Intro to Molecular Dynamics

Review of classical mechanics:

- Newton's 2nd law $\vec{F} = m\vec{a} = m\frac{d^2\vec{r}}{dt^2}$

- position $= \vec{r}$, velocity $\vec{v} = \frac{d\vec{r}}{dt}$, acceleration $\vec{a} = \frac{d\vec{v}}{dt} = \frac{d^2\vec{r}}{dt^2}$

- If acceleration doesn't depend on time, can write const. acceleration equations relating initial (x_0, v_0) to values (x, v) after time interval t:

$$v(t) = v_0 + \int_0^t a\,dt' = v_0 + at$$

$$x(t) = x_0 + \int_0^t v(t')\,dt' = x_0 + \int_0^t (v_0 + at')\,dt'$$

$$= x_0 + v_0 t + \frac{1}{2}at^2$$

- Conservative force, only depends on positions (not velocities)
Then relate force F and potential energy U

$$\vec{F} = -\vec{\nabla}U = -\left(\frac{\partial U}{\partial x}\hat{x} + \frac{\partial U}{\partial y}\hat{y} + \frac{\partial U}{\partial z}\hat{z}\right)$$

- Conservation of energy $E = K + U$

kinetic energy $K = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2$

- E.g. Simple harmonic oscillator

$$U = \frac{1}{2}kx^2 \qquad F = -\nabla U = -kx = m\frac{d^2x}{dt^2}$$

$$\frac{d^2x}{dt^2} = \frac{-k}{m}x$$

Basics of MD

Inputs

- system of N atoms, each atom has an initial position $\vec{r}_{0,i}$ and initial velocity $\vec{v}_{0,i}$
- interatomic potential giving interactions between atoms $\phi(r_{ij})$

1. Calculate potential energy of initial configuration of atoms

   e.g. $u(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \phi(r_{ij})$

2. Calculate force on each atom

   $\vec{F}_i = -\vec{\nabla}_i u(\vec{r}_1 \cdots \vec{r}_N)$ note $\vec{\nabla}_i$ means gradient wrt coordinates of atom i.

   e.g. $\vec{F}_3 = -\vec{\nabla}_3 u = -\left(\frac{\partial u}{\partial x_3} \hat{x} + \frac{\partial u}{\partial y_3} \hat{y} + \frac{\partial u}{\partial z_3} \hat{z} \right)$

3. Solve $3N$ Newton's eq $\vec{F}_i = m_i \frac{d^2 \vec{r}_i}{dt^2}$ to get $\vec{r}_i(t)$

We have a set of $3N$ coupled differential equations (each eq'n depends on all coords $\vec{r}_i$) → numerical integration

Approach: we will divide time t into intervals of length dt.
Given positions x(t) and velocities v(t) at time t, we will find the positions and velocities at time t+dt using a numerical integration algorithm (Euler or Verlet)
The output of this algorithm will be the positions and velocities of each atom at each timestep 0, dt, 2dt, 3dt,....Ndt, where Ndt = t.

Choice of time-step

- accuracy - want dt as short as possible
- computation time - want dt as long as possible
- Typical time step in MD simulation: 0.5 - 10 fs ($1\,fs = 10^{-15}\,s$)
- Timescales

1 fs - atomic motions	$(10^{-15}\,s)$
1 ps - molecular motions	$(10^{-12}\,s)$
1 ns - H_2O dynamics	$(10^{-9}\,s)$
1 μs - ionic diffusion	$(10^{-6}\,s)$
1 ms - protein folding	

e.g. w/ 1 fs timestep, a 1 ns simulation takes

$$\frac{10^{-9}\,s}{10^{-15}\,s} = 10^{6} \text{ time steps}$$

Choosing initial positions and velocities

(4)

- set size and shape of simulation cell and # of atoms N
- choose initial position and velocity of all N atoms
- important because this sets the total energy $E = K + U$ which will be conserved throughout the simulation
- typically choose initial positions to be close to what you think the final positions will be
- choice of velocities, e.g. from Maxwell-Boltzman distribution - prob. distribution of speeds in an ideal gas - at desired starting temp.

$$P_{MB}(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/k_B T} \qquad k_B = 1.38 \times 10^{-23}\,J/K$$

Note on conservation laws and temperature in MD

- U does not depend on velocity → energy $E = k + U$ is conserved
- making sure E is conserved is an important test that a MD simulation is working
- In standard MD, N, V, and E are fixed → NVE or Microcanonical ensemble
- Temperature is not fixed, it is related to kinetic energy

$$\langle T \rangle = \frac{2\langle K \rangle}{3Nk_B}$$

where $\langle K \rangle$ is computed by averaging over all timesteps

$$\langle k \rangle = \frac{1}{t_{max}} \sum_{t=1}^{t_{max}} k(t)$$