

Lecture V: Molecular Dynamics

Short interlude about Classical Mechanics

A brief timeline of developments in classical mechanics:

- **Newton:** 1687
- **Lagrange:** 1760
- **Hamilton:** 1834

Newtonian Mechanics

- **Second Law:** In Cartesian coordinates, the force on a particle is given by $\underline{F}_i = m \cdot \underline{a}_i$, where the acceleration is $\underline{a}_i = \ddot{\underline{r}}_i$.
- **Linear Momentum:** The momentum is defined as $\underline{p}_i = m_i \underline{v}_i = m \dot{\underline{r}}_i$.
- **Total Energy:** The total energy $E = T + V$ is the sum of kinetic energy (T) and potential energy (V).
 - $T = \sum_{i=1}^N \frac{1}{2} m v_i^2$
 - $V = V(\{\underline{r}_i\})$
- For conservative systems, the force is the negative gradient of the potential energy: $\underline{F}_i = -\frac{\partial V}{\partial \underline{r}_i}$.

Lagrangian Mechanics

This formulation is independent of the coordinate system.

- The Lagrangian (L) is defined as the difference between kinetic and potential energy: $L := T(\{\dot{\underline{r}}_j\}) - V(\{\underline{r}_j\})$.
- Using generalized coordinates q_i and generalized velocities \dot{q}_i , the equations of motion are given by the **Euler-Lagrange equation**:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

Hamiltonian Mechanics

This is a reformulation in terms of coordinates and their conjugate momenta.

- The **canonical momentum** is defined as $\tilde{p}_i = \frac{\partial L}{\partial \dot{q}_i}$.
- The **Hamiltonian** (H) is defined via a Legendre transformation of the Lagrangian:

$$H = \sum_{i=1}^N \tilde{p}_i \dot{q}_i - L(\{\dot{q}_i\}, \{q_i\}) = H(\{\tilde{p}_i\}, \{q_i\})$$

- **Hamilton's Equations of Motion** are a set of first-order differential equations:

$$\frac{\partial H}{\partial p_i} = +\dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i$$

Conservation Laws and Symmetries

- According to **Noether's theorem**, every continuous symmetry of a system corresponds to a conserved quantity.
- If the Hamiltonian has no explicit time dependence, it is a conserved quantity, which physically represents the total energy of the system.
- **Symmetries and Conserved Quantities (CQ):**
 - **Homogeneity of time** (invariance under a time shift $t \rightarrow t' = t + \tau$) corresponds to the conservation of **energy**.
 - **Homogeneity of space** (invariance under a spatial translation $\underline{r}' = \underline{r} + \underline{d}$) corresponds to the conservation of **momentum**.

Phase Space and the Liouville Equation

- **Phase Space:** This is a $6N$ -dimensional space spanned by the generalized coordinates and their conjugate momenta for an N -particle system. A single point in phase space completely defines the state of a classical system, and its path over time describes the system's evolution.
- The **Liouville equation** describes the time evolution of the phase space probability density function, $\rho(p, q, t)$:

$$\frac{\partial \rho}{\partial t} = - \sum_{j=1}^{3N} \left(\frac{\partial H}{\partial p_j} \cdot \frac{\partial \rho}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial \rho}{\partial p_j} \right)$$

- Using the Poisson bracket, $\{A, B\} := \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right)$, the equation can be written more compactly:

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\} = -i\hat{L}\rho$$

where \hat{L} is the Liouville operator.

- **Liouville's Theorem:** The total time derivative of the phase space density is zero, $\frac{d\rho}{dt} = 0$, which implies that the density of states in the vicinity of a system's trajectory is constant over time. For a system in thermal equilibrium, the state is stationary, meaning $\frac{\partial \rho}{\partial t} = 0$.

Molecular Dynamics (MD)

MD simulations solve Newton's equations of motion, $m_i \ddot{\underline{r}}_i = \underline{F}_i = -\underline{\nabla}_i V(\{\underline{r}_i\})$, by discretizing them in time.

- **Time Step (δt):** Must be small compared to the fastest dynamics in the system.
- **Total Time (t_{max}):** Must be large compared to the slowest dynamics of interest.

Integration Algorithms

The goal is to find an efficient and accurate method to integrate the equations of motion.

- **Euler Algorithm:** This is the simplest method, based on a first-order Taylor expansion:

$$\underline{r}(t_0 + \delta t) \approx \underline{r}(t_0) + \underline{v}(t_0)\delta t + \frac{1}{2m}\underline{F}(t_0)\delta t^2$$

However, it is not time-reversible, does not conserve energy, and does not conserve phase space volume.

- **Verlet Algorithm:** This algorithm overcomes the limitations of the Euler method and possesses the correct physical properties. It is derived by combining forward and backward Taylor expansions:

- $\underline{r}(t_0 + \delta t) = \underline{r}(t_0) + \underline{v}(t_0)\delta t + \frac{1}{2m}\underline{F}(t_0)\delta t^2 + \mathcal{O}(\delta t^3)$
- $\underline{r}(t_0 - \delta t) = \underline{r}(t_0) - \underline{v}(t_0)\delta t + \frac{1}{2m}\underline{F}(t_0)\delta t^2 - \mathcal{O}(\delta t^3)$

Adding these two equations yields the position update formula:

$$\underline{r}(t + \delta t) = 2\underline{r}(t) - \underline{r}(t - \delta t) + \frac{1}{m}\underline{F}(t)\delta t^2$$

The local error for this algorithm is on the order of $\mathcal{O}(\delta t^4)$.