Molecular Dynamics Simulations

Said calculate $\langle A \rangle \approx \frac{1}{N} \sum_{i=1}^{N} A(x_i)$

x_i sampled from thermodynamic dist.

Get x_i sampled from Newtonian dynamics

We know: $\{\vec{q}(0), \vec{p}(0)\}$ and $\mathcal{H}$

then we know $\{\vec{q}(t), \vec{p}(t)\}$

Closed isolated system, micro canonical

constant N, V, E

$$\vec{F} = m\ddot{\vec{q}} \qquad \vec{F} = -\frac{\partial U}{\partial \vec{q}} = -\nabla U$$

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

Start with some p, q at time $t=0$ and go until $t \to \infty$, if ergodic

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

$$\langle A \rangle_{\text{ensemble}} = \int d\vec{x}\, A(\vec{x})\, P(\vec{x})$$

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

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

<u>if</u> ergodic

$$\langle A \rangle_{\text{ens}} = \langle A \rangle_{\text{time}} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, A(p(t),q(t))$$

In practice: 1) initial starting structure

- gen velocities from Bolzmann distribution

2) Interaction energy

$U(\vec{q})$ "forcefield"

Formal dynamics, for observable A

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

$$= \sum_{i=1}^{N} \left(\frac{\partial A}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right)$$

$$i\mathcal{L}A = \{H, A\}, \quad i\mathcal{L} = \{H, -\}$$

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

first: Newtonian dynamics, a taylor series in time

(1) $$\vec{q}(t+d\tau) \approx \vec{q}(t) + d\tau \underbrace{\left.\frac{d\vec{q}}{dt}\right|_t}_{v(t)} + \frac{(d\tau)^2}{2} \underbrace{\left.\frac{d^2 q}{dt^2}\right|_t}_{a(t)} \ldots$$

$$\approx \vec{q}(t) + \vec{v}(t)\,d\tau + \vec{a}(t)\frac{d\tau^2}{2} + \ldots$$

$$\vec{q}(t+d\tau) - \vec{q}(t) = \underline{d = vt + \tfrac{1}{2}at^2}$$

at short times "ballistic"

① $q(t+d\tau) = q(t) + d\tau\, \dot{q}(t) + \frac{dt^2}{2} \cdot \frac{F_i}{m}$

$$a_i(t) = -\frac{\partial U(\vec{q}(t))}{\partial q_i} \cdot \frac{1}{m} = \frac{F_i}{m}$$

② $q(t-d\tau) = q(t) - d\tau\, \dot{q}(t) + \frac{dt^2}{2} F_i/m$

add ①&②

$$q(\tau+d\tau) + q(t-d\tau) = 2q(t) + dt^2 F_i/m$$

$$q(\tau+d\tau) = 2q(t) - q(t-d\tau) + dt^2 F_i/m$$

no velocities

① - ② $\Rightarrow q(t+d\tau) - q(t-d\tau)$

$$= 2\dot{q}(t)\,d\tau$$

$$\dot{q}(t) = v(t) = \frac{q(t+d\tau) - q(t-d\tau)}{2\,d\tau}$$

Verlet 1967: alternate these two equations

Go back to formal description

$$\mathcal{H} = \frac{p^2}{2m} + U$$

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

$$-i\mathcal{L} = \sum_{i=1}^{N} \left(\underbrace{\frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial}{\partial p_i}}_{\text{mom}} - \underbrace{\frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial}{\partial q_i}}_{\text{pos}} \right)$$

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

$$= +F \frac{\partial}{\partial p} = \frac{F}{m} \frac{\partial}{\partial V} \qquad i\mathcal{L}_q = V \frac{\partial}{\partial q}$$

$$e^{i\mathcal{L}_q + i\mathcal{L}_p}$$ what does this do?

$$e^{A+B} \neq e^{A} e^{B}$$ unless $[A,B] = AB - BA = 0$

can show $[i\mathcal{L}_p, i\mathcal{L}_q] \neq 0$

Trotter factorization

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

$$e^{i\mathcal{L}t} \stackrel{?}{=} \approx \left[e^{i\mathcal{L}_p \frac{\Delta t}{2}} e^{i\mathcal{L}_q \Delta t} e^{i\mathcal{L}_p \Delta t/2} \right]^M + O(M\Delta t^3) \sim O(t\Delta t^2)$$

$\Delta t = t/M$

$$e^{i\mathcal{L}t} \approx \Big[\underbrace{e^{i\mathcal{L}_p \frac{\Delta t}{2}}}_{P} \; \underbrace{e^{i\mathcal{L}_q \Delta t}}_{Q} \; \underbrace{e^{i\mathcal{L}_p \Delta t/2}}_{P} \Big]^M$$

$$e^{A+B} = e^{B+A}$$

Can show $e^{c\frac{d}{dx}} g(x) = g(x+c)$

why?
$$g(x+c) \approx g(x) + c\frac{d}{dx}g(x) + \frac{c^2}{2}\frac{d^2}{dx^2}g(x) \; \ldots$$

$$e^{c\frac{d}{dx}} = \left(1 + c\frac{d}{dx} + \frac{c^2}{2}\frac{d^2}{dx^2} + \cdots\right)$$

$$e^{i\mathcal{L}t} \approx \left[e^{i\mathcal{L}_p \frac{\Delta t}{2}} \; e^{i\mathcal{L}_q \Delta t} \; e^{i\mathcal{L}_p \Delta t/2} \right]^M$$

$$i\mathcal{L}_p = \frac{F}{m}\frac{\partial}{\partial v} \qquad i\mathcal{L}_q = v\frac{\partial}{\partial q}$$

$$\underline{\underline{P}} = e^{\frac{F\Delta t}{2m}\frac{\partial}{\partial v}} \qquad \underline{\underline{Q}} = e^{v\Delta t\frac{\partial}{\partial q}}$$

$$X_0 = \{q_0 ; v_0\}$$

$$\underline{\underline{P}}\, X_0 = \Big\{ q_0 ,\; \overbrace{v_0 + \frac{F_0 \Delta t}{2m}}^{v_1} \Big\}$$

$$\underline{\underline{Q}}\left(\underline{\underline{P}}\, X_0\right) = \Big\{ q_0 + v_1 \Delta t ,\; v_0 + \frac{F\Delta t}{2m} \Big\}$$

$$\underset{=}{P} x_0 = \Big\{ q_0,\ \overbrace{v_0 + \frac{F_0 \Delta t}{2m}}^{v_1} \Big\}$$

$$\underset{=}{Q}(\underset{=}{P} x_0) = \Big\{ q_0 + v\Delta t,\ v_0 + \frac{F\Delta t}{2m} \Big\}$$

$$= \Big\{ q_0 + v_0\Delta t + \frac{F_0 \Delta t^2}{2m},\ \underbrace{v_0 + \frac{F_0\Delta t}{2m}}_{v_1} \Big\}$$

$$\underset{=}{P}\,\underset{=}{Q}\,\underset{=}{P} = \Big\{ q_0 + v_0\Delta t + \frac{F_0\Delta t^2}{2m},\ v_0 + \frac{F_0 \Delta t}{2m} + \frac{F_1 \Delta t}{2m} \Big\}$$

Velocity verlet

$$= \Big\{ q_0 + v_0\Delta t + \frac{F_0 \Delta t^2}{2m},\ v_0 + \frac{F_0 + F_1}{2m}\Delta t \Big\}$$

RESPA - Reversible multiple time scale molecular dynamics

split "cheap" forces

"expensive, slow" forces

$$U(q) = U_{springs}(q) + U_{other}(q)$$

$$i\mathcal{L}^{fast} = F^{fast}\frac{d}{dp} + iLq \quad , \quad iL^{slow} = F^{slow}\frac{d}{dp}$$

$$e^{i\mathcal{L}^{fast} + i\mathcal{L}^{slow}} \approx \left[e^{iL^{slow}\frac{\Delta t}{2m}}\, e^{iL^{fast}\frac{\Delta t}{m}}\, e^{iL^{slow}\frac{\Delta t}{m}}\right]^{m}$$

$$e^{i\mathcal{L}^{fast}\Delta t/m} \approx \left[e^{\frac{\delta t}{2n} F^{fast} \frac{d}{dp}} \, e^{\frac{\delta t}{n} v \frac{\partial}{\partial q}} \, e^{\frac{\delta t}{2n} F^{fast} \frac{\partial}{\partial p}} \right]^n$$

$\Delta t/m - \delta t$

$$A^{slow} \; B^{fast} \; A^{slow}$$

$$\left(P^{fast} Q P^{fast} \right)^n$$

how small should Δt be?

shorter than fast time scale, C–H bond $\tau = 2\pi/\omega \sim 10$ fs