What is MD simulation?

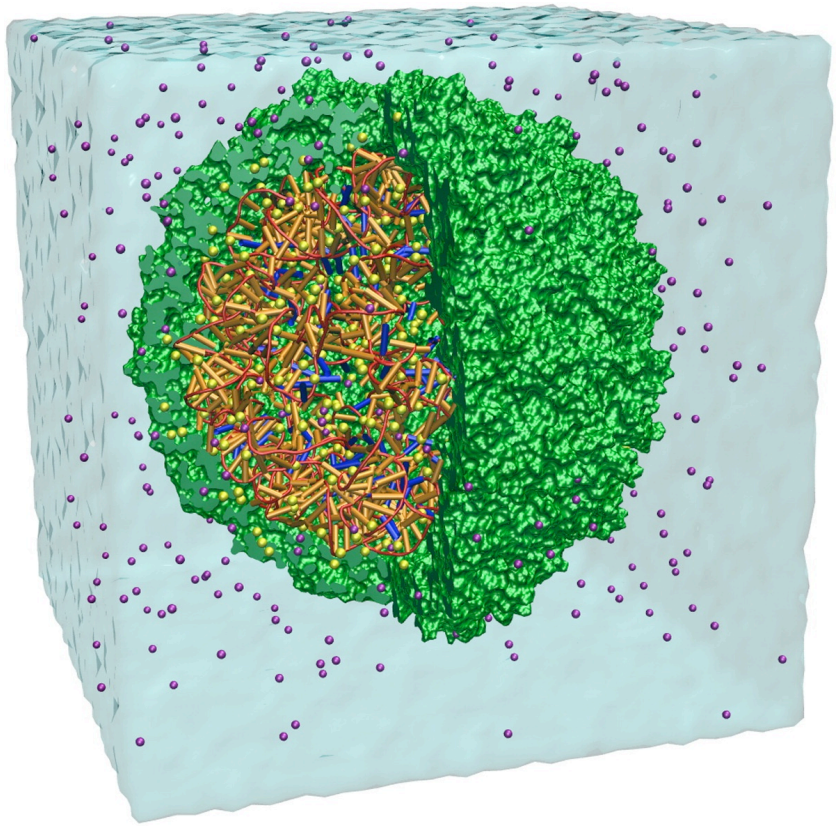
- A form of molecular simulation where atoms and molecules interact through a classical force field
- Electronic (quantum) effects are incorporated into the potential that defines the force, $V(r^N)$.
- Newton's Laws are integrated numerically to yield the individual trajectories of all the particles.
- At each step in time, particle positions and velocities are known.
- Thermodynamic properties are obtained based on the ergodic hypothesis, namely, that a long enough time average is equivalent to an ensemble average.
- MD allows for the determination dynamical properties of the system, e.g. transport coefficients.

Why simulate?

- Necessary when analytic approaches are insufficient
- MD provides very detailed microscopic information, typically unavailable in experiment.
- Provides a way to test theories
- Predict system properties of material at conditions outside of easy experimental reach, or of new materials
- Virtual workbench to explore new ideas - computer experiments!
- Drawback: simulations used to quantitatively determine properties of real systems are only as good as the model [$V(r^N)$].
- However, qualitative relations can still be determined if the model interactions capture the essential features of the real systems.

Some more recent examples

Simulation of an entire virus



Peter L. Freddolino, Anton S. Arkhipov, Steven B. Larson, Alexander McPherson, and Klaus Schulten. Molecular dynamics simulations of the complete satellite tobacco mosaic virus. *Structure*, 14:437-449, 2006.This work presents an all-atom molecular dynamics simulation of a complete virus, the satellite tobacco mosaic virus. Simulations with up to 1 million atoms for over 50 ns demonstrate the stability of the whole virion and of the RNA core alone, while the capsid without RNA exhibits a pronounced instability. Physical properties of the simulated virus particle including electrostatic potential, radial distribution of viral components, and patterns of correlated motion are analyzed and the implications for the assembly and infection mechanism of the virus are discussed.

F=ma

$$\frac{d^2 x_i}{dt^2} = \frac{1}{m_i} F_{x,i}(r^N)$$

- For N particles in 3D, this is a set of 3N coupled ODE's (force on a particle is a function of, in principle, all of the other particles in the system).
- Newton's laws are time reversible, so should the ODE solver be (reversing the direction of time should result in tracing back over the trajectory).
- Energy and momentum should be conserved
- Other desirable features of the algorithm: duplicate classical trajectories, fast, low memory requirement, permit long time step, simple to implement

Verlet Algorithm

$$r(t+\Delta t) = r(t) + \Delta t\, r'(t) + \tfrac{1}{2}\Delta t^2 r''(t) + \tfrac{1}{6}\Delta t^3 r'''(t) + O(\Delta t^4)$$

$$r(t-\Delta t) = r(t) - \Delta t\, r'(t) + \tfrac{1}{2}\Delta t^2 r''(t) - \tfrac{1}{6}\Delta t^3 r'''(t) + O(\Delta t^4)$$

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \Delta t^2 r''(t) + O(\Delta t^4)$$

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \Delta t^2 \frac{F(t)}{m} + O(\Delta t^4)$$

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + O(\Delta t^2)$$

Verlet variants

Leap Frog

$$r(t+\Delta t) = r(t) + \Delta t\, v(t+\tfrac{1}{2}\Delta t)$$

$$v(t+\tfrac{1}{2}\Delta t) = v(t-\tfrac{1}{2}\Delta t) + \Delta t\, F(t)/m$$

$$v(t) = \frac{v(t+\tfrac{1}{2}\Delta t) + v(t-\tfrac{1}{2}\Delta t)}{2}$$

Velocity Verlet

$$r(t+\Delta t) = r(t) + \Delta t\, v(t) + \tfrac{1}{2}\Delta t^2 F(t)/m$$

$$v(t+\Delta t) = v(t) + \tfrac{1}{2}\Delta t[F(t) + F(t+\Delta t)]/m$$

Periodic Boundary Conditions

- Eliminate surface effects from simulations of bulk systems
- Distance between two particles in the simulation box is really the distance between closest images
- The simulation can still suffer finite size effects
- Long wavelength properties still not accessible

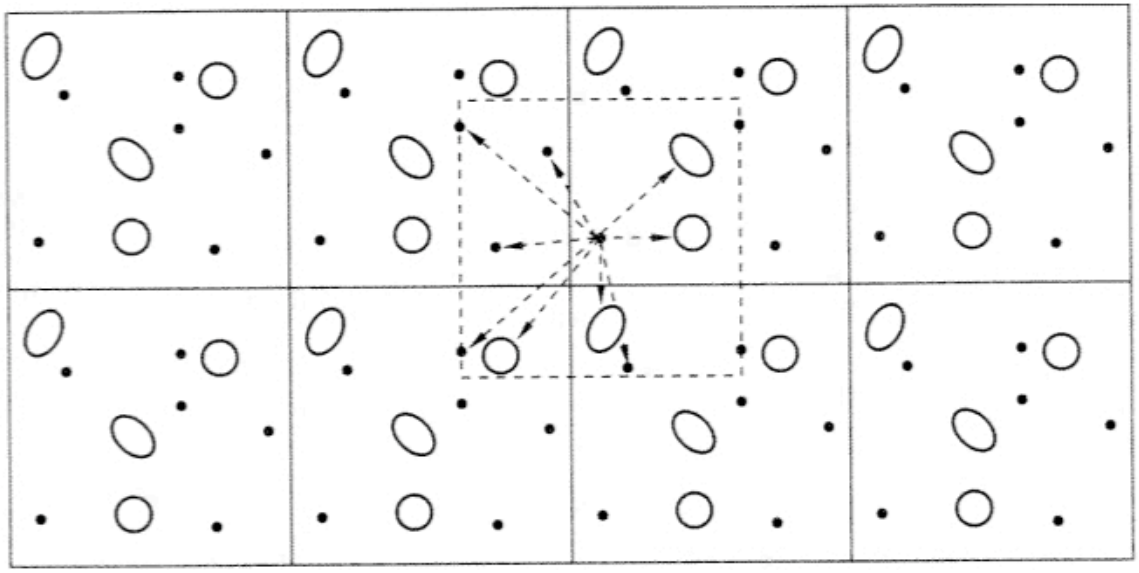
$$\Delta x = x_2 - x_1$$

$$\Delta x \leftarrow \Delta x - box * NINT(\Delta x / box)$$

$$box = 10$$

$$\Delta x = 8$$

$$\Delta x \leftarrow 8 - 10 * NINT(0.8) = -2$$

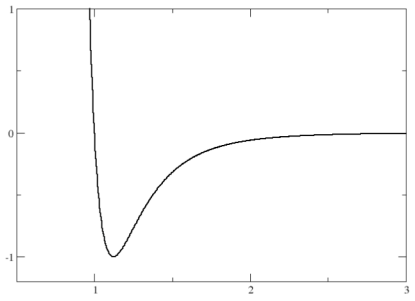


Reduced Units

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\varepsilon \rightarrow unit\ energy$$
$$\sigma \rightarrow unit\ length$$
$$m \rightarrow unit\ mass$$
$$time \leftarrow \sigma\sqrt{m/\varepsilon}$$
$$temperature \leftarrow \varepsilon / k_B$$
$$pressure \leftarrow \varepsilon / \sigma^3$$

$$V^*_{LJ}(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$



- Convenient: (inifinitely) many combinations of ρ, T, ε and σ correspond to the same state.
- Gives values near 1 (from 10^{-3} to 10^{3}), resulting in reduced likelihood of overflow and underflow errors, and
- sometime makes errors easier to spot; e.g. a big number is probably wrong.

$$T^* = k_B T / \varepsilon$$
$$U^* = U / \varepsilon$$
$$P^* = P\sigma^3 / \varepsilon$$
$$\rho^* = \rho\sigma^3$$

$$\sigma_{Ar} = 0.341nm$$
$$\varepsilon_{Ar} / k_B = 119.8K$$
$$\sigma_{Kr} = 0.338nm$$
$$\varepsilon_{Kr} / k_B = 164.0K$$

$$\Delta t^* = 0.001 \rightarrow \Delta t_{Ar} = 2 \times 10^{-15} s$$

Ar at 60K and 850 kg/m^3 and Kr at 82K and 1800 kg/m^3 both correspond to T*=0.5 and ρ*=0.5

Physical quantities

- We must express are the quantities we wish to calculate in terms of particle coordinates and velocities
  - Temperature
  - Potential energy
  - Pressure

$$k_B T_{inst} \equiv \frac{2K}{N_f} = \frac{1}{3N-3}\sum_{i=1}^{N} m_i (v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2)$$

$$U = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} V(r_{ij})$$

$$P_{inst} = \rho k_B T_{inst} + \frac{1}{dV}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \vec{f}_{ij} \cdot \vec{r}_{ij}$$

- Some other quantities we will consider are
  - g(r)
  - Mean square displacement
  - Velocity autocorrelation function
  - Diffusion coefficient, viscosity
  - S(q)