Short Course on Molecular Dynamics Simulation

Lecture 4: Temperature Control

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High Level Course Outline

1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

Temperature Control

- Macroscopic systems
  - Conduction
  - Convection
  - Radiation
- Model atomic system
  - Numerical temperature control (thermostats)
    - Velocity scaling
    - Berendsen
    - Andersen
    - Langevin dynamics
    - Nose-Hoover

Velocity Scaling

- Energy and temperature in an N-body system

$$H(p,r) = E_k(p_N) + U(r_N) = const$$

$$\langle E_k \rangle = \left\langle \frac{1}{2m} \sum_i^N \vec{p}_i^{\,2} \right\rangle = \frac{3}{2} N k_b T$$

$$\left\langle \sum_i^N (m_i \vec{v}_i)^2 \right\rangle = 3MNk_bT$$

$$M \left\langle \sum_i^N \vec{v}_i^{\,2} \right\rangle = 3Nk_bT \quad \Rightarrow \quad T = \frac{M}{3Nk_b} \left\langle \sum_i^N \vec{v}_i \cdot \vec{v}_i \right\rangle$$

Velocity Scaling

- Controlling temperature during an NVE simulation

$$\frac{T^{new}}{T^{old}} = \frac{\frac{M}{3Nk_b}\left\langle \sum_i^N \vec{v}_i^{new} \cdot \vec{v}_i^{new} \right\rangle}{\frac{M}{3Nk_b}\left\langle \sum_i^N \vec{v}_i^{old} \cdot \vec{v}_i^{old} \right\rangle}$$

$$\frac{T^{new}}{T^{old}} = \frac{\left\langle \sum_i^N \vec{v}_i^{new} \cdot \vec{v}_i^{new} \right\rangle}{\left\langle \sum_i^N \vec{v}_i^{old} \cdot \vec{v}_i^{old} \right\rangle} \quad \Rightarrow \quad v_i^{new} = v_i^{current} \sqrt{T^{new} / T^{current}}$$

Berendsen

- Berendsen; adjustable parameter determines how tightly bath and system are coupled
  - Simple velocity scaling as the coupling parameter approaches the integration timestep
  - Suggested value $\Delta t / \tau \sim 0.0025$

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_{bath} - T(t)\right) \qquad \Delta T = \frac{\Delta t}{\tau}\left(T_{bath} - T(t)\right)$$

Andersen

- Andersen heat bath → stochastic impulsive forces acting on randomly selected particles
  - Coupling strength → frequency of stochastic collisions, ν

1. Start with a set of positions and momenta
2. Integrate equations of motion
3. Select particles to undergo collision with heat bath; probability of selection $\nu\Delta t$
4. The velocities of particles selected for collision are taken from a Boltzmann distribution at the desired temperature

Andersen

- Coupling strength → frequency of stochastic collisions, ν
  - The value of ν is related to the intermolecular collision frequency ν_c (a function of the density and thermal conductivity)

$$\nu = \frac{\nu_c}{N^2/3}$$

  - For each particle, a random number is selected between 0 and 1
  - If that number is less than $\nu\Delta t$, its momenta are reset

Langevin Dynamics

- Langevin method simulates interactions with a solvent
- Two terms added to the equation of motion
  - Friction term removes energy → frictional drag on the system moving through a solvent
  - Random term adds energy → collisions/interactions with solvent molecules

$$m\vec{a} = \vec{F} - m\gamma\vec{v} + \vec{R}$$

Nosé-Hoover

- Includes the heat bath explicitly as an additional degree of freedom
- Widely used algorithm
- Introduce an artificial variable s that plays the role of a time scaling parameter
  - "mass" Q
  - "velocity" $\dot{s}$

Nosé-Hoover

- Nosé-Hoover Hamiltonian

$$H_{Nose-Hoover} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i s^2} + U(\vec{r}^{\,N}) + \frac{p_s^2}{2Q} + (f+1)k_b T \ln s$$

- Magnitude of Q controls coupling strength
  - Too large → loose coupling → poor temperature control
  - Too small → tight coupling → high frequency temperature oscillation
  - Can be related to effective relaxation time

$$Q = Cfk_bT$$

found by testing the system oscillation about a desired T