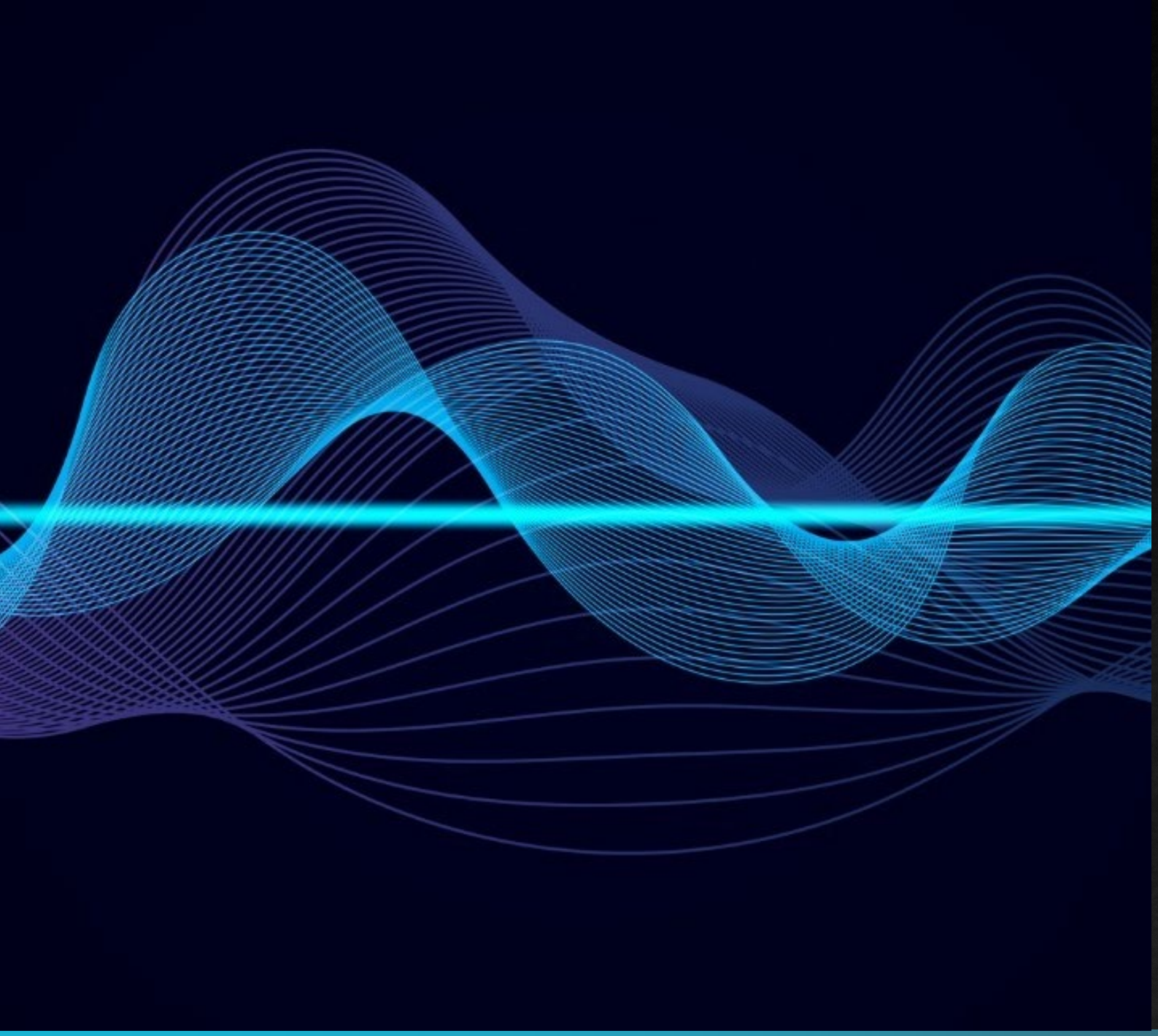


Computational Physics

PHYS 6260

Molecular Dynamics

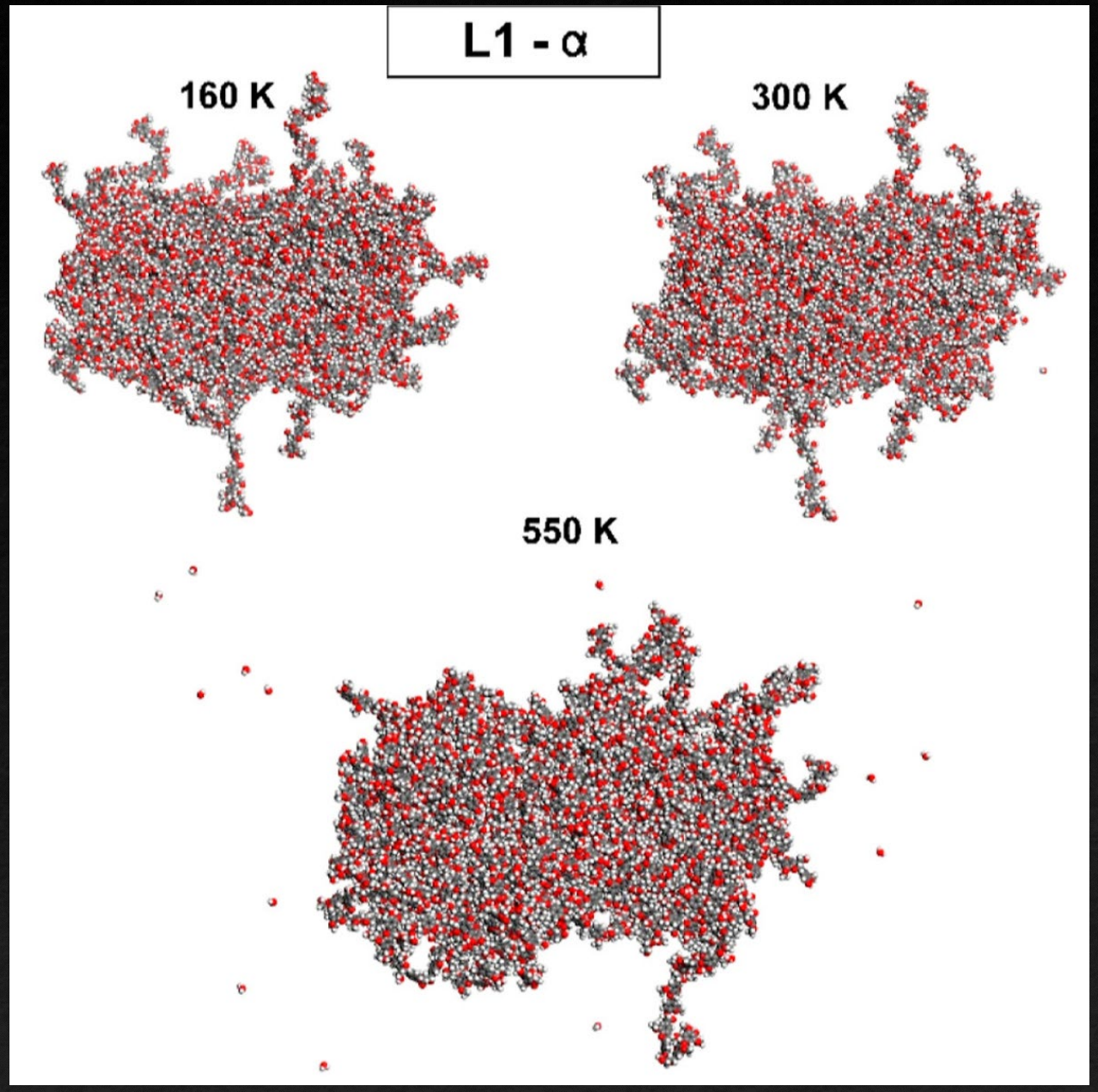
Announcements:

- HW7: Due today (4/7)
- No class: Mon 4/14
- Poster presentations: Wed 4/16

Lecture Outline

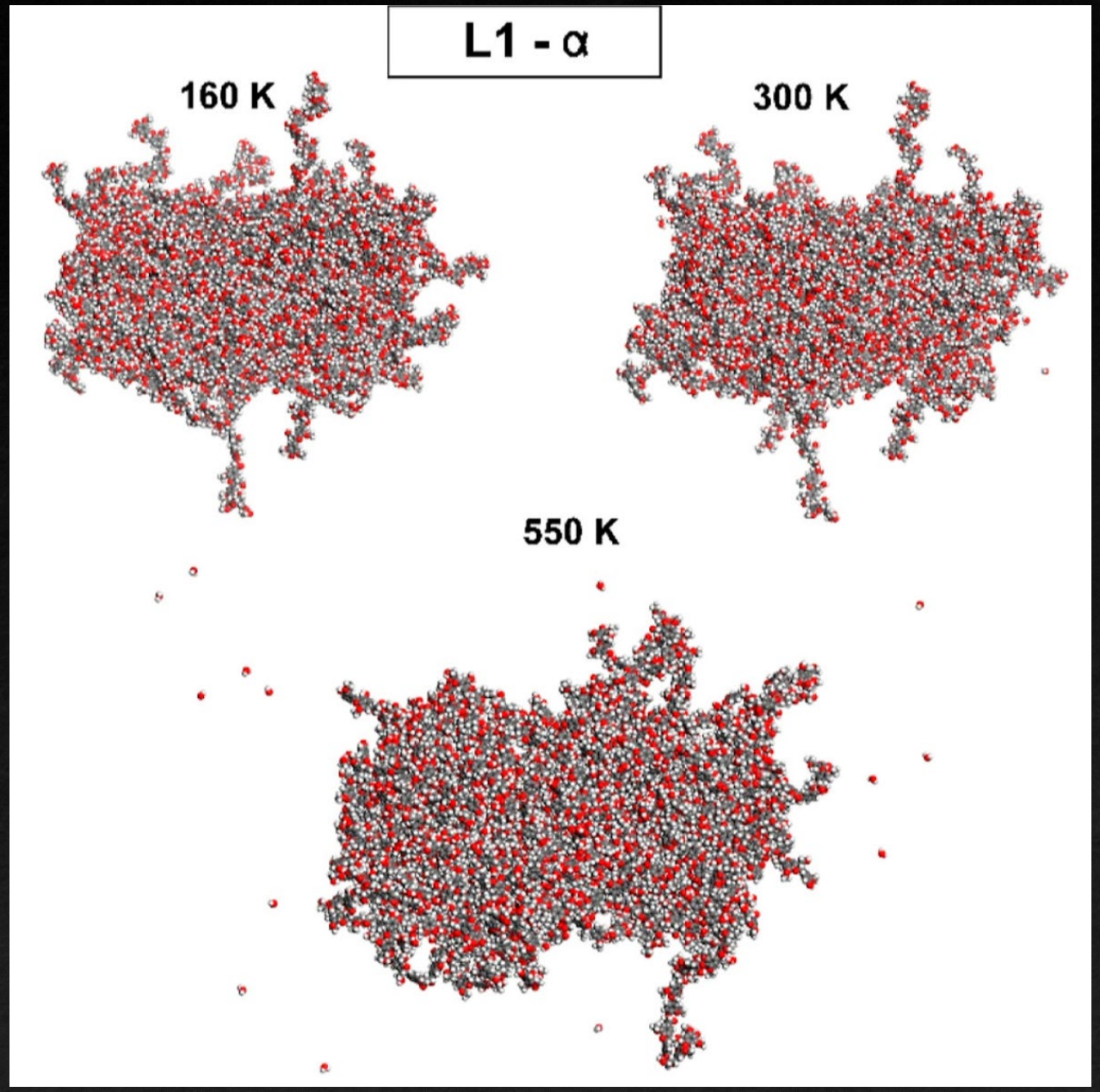
We will cover these topics

- What is Molecular Dynamics (MD)?
- Components of MD simulations
  - Potential energy
  - Verlet algorithm
  - Ensembles of configurations
  - Boundary conditions
- Examples



What is MD?

- Simulation method for analyzing physical movement of atoms and molecules
- Atoms and molecules are allowed to interact for a fixed time
- Trajectories of particles are solved using Newton's equation of motion
- Forces are given by interatomic and intermolecular potentials
- Accuracy depends highly on interatomic potentials



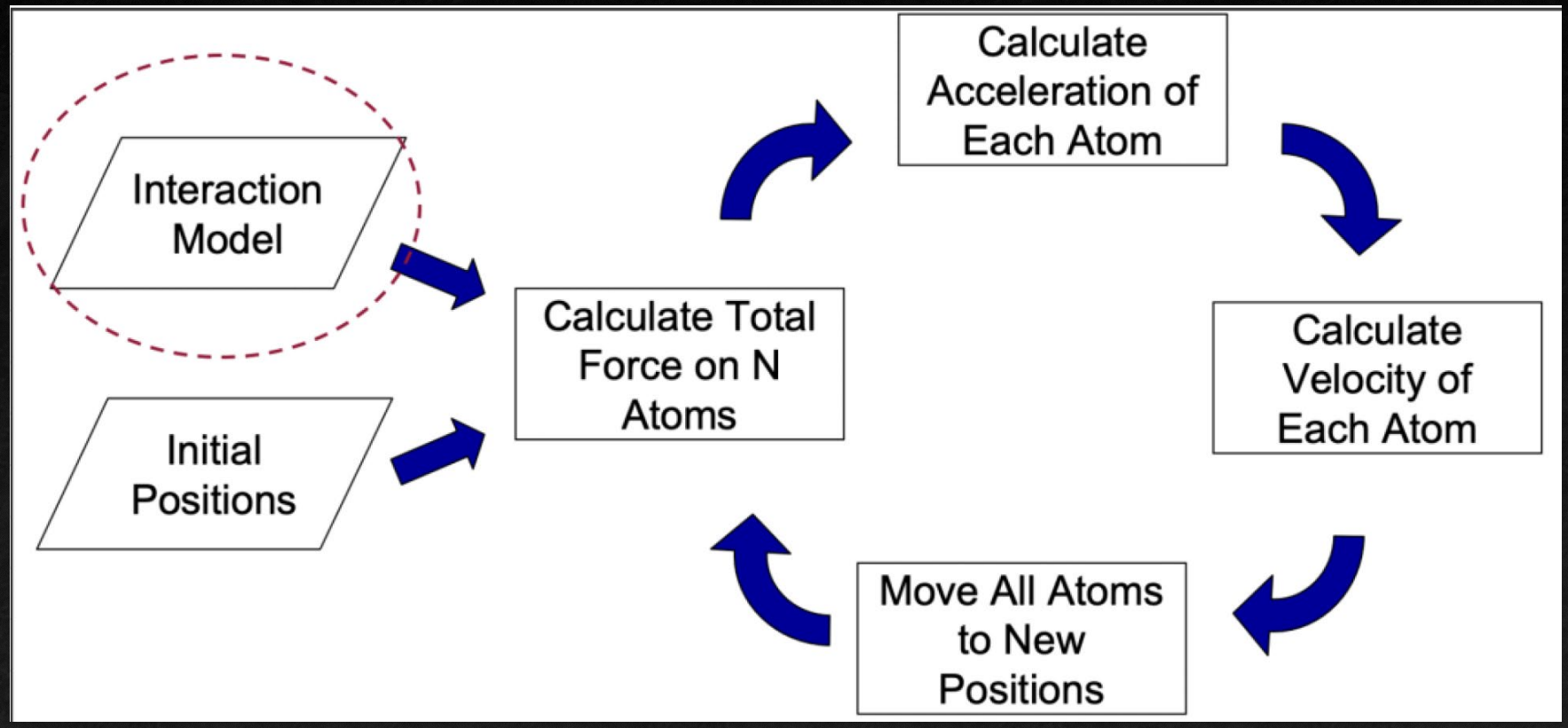
MD Timescales

- Limited to the femto- to nanosecond scales
- Short timescale is needed to ensure numerical stability and accuracy when conserving energy
- Need timescales an order of magnitude shorter than the fastest timescales in the system

MD Modeling

Assumptions

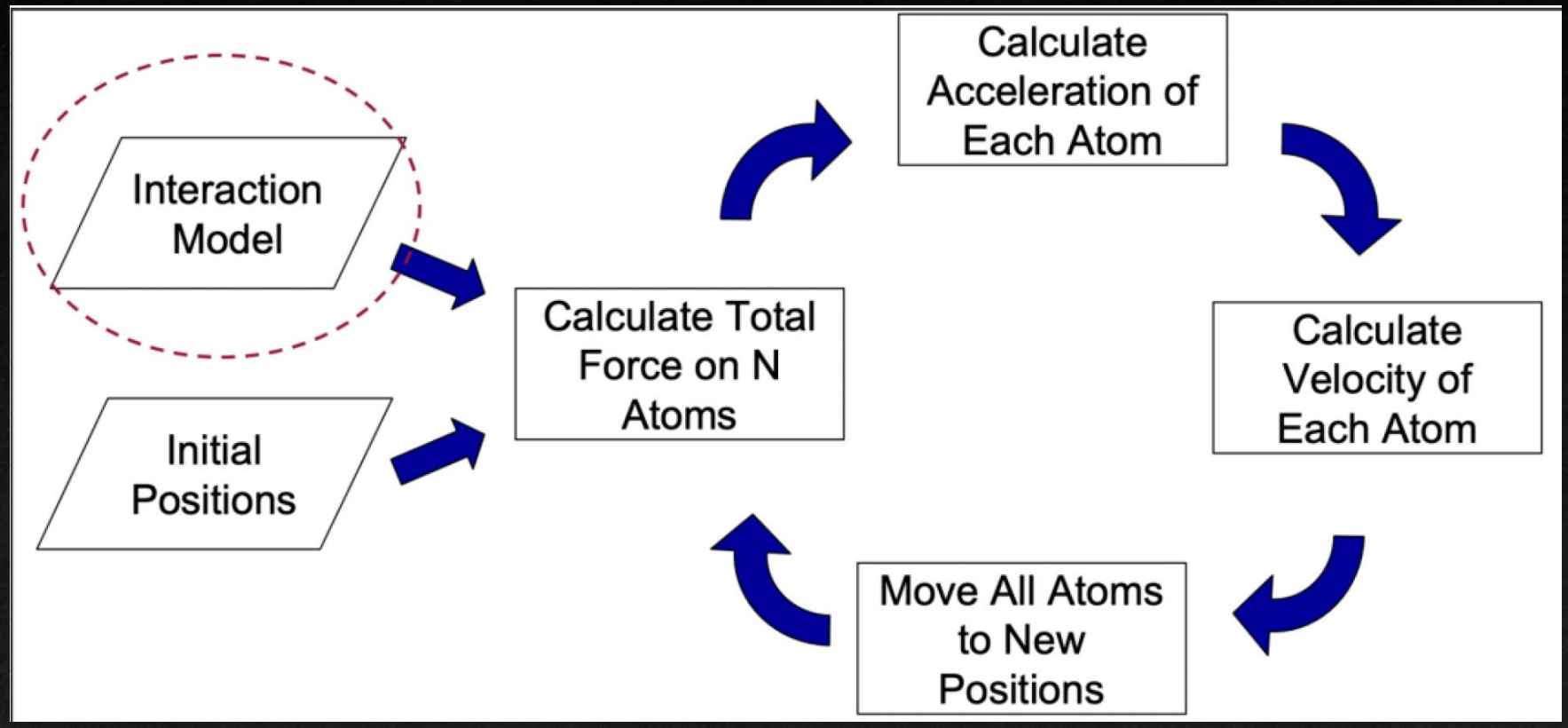
- Atoms are treated like balls connected on springs
- Neglects QM effects



MD Modeling

Basic problems

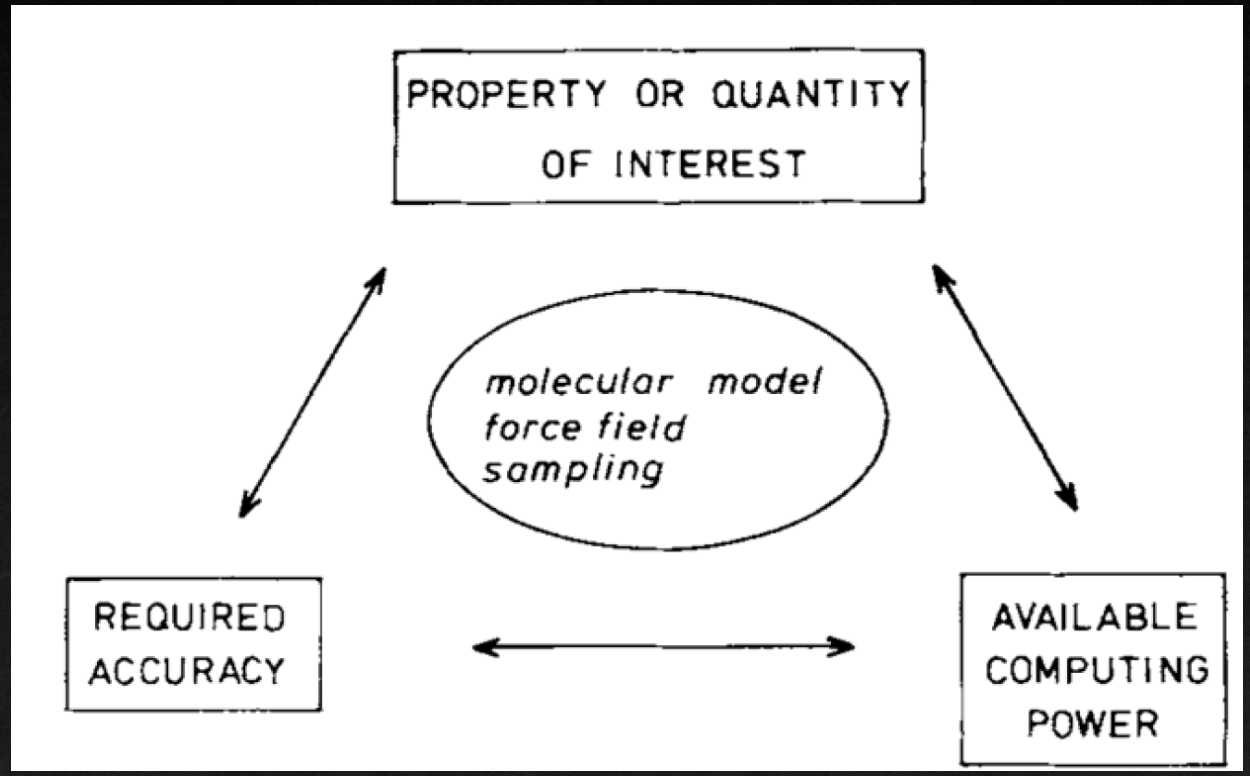
- Size of configuration space
- Accuracy of molecular model or interatomic potential



MD Modeling

Successful simulation reqs

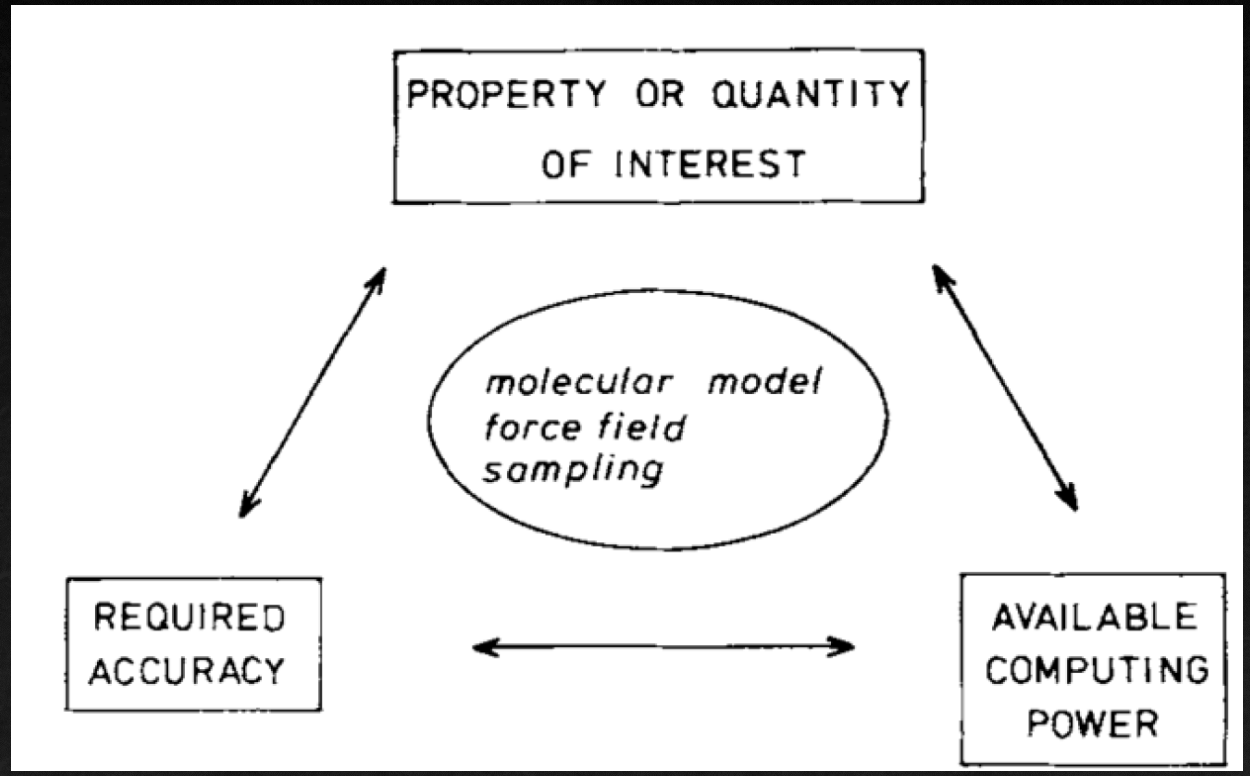
- Fast & memory efficient
- Permit the use of long timesteps
- Duplicate classical treatments
- Satisfy known energy laws
- Time reversible <-> energy conservation
- Simple and easy to program



MD Modeling

Successful simulation reqs (cont'd)

- Good algorithms permit both large dt & accuracy
  - Energy conservation is degraded with increasing dt
  - Measure "acceptable" MD simulation by preserving energy conservation
- Simplicity of algo increases speed
  - No point in calculating unused variables



Components of MD Simulations: Force law

- Newton's 2nd law for particle motion

$$F_i = m_i \dot{v}_i = -\frac{\partial}{\partial x_i} V\left(\sum_i \{x_i\}\right)$$

- Equation of motion (EoM) for atomic systems in classical MD

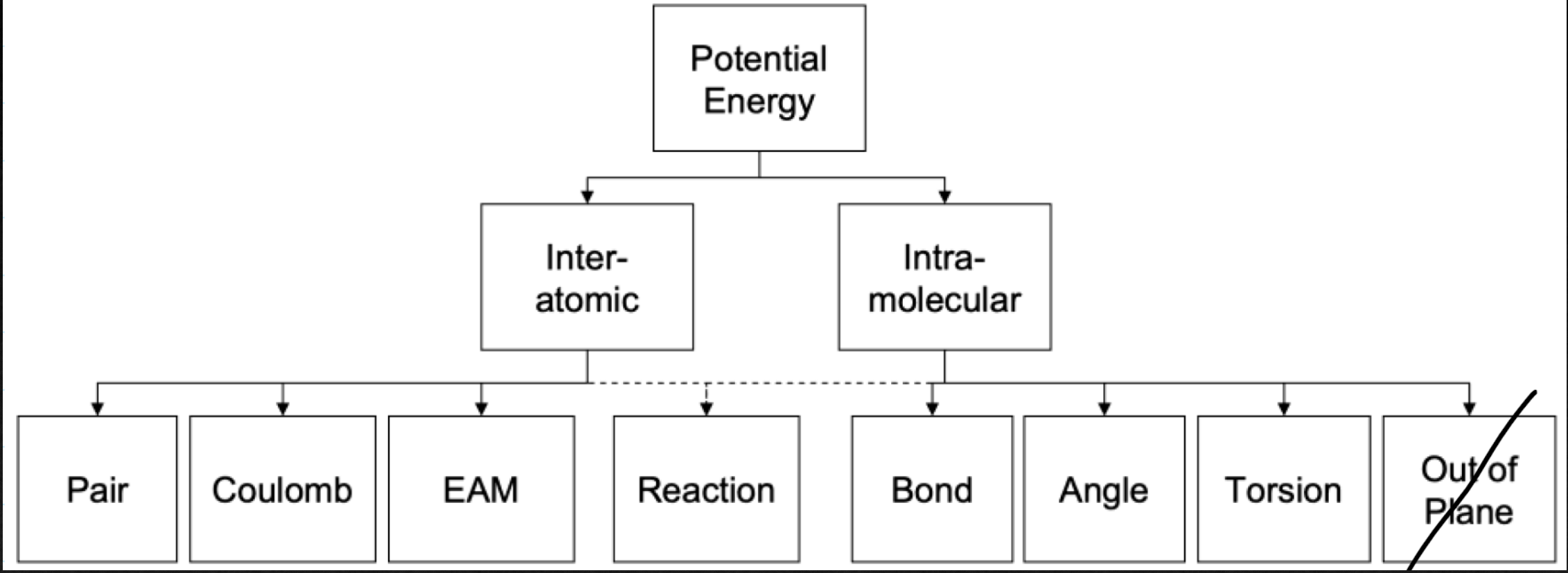
$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

- Here q_i is the generalized coordinate and p_i is the momentum
- The Hamiltonian is given by the standard

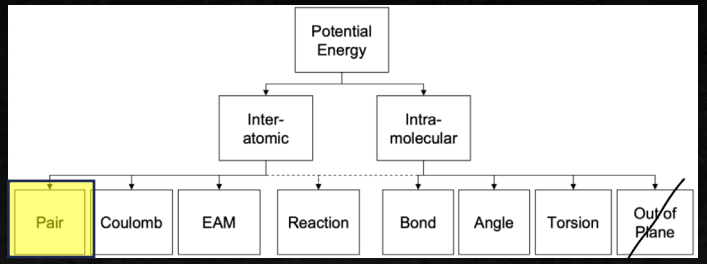
$$H = \sum_i [p_i^2/2m_i + V(\{x_i\})]$$

- For a given potential and initial condition, we solve for
  - Force (F_i) → acceleration (a_i) → new positions (x_i)

Components of MD Simulations: Potentials



Components of MD Simulations: Potentials

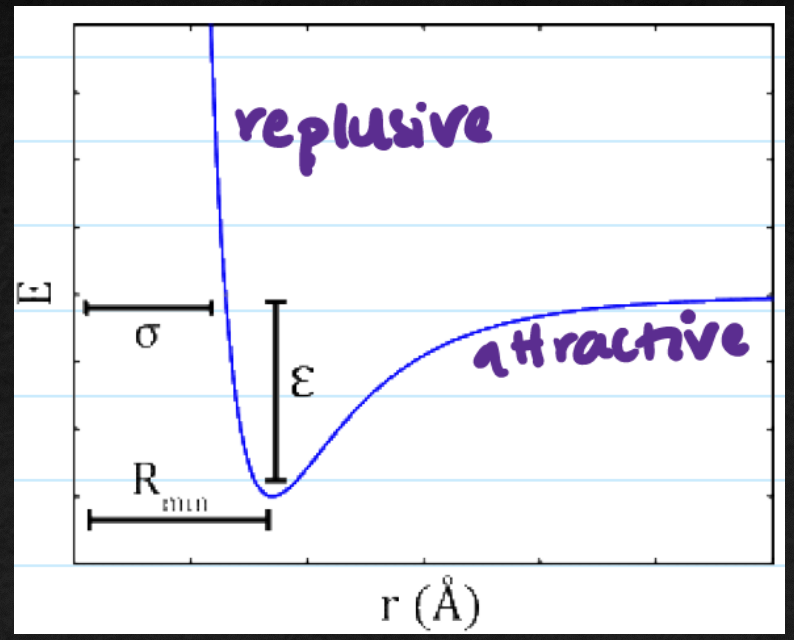


Pair potential

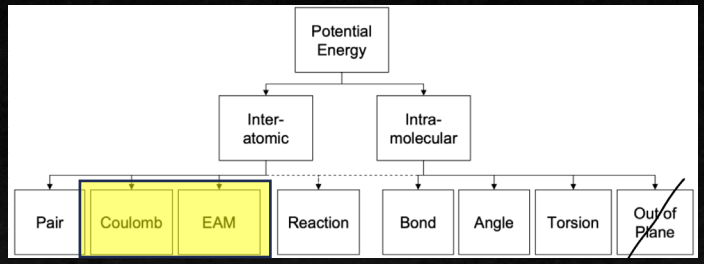
- Attraction: long distance; instantaneous dipoles arise during fluctuations of e-cloud
- Repulsive: short distance; overlap of e-cloud such that nuclei are shielded

$$U(r) = K\epsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{m}\right]; \quad K = \frac{n}{n-m}\binom{n}{m}^{\frac{m}{n-m}}$$

- Example: Lennard-Jones (LJ)
  - n = 12; m = 6; decays rapidly with distance
  - Save computational time by neglective pair potential at a specific radius (usually 2.5σ Angströms)



Components of MD Simulations: Potentials



Coulombic interactions

- Included if electrostatics between atoms are significant

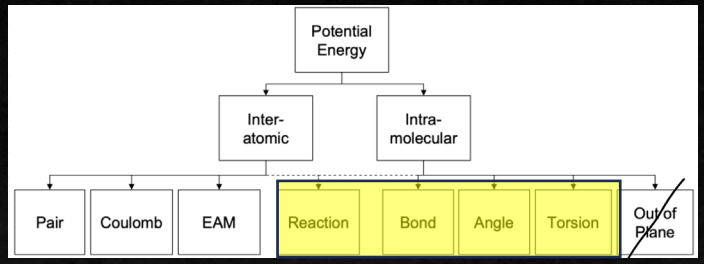
$$U_i = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}$$

- For full potential calculations, we need to correct for screening e-clouds surrounding the point charges

Embedded atom model

- Each atom is considered to be embedded in an electron sea, where the energy of the system is expressed as a function of e^- density at each position
- Allows to capture bounding and repulsion between atoms

Components of MD Simulations: Potentials

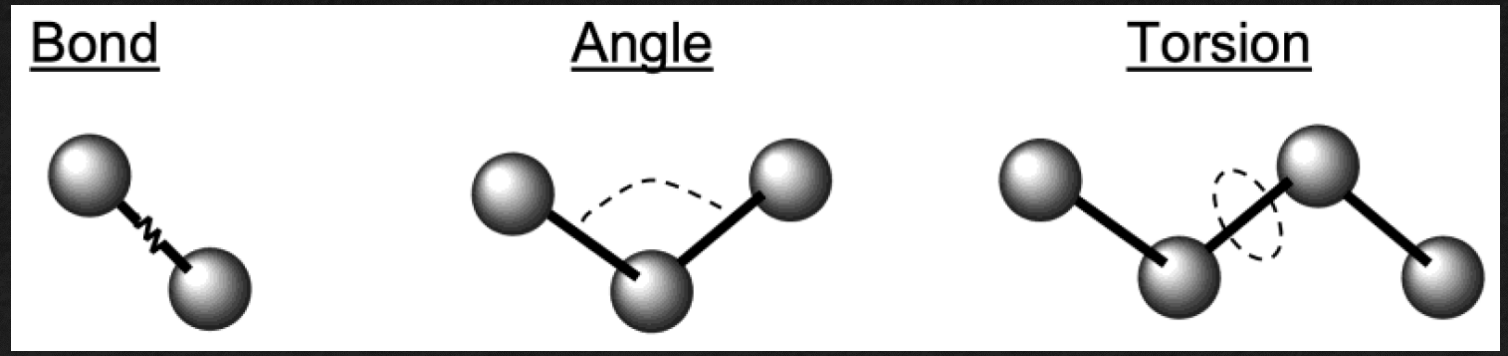


Reactive potentials

- Specifically designed to model bond breaking and forming
- Combines empirical parameters

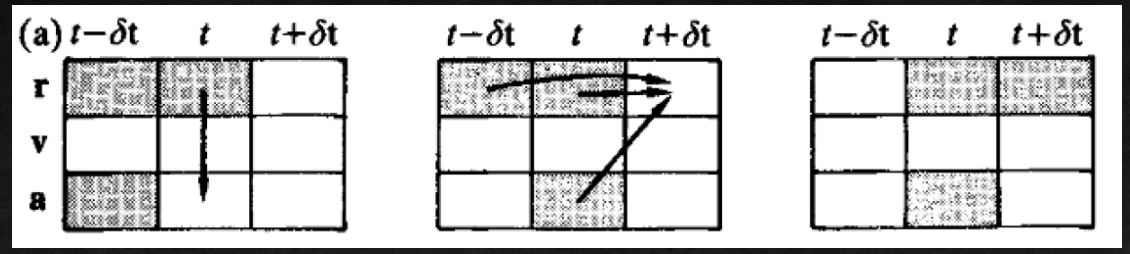
Intermolecular

- Models describe behavior between covalent bonds (stretching, bending, rotation modes)



Components of MD Simulations: Verlet algorithm

- Most widely used method for integrating EoM – covered very early in the semester
- Direct solution of 2nd order equations (special case of leapfrog method)

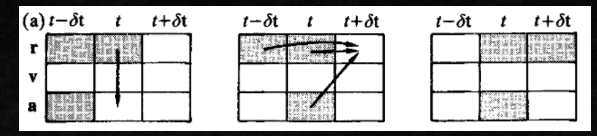


- Disadvantages
  - Awkward handling of velocity
  - Some numerical imprecision

```python
import numpy as np

n=100
t0=0
tstop=2*np.pi
deltat = (tstop-t0)/float(n)

t = np.linspace(t0,tstop,n+1)
rx, ry, rz = np.zeros(n+1),np.zeros(n+1),np.zeros(n+1)
ax, ay, az = np.zeros(n+1),np.zeros(n+1),np.zeros(n+1)

sum_vx, sum_vy, sum_vz = 0,0,0

rx[0],ry[0],rz[0] = 0.1,0.1,0.1

for i in range(1,n):

    rx[i+1] = 2*rx[i]-rx[i-1]+deltat*ax[i]
    ry[i+1] = 2*ry[i]-ry[i-1]+deltat*ay[i]
    rz[i+1] = 2*rz[i]-rz[i-1]+deltat*az[i]

    vx = (rx[i+1] - rx[i])/(2*deltat)
    vy = (ry[i+1] - ry[i])/(2*deltat)
    vz = (rz[i+1] - rz[i])/(2*deltat)

    sum_vx += vx
    sum_vy += vy
    sum_vz += vz
```

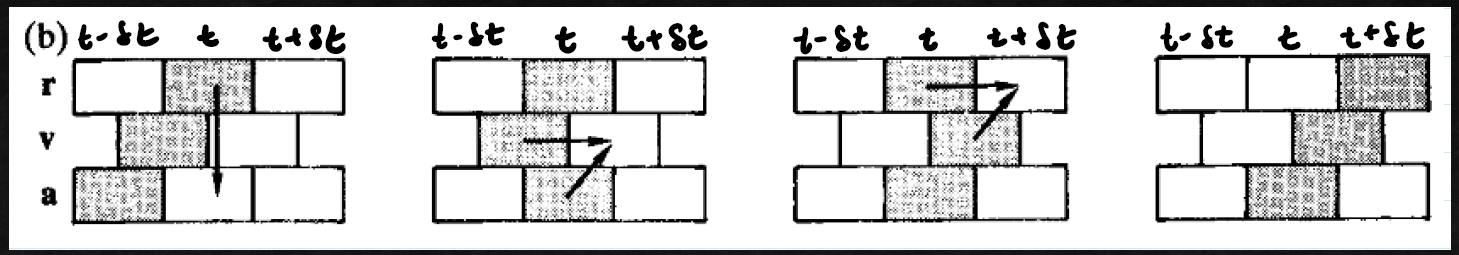
use these to calculate the kinetic energy

Components of MD Simulations: Verlet common mods



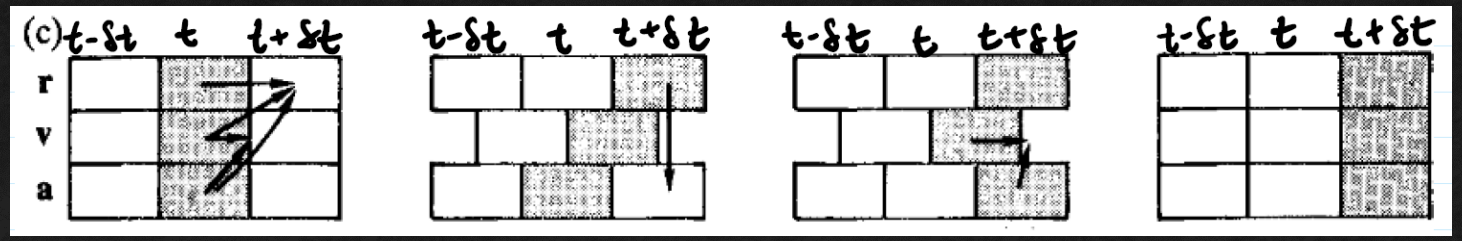
Half-step leapfrog

- Reduces $O(dt^2)$ error term, however we are not storing the velocities at the same timestep



Velocity-Verlet algorithm

- Requires 2 stages and storage of $\vec{r}$, $\vec{v}$, $\vec{a}$
- Calculate new potential and forces at t+dt, velocities at t+dt/2



Ensemble of Configurations

- Collection of possible conditions that the system can occupy under specific circumstances
- For example, what thermodynamic parameters do we keep constant (pressure, temperature, volume?)

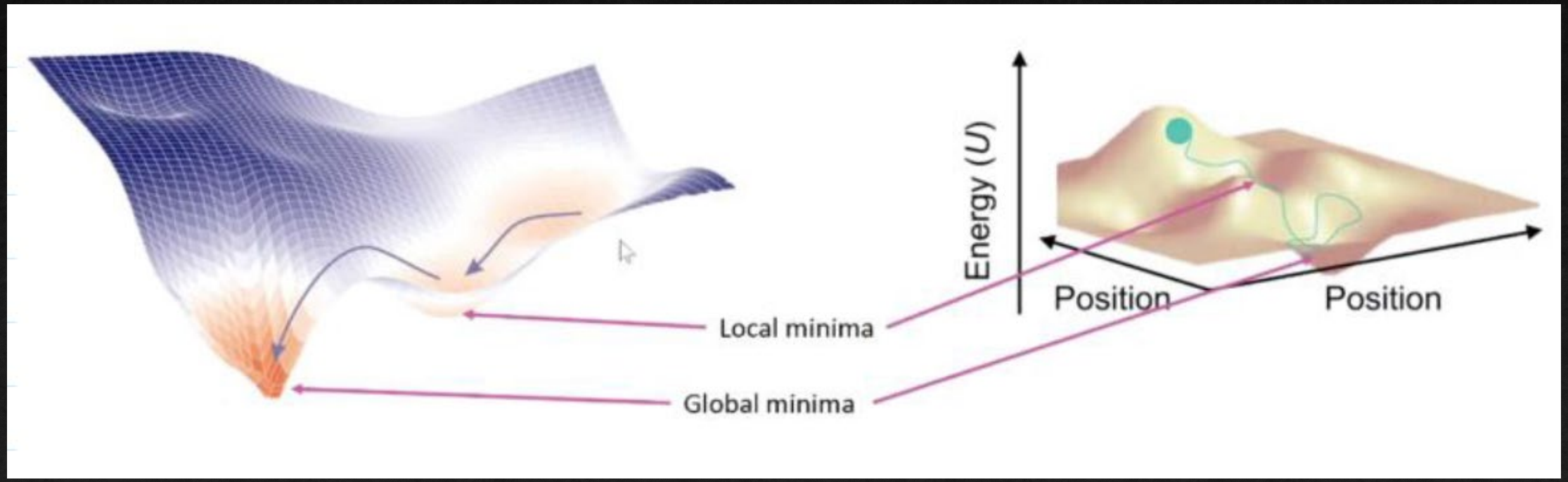
A few common ensembles

- Micro-canconical ensemble (NVE): const # of particles (N), volume (V), energy (E)
- Canonical ensemble (NVT): const # of particles (N), volume (V), temperature (T)
- Isothermal-isobaric ensemble (NPT): const # of particles (N), pressure (P), temperature (T)

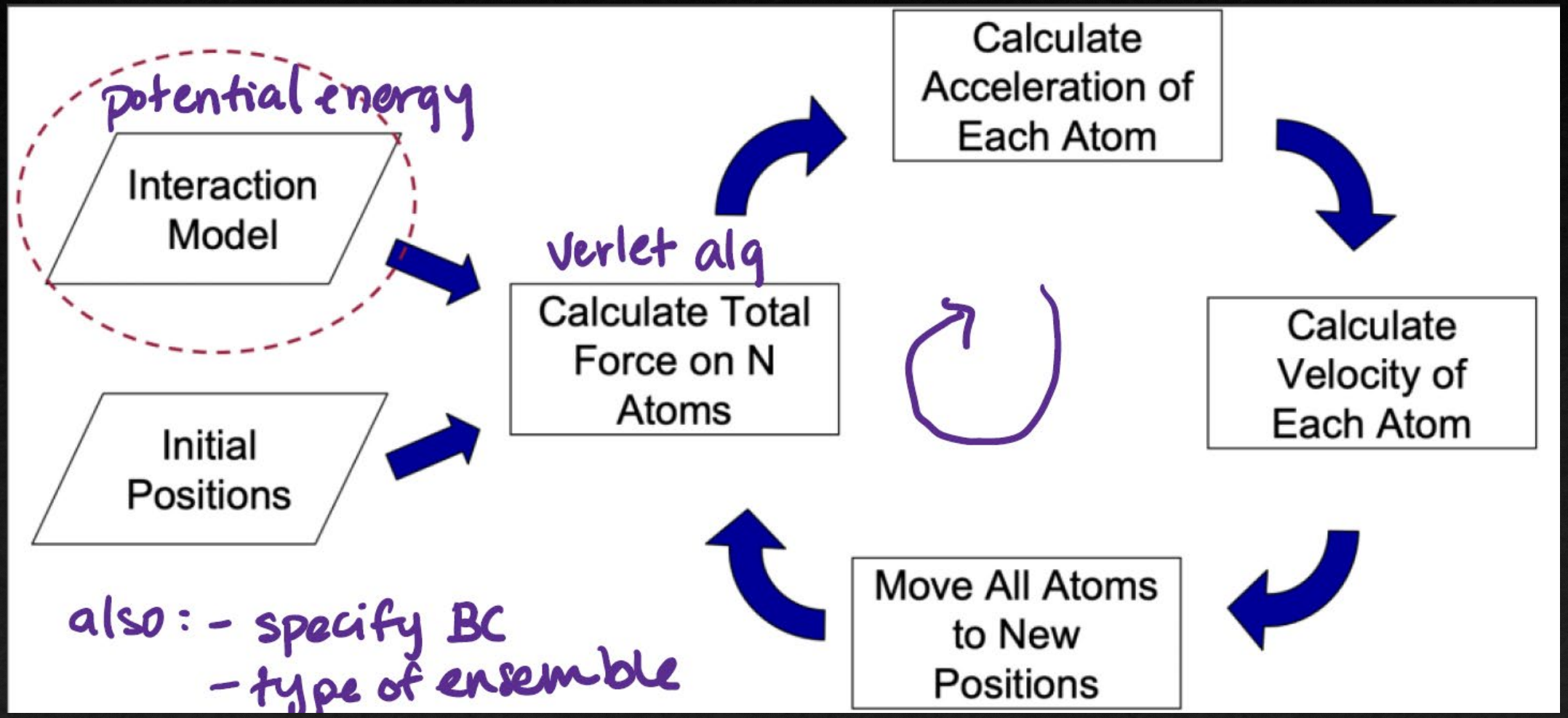
- **Boundary conditions:** usually periodic in a single or multiple dimensions, depending on the system

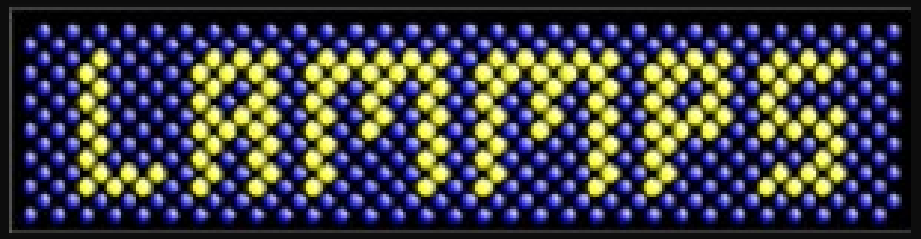
Energy minimization

- Useful when initial configuration is unfavorable
- Energy minimization allows the system to be relaxed before MD simulation
- Can also be performed during a MD simulation to obtain a more favorable configuration

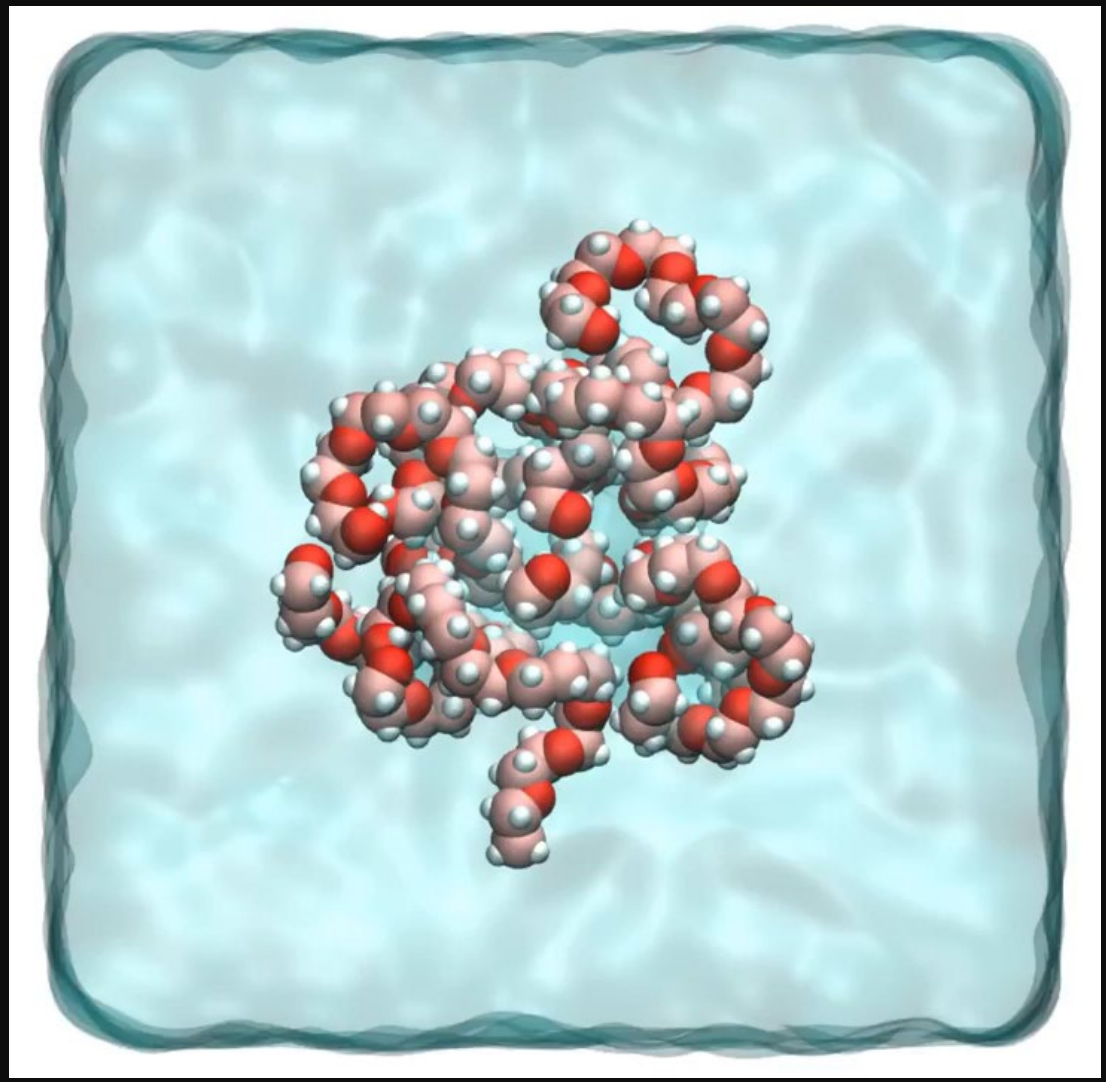


How does everything fit together?

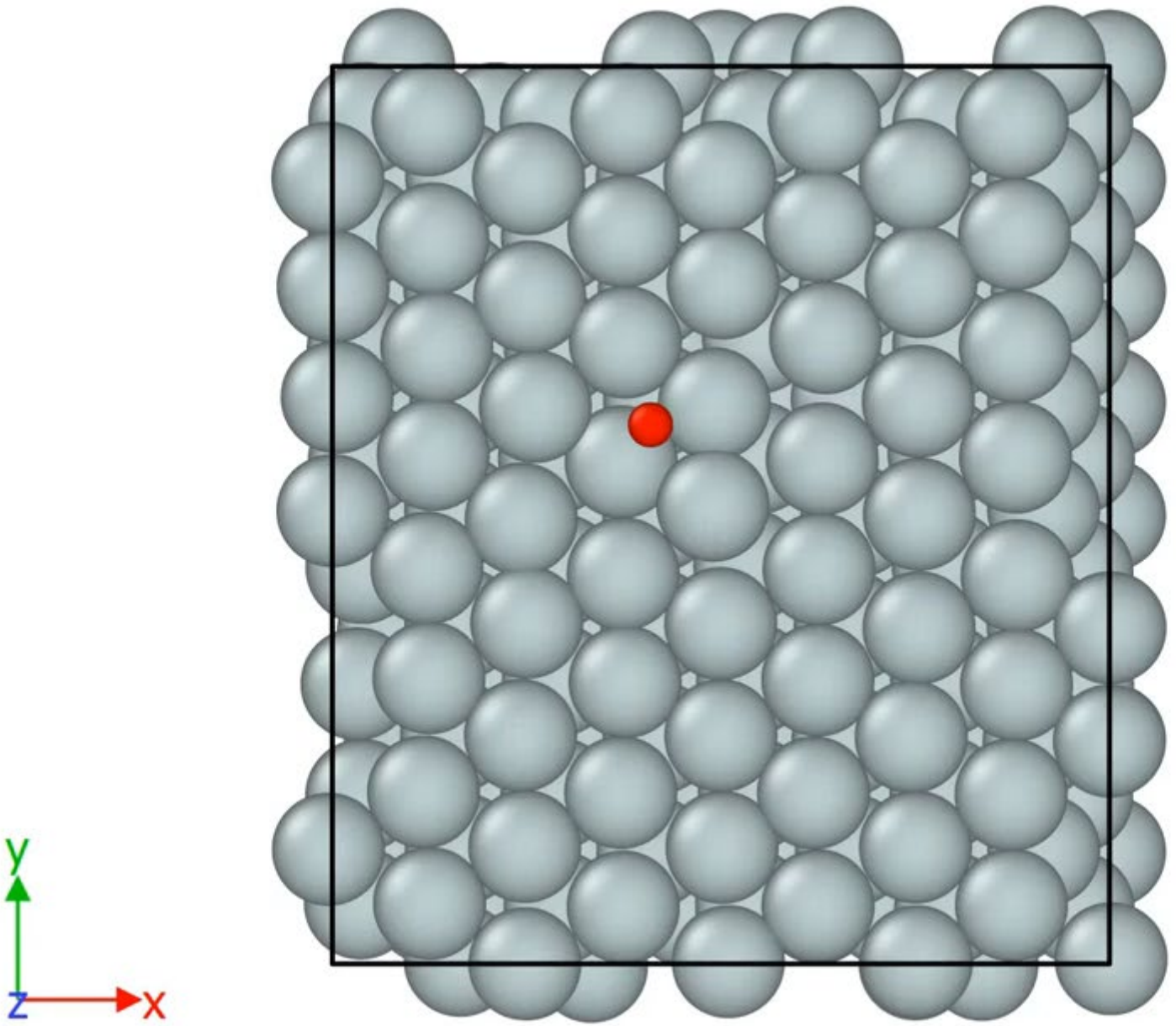


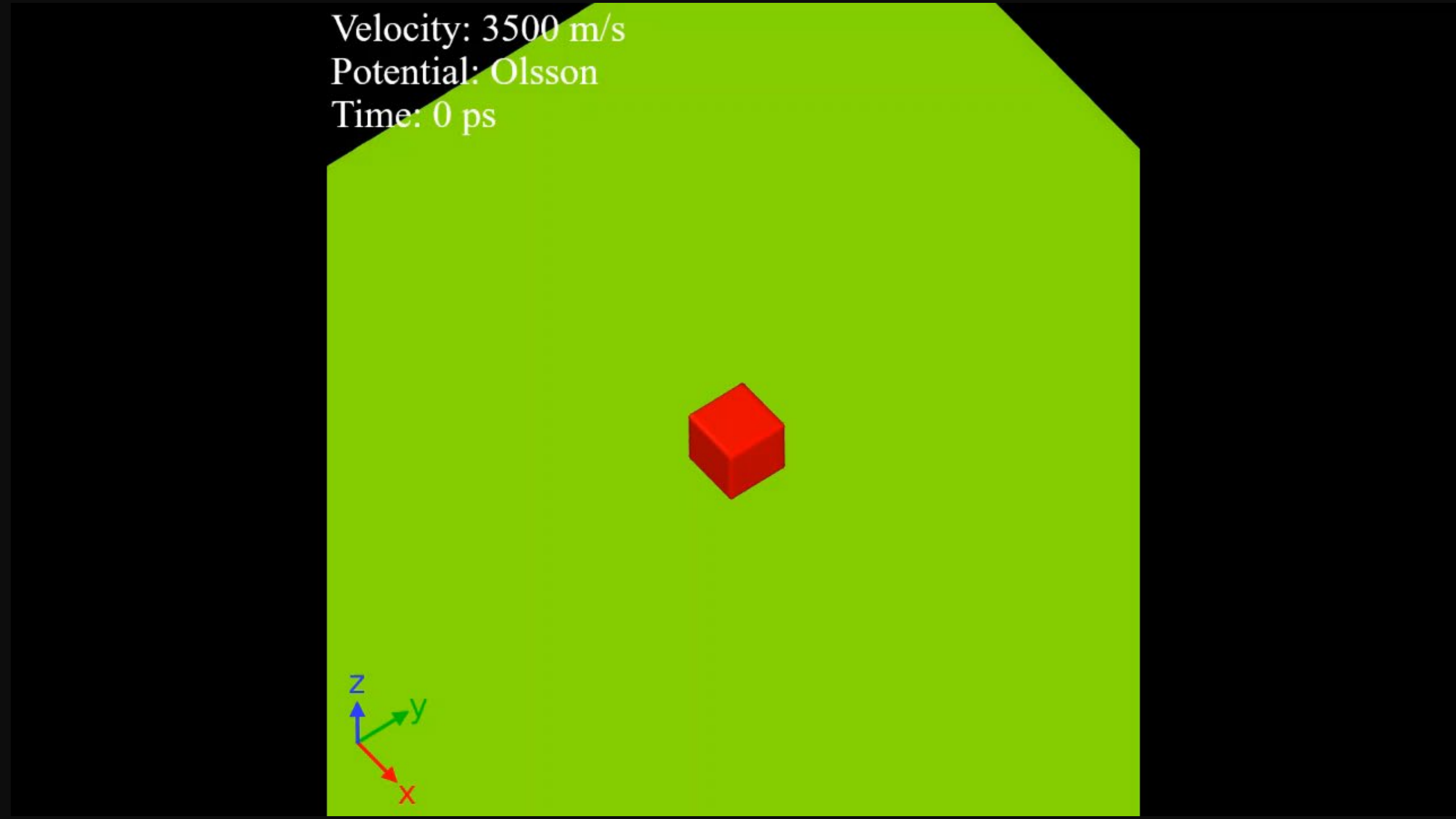


```
boundary p p p
units real

atom_style full
bond_style harmonic
angle_style hybrid harmonic charmm
dihedral_style hybrid harmonic charmm
pair_style lj/cut/coul/long 12

read_data mixture.data

# first equilibration at large temperature
fix mynpt all npt temp 360 360 100 iso 1000 1000 1000
timestep 1.0
thermo 1000
run 20000
```



Carbon Deposition on Nickel surface




Velocity: 3500 m/s
Potential: Olsson
Time: 0 ps
z
y
x

Recent (random) examples

- MD + AI for COVID-19
- MD in drug discovery review
- Food science
- Prof. Gumbart's group at GT