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

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

Simple and robust integration scheme based on Taylor expansions:

Big-O notation

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

Position   Timestep   Velocity   Acceleration

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

Adding both equations:

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

More practical variant that gives direct access to velocities:

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

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

⚖ Temperature control

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

Mass of atom i, Boltzmann constant, Temperature

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

Kinetic energy   Velocity   number of degrees of freedom

Challenges:

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

$\bigcirc$ Idea

– Weak coupling to external heat bath

– Rescales velocities to target temperature

– Simple but not rigorous

$$\mathsf{v_i}' = \mathsf{v_i}\sqrt{\frac{\langle E_{\mathsf{kin}}\rangle}{E_{\mathsf{kin}}(t)}} \qquad (45)$$

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

Andersen parameter

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

Particle collision frequency

Andersen, J Chem Phys, 1980.

◯ 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

$$\mathsf{v}_i = \mathsf{p}_i/m_i \qquad \dot{\mathsf{p}}_i = \mathsf{F}_i - \underset{\text{Friction coefficient}}{\gamma}\mathsf{p}_i + \overset{\text{Random kicks}}{\mathsf{f}_i} \tag{47}$$

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

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: $\Delta t < 2\sqrt{m/k_{\max}}$

⇄ 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