

MOLECULAR DYNAMICS OF WATER

Group2

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1. Familiarize with the given dynamical system and discuss the properties.
 - Explain the dynamics induced by each of the terms of the potential energy V and determine the equations of motion for this Hamiltonian system.

Molecular dynamics

Molecular dynamics simulation consists of the numerical, step-by-step, solution of the classical equations of motion.

For an N-body system we employ the vector notation:

$$\mathbf{f} = \mathbf{M}\mathbf{a}$$

with the acceleration

$$\mathbf{a} = \frac{d}{dt}\mathbf{v} = \mathbf{M}^{-1}\frac{d}{dt}\mathbf{p}$$

we get just

$$\mathbf{f} = \frac{d}{dt}\mathbf{p} \quad (1)$$

and using

$$\mathbf{p} = \mathbf{M}\frac{d}{dt}\mathbf{q} \quad (2)$$

we have

$$\mathbf{f} = \mathbf{M}\frac{d^2}{dt^2}\mathbf{q}$$

Thus, given a starting condition $q_i(0), p_i(0)$, by applying a suitable numerical integration scheme to equations (1)(2), we can get the entire dynamical trajectory $q_i(t), p_i(t)$ for anytime $t \in 0^+$.

For this purpose we need to be able to calculate the forces f_i acting on the atoms and these are usually derived from a potential energy $V(q^n)$, where $q^n = (q_1, q_2, \dots, q_n)$ represents the complete set of \mathbb{R}^3 atomic coordinates.

Bonding Potentials

$V_{\text{int}}(q^n)$ representing intra-molecular potential and this part includes harmonic valence potential and bond potential respectively.

$$V_{\text{int}}(q^n) = \frac{1}{2} \sum_{(h_1, o, h_2) \in \mathcal{M}} k_{\theta}(\theta(q_{h_1}, q_o, q_{h_2}) - \theta_{eq})^2 + \frac{1}{2} \sum_{l=1}^2 k(q_{h_l} - q_o - q_{eq})^2 \quad (3)$$

Non-bonded Interactions

The part of the potential energy $V_{\text{ext}}(q^n)$ representing non-bonded interactions between atoms. While in the flexible SPC water model, it is written

$$V_{\text{ext}}(q^n) = \sum_{i \neq j \in \mathcal{O}} \frac{A}{\|q_i - q_j\|^{12}} - \frac{B}{\|q_i - q_j\|^6} + C \sum_{M_1 \neq M_2 \in \mathcal{M}} \sum_{\substack{i \in M_1 \\ j \in M_2}} \frac{c_1 c_2}{\|q_i - q_j\|} \quad (4)$$

The first term is the Lennard-Jones interaction between the oxygen atoms while the second term represents the reaction field corrected Coulomb interaction between all pairs of charges on different molecules.

Force Calculation

Since we have specified the potential energy function $V(q^n)$, the next step is to calculate the atomic forces.

$$f_i = -\frac{\partial}{\partial q_i} V(q^n)$$

In part of the potential energy $V_{\text{ext}}(q^n)$, it is simple site-site potentials, we can take derivation on both Lennard-Jones potential and Coulomb potential to get the force.

– Lennard-Jones interaction:

$$\begin{aligned} LJ(q_{ij}) &= \frac{A}{\|q_i - q_j\|^{12}} - \frac{B}{\|q_i - q_j\|^6} \\ &= 4\epsilon \left[\left(\frac{\sigma}{\|q_i - q_j\|} \right)^{12} - \left(\frac{\sigma}{\|q_i - q_j\|} \right)^6 \right] \\ \frac{dLJ(q_{ij})}{dq_{ij}} &= 4\epsilon \left[-12 \frac{\sigma^{12}}{\|q_i - q_j\|^{13}} + 6 \frac{\sigma^6}{\|q_i - q_j\|^7} \right] \\ \vec{F}_i &= - \sum_{j \neq i} 24 \frac{\epsilon \sigma^6 (\vec{q}_i - \vec{q}_j)}{\|q_i - q_j\|^8} \left[1 - 2 \left(\frac{\sigma}{\|q_i - q_j\|} \right)^6 \right] \end{aligned}$$

– Coulomb interaction:

$$\vec{F}_i = \frac{c_i}{4\pi\epsilon_0} \sum_{M_1 \neq M_2 \in \mathcal{M}} \sum_{\substack{i \in M_1 \\ j \in M_2}} c_j \frac{\vec{q}_i - \vec{q}_j}{\|q_i - q_j\|^3}$$

In part of the potential energy $V_{\text{int}}(q^n)$, atoms interact within their own molecule.

– Bond potential:

the force produced on one hydrogen atom is

$$\vec{f}_h = -k(q_h - q_o - q_{eq}) \cdot \frac{\vec{q}_h - \vec{q}_o}{\|q_h - q_o\|} \quad (5)$$

the force produced on the oxygen atom is the join of the two opposite force on hydrogen atoms.

- Valence potential:

The partial derivative of valence potential $V(\theta)$ according to the angle θ is

$$\frac{\partial V(\theta)}{\partial \theta} = k_\theta(\theta(q_{h_1}, q_o, q_{h_2}) - \theta_{eq})$$

The partial derivative of valence potential $V(\theta)$ according to the position q_{h_1} of h_1 is

$$\frac{\partial V(\theta)}{\partial q_{h_1}} = k_\theta(\theta(q_{h_1}, q_o, q_{h_2}) - \theta_{eq}) \cdot \frac{\partial \theta}{\partial q_{h_1}}$$

we have

$$\frac{\partial \theta}{\partial q_{h_1}} = \frac{1}{\|q_{h_1} - q_o\|}$$

Let \vec{N}_{h_1} be the normalized vector in the water molecule plane, orthogonal to $\vec{q}_{h_1} - \vec{q}_o$

$$\vec{N}_{h_1} = \text{norm}((\vec{q}_{h_1} - \vec{q}_o) \times ((\vec{q}_{h_1} - \vec{q}_o) \times (\vec{q}_{h_2} - \vec{q}_o)))$$

The force applied on h_1 is then:

$$\vec{f}_{h_1} = -k_\theta(\theta(q_{h_1}, q_o, q_{h_2}) - \theta_{eq}) / (\|q_{h_1} - q_o\|) \cdot \vec{N}_{h_1} \quad (6)$$

In the same way, the force applied on h_2 can be calculated.

The sum of the forces should be null, thus the force applied on oxygen atom is:

$$\vec{f}_o = -\vec{f}_{h_1} - \vec{f}_{h_2} \quad (7)$$

- Discuss the computational restrictions raised by the individual terms in the potential energy function.