Molecular Dynamics Sims

Last time, discussed monte carlo sims
$\Rightarrow$ Molecular dynamics is an alternative idea
Solve newton's equations approximately, with the same idea of computing $\langle A \rangle = \int dx P(x) A(x)$

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

If the system is "ergodic", then as $t \to \infty$ will sample all configurations $\{p(t), q(t)\}$ st $\mathcal{H}(p(t), q(t)) = \mathcal{E}$ with equal prob, ie $P(\vec{X}) = P(\vec{p}, \vec{q}) = 1/\Omega(N, V, \mathcal{E})$

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

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

& 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 cfg (gen vel from Boltzmann dist)
2) interaction energy

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

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \frac{dq_i}{dt} = \partial H/\partial p_i, \quad \frac{dp_i}{dt} = -\partial H/\partial q_i$

and defined $i\mathcal{L}A = \{H, A\}$, $i\mathcal{L} = \{H, \_\}$

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

$\left[\vec{v} = d\vec{q}/d\tau \approx \frac{\vec{q}(t + d\tau) - \vec{q}(t)}{d\tau} \right]$ 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.

Example, could have written:

no vel

(2) $\vec{q}(\tau - d\tau) = \vec{q}(\tau) - d\tau \frac{d\vec{q}}{dt}\Big|_{t=\tau} + \frac{d\tau^2}{2}\frac{d^2\vec{q}}{dt^2}\Big|_{t=\tau} + O(d\tau^3)$

add (1)+(2) $\Rightarrow \vec{q}(\tau+d\tau) + \vec{q}(\tau-d\tau) = 2\vec{q}(\tau) + d\tau^2/m \, \vec{F}(t)$

(3) $\frac{(1)-(2)}{d\tau} \Rightarrow \vec{v}(\tau) \approx (q(\tau+d\tau) - q(\tau-d\tau))/2d\tau$

Verlet 1967, alternate these two eqns

→ Good idea to have time reversibility
these equations are invariant under $d\tau \to -d\tau$

Another variant, using this backwards idea
$(q(\tau+d\tau), -v(\tau+d\tau)) \to \{q(\tau), -v(\tau)\}$

note
$v = dq/dt$
$-v = dq/d(-t)$

(4) $\vec{q}(\tau) = \vec{q}(\tau+d\tau) - d\tau\,\vec{v}(\tau+d\tau) + \frac{d\tau^2}{2}\vec{F}(\tau)/m$

(5) Sub 1→4 $\Rightarrow v(\tau+d\tau) = v(\tau) + \frac{d\tau}{2m}[F(\tau+d\tau) + F(\tau)]$

Alternate 1 & 5,

Lets go back to formal description

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

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

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

can rewrite $\mathcal{L} = \mathcal{L}_p + \mathcal{L}_q$ ↙ analogous for N particles

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

if $H = p^2/2m + U \Rightarrow +i\mathcal{L}_p = +F\,\partial/\partial(mv) = +\frac{F}{m}\frac{\partial}{\partial v}$

$\Rightarrow +i\mathcal{L}_q = +v\,\partial/\partial q$

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

so $e^{+iLt} \approx \left[\underbrace{e^{+i\mathcal{L}_p \frac{\Delta t}{2}}}_{\underline{\underline{P}}} \underbrace{e^{+i\mathcal{L}_q \Delta t}}_{\underline{\underline{Q}}} \underbrace{e^{+iL_p \Delta t/2}}_{\underline{\underline{P}}} \right]^M + O(M\Delta t^3)$
$(\Delta t = t/M)$ $\qquad O(M\Delta t^3) = O(t\Delta t^2)$
(one scheme) $\qquad$ error increases w/ time

Now $e^{c\, d/dx} g(x) = g(x+c)$

why? $g(x+c) = g(x) + c\frac{d}{dx}g(x) + \frac{c^2}{2}\frac{d^2}{dx^2}g(x) + \cdots = e^{c\,d/dx} g(x)$

$e^{c\,d/dx} = 1 + c\cdot\frac{d}{dx} + \frac{c^2}{2}\frac{d^2}{dx^2} + \cdots$

Applying once to $A = \{q_0, v_0\}$, $\quad \underline{\underline{P}}A = \{q_0, \overbrace{v_0 + F_0/m\, \Delta t/2}^{v_1}\}$ $\qquad F_0 = F(q_0)$

$\underline{\underline{Q}}\underline{\underline{P}}A = \{q_0 + v_1\Delta t, v_0 + F_0/m\, \Delta t/2\} = \{\underbrace{q_0 + v_0\Delta t + \frac{F_0}{m}\Delta t^2/2}_{q_1}, v_1\}$

$\underline{\underline{P}}\underline{\underline{Q}}\underline{\underline{P}} = \{q_0 + v_0\Delta t + F_0\, \Delta t^2/m, v_0 + \frac{F_0 + F_1}{2m}\Delta t\}$ $\quad$ velocity verlet again

Seems overly complicated, but this formulation allowed for many advanced methods to be derived using splitting schemes.

Eg. RESPA, evolve slow and fast forces separately, eg $U(q) = U_{spring}(q) + U_{other}(q)$ ← expensive

$$iL^{fast} = F^{fast}\frac{d}{dp} + iL_q \quad , \quad iL^{slow} = F^{slow}\frac{\partial}{\partial p}$$

Then can do

$$e^{iLt} \approx \left[e^{iL^{slow} t/2n} \, e^{iL^{fast} t/n} \, e^{iL^{slow} t/2n} \right]^n$$

(Tuckerman 1992)

but

$$\underbrace{e^{iL^{fast} t/n}}_{\delta t} \approx \left[e^{\frac{\delta t}{2n} F^{fast}\frac{d}{dp}} \, e^{\frac{\delta t}{n} v \frac{\partial}{\partial q}} \, e^{\frac{\delta t}{2n} F^{fast}\frac{d}{dp}} \right]^n$$

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

Also, error in methods grow as $\Delta t^{2 \text{ or } 3}$, how small should Δt be. In practice, for fastest motion in system, $\omega = \sqrt{k/m}$,

$\tau = 2\pi/\omega$, want $\Delta t < \tau$, maybe $\Delta t < \tau/5$

* C-H bond $\tau < 10 fs$ so MD sims $\Delta t \sim 2 fs$ w/ rigid CH ...

Enhanced Sampling

We said before that the time avg

$$\langle A \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} A(X_i) \quad \text{for } N \text{ mc samples}$$

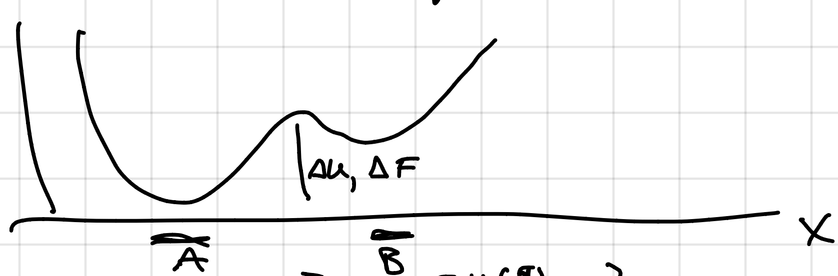
or $N = T/\Delta t$ md time steps is true if the system is ergodic, ie sees all the states

The problem in real simulation is $N \neq \infty$,

$N \sim (1 - 10^{10})$

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

Suppose $U(x)$ or $F(x)$



$$F(\vec{x}) = -kT \log \int \delta(M(\vec{q}) - \vec{x})\, e^{-\beta U(\vec{q})} d\vec{q} - F_0$$

(Potential of mean force)

$$\text{Rate}_{A \to B} \propto e^{-\beta \Delta U^{\ddagger}} \text{ or } e^{-\beta \Delta F^{\ddagger}}$$

So if $1/\text{rate} \gg N\Delta t$, then you will be trapped in A (or B)

(rare event problem)

We need tricks to overcome this problem!