Molecular Dynamics

Statistical mechanics

- Need ensemble averages for thermodynamic properties
- Ergodic hypothesis: time average = ensemble average
- Classical simulation of atomic motion over time

Propagation

- Integrate Newton's equations of motion
- Small time steps (femtoseconds)
- Repeated force evaluations from potential energy surface

Newton's Equations of Motion

Classical mechanics governs molecular motion:

Acceleration of atom i — Position of atom i

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{38}$$

Force on atom i — Gradient of potential energy

Requirements for MD integrator

- Stability over long time scales
- Time reversibility (energy conservation)
- Computationally efficient
- Access to positions and velocities

Verlet Algorithm

Simple and robust integration scheme based on Taylor expansions:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\,\Delta t + \tfrac{1}{2}\mathbf{a}(t)\,\Delta t^2 + \mathcal{O}(\Delta t^4) \tag{39}$$

Position — Timestep — Velocity — Acceleration — Big-O notation

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\,\Delta t + \tfrac{1}{2}\mathbf{a}(t)\,\Delta t^2 + \mathcal{O}(\Delta t^4) \tag{40}$$

Adding both equations:

$$\mathbf{r}(t + \Delta t) = 2\,\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \mathbf{a}(t)\,\Delta t^2 \tag{41}$$

More practical variant that gives direct access to velocities:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\,\Delta t + \tfrac{1}{2}\mathbf{a}(t)\,\Delta t^2 \tag{42}$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \tfrac{1}{2}[\mathbf{a}(t) + \mathbf{a}(t + \Delta t)]\,\Delta t \tag{43}$$

Temperature control

- Canonical ensemble (NVT): constant temperature
- Microcanonical ensemble (NVE): constant energy

Mass of atom i · Boltzmann constant · Temperature

$$E_{\text{kin}}(t) = \frac{1}{2}\sum_i m_i \mathbf{v_i}^2 = \langle E_{\text{kin}} \rangle = \frac{1}{2} n k_B T \tag{44}$$

Kinetic energy · Velocity · number of degrees of freedom

Challenges:

- Continuous trajectory
- Conserve Autocorrelation / dynamic properties
- Instantaneous temperature

Idea

- Weak coupling to external heat bath
- Rescales velocities to target temperature
- Simple but not rigorous

$$\mathbf{v}_i' = \mathbf{v}_i \sqrt{\frac{\langle E_{\text{kin}} \rangle}{E_{\text{kin}}(t)}} \tag{45}$$

Problems

- Flying ice cube
- Jumps

Berendsen et al. J Chem Phys, 1984.

Idea

- virtual random collisions
- sample target momentum of particles from Boltzmann distribution
- effectively: adding random forces

$$P(t) = \nu \exp(-\nu t) \tag{46}$$

ν: Andersen parameter

$P(t)$: Particle collision frequency

Andersen, J Chem Phys, 1980.

Canonical Sampling through velocity rescaling (CSVR)

Idea

- Scale not exactly, but with noise
- Coupling timescale τ

Properties

- Samples canonical ensemble
- Has conserved quantity, close to true energy

Bussi et al. J Chem Phys, 2007.

Idea

- random kicks per atom
- added friction term in equations of motion

$$\mathbf{v}_i = \mathbf{p}_i / m_i \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i - \gamma \mathbf{p}_i + \mathbf{f}_i \tag{47}$$

Random kicks

Friction coefficient

$$|\mathbf{f}_i| \in \mathcal{N}(0, 2\, m_i\, \gamma\, k_B\, T / \Delta t) \tag{48}$$

Hoover, Phys Rev Lett, 1982.

Idea

- Scale velocities by dynamic virtual coordinate s
- Propagate s
- Controll through mass

$$\mathcal{L}_s = \frac{1}{2} Q \dot{s}^2 - n k_B T \ln s \tag{49}$$

Degrees of freedom

Ficticious mass

Nosé, J Chem Phys, 1984. Hoover, Phys Rev A, 1985.

Time step selection

- Typically 0.5-2 fs for organic molecules
- Must resolve fastest motions (C-H stretching)
- Stability criterion: $\Delta t < 2\sqrt{m/k_{\text{max}}}$

Boundary conditions

- Periodic boundary conditions for bulk systems
- Minimum image convention for interactions

Equilibration

- Initial relaxation period before data collection
- Monitor energy, temperature, and structural properties

Molecular Dynamics

- Classical simulation of atomic motion using Newton's equations
- Time evolution through numerical integration (Verlet algorithms)
- Access to dynamic properties and ensemble averages

Control

- Thermostats maintain constant temperature
- Time step selection critical for stability
- Equilibration required before data collection