

MOLECULAR DYNAMICS OF WATER

1. INTRODUCTION

Solving Newton's equations of motion does not immediately suggest activity at the cutting edge of research. The molecular dynamics algorithm in most common use today may even have been known to Newton. [1] In strong contrast to the prepping quote, taken from an introductory text on molecular dynamics, one can argue that the simulation of large particle systems on multiple scales is non trivial and an ongoing endeavour. To familiarize with the computational tasks, this project considers one of the most ubiquitous molecules, water. Despite its relative simple structure, the importance of water as solvent results in a whole zoo of available models.

2. MODEL

Consider n particles which positions and momenta are denoted by $q_i \in \mathbb{R}^3$ and $p_i \in \mathbb{R}^3$ respectively. Let $I := \{1, \dots, n\}$, then the set of all indices describing Oxygen atoms is denoted by $\mathcal{O} \subseteq I$, the set of indices for Hydrogen atoms by $\mathcal{H} \subseteq I$ and the set of index triples (H, O, H) for water molecules \mathcal{M} . The Hamiltonian energy functional for a flexible SPC water model is given by

(1)

$$H(p_1, \dots, p_n, q_1, \dots, q_n) = T(p_1, \dots, p_n) + V_{\text{int}}(q_1, \dots, q_n) + V_{\text{ext}}(q_1, \dots, q_n)$$

$$(2) \quad T(p_1, \dots, p_n) = \frac{1}{2} \sum_{i \in I} \frac{\|p_i\|^2}{m_i}$$

$$(3) \quad V_{\text{int}}(q_1, \dots, q_n) = \sum_{(h_1, o, h_2) \in \mathcal{M}} k_\theta (\theta(q_{h_1}, q_o, q_{h_2}) - \theta_0)^2 + \sum_{l=1}^2 k(q_{h_l} - q_o)^2$$

$$(4) \quad V_{\text{ext}}(q_1, \dots, q_n) = \sum_{i \neq j \in \mathcal{O}} \frac{A}{\|q_i - q_j\|^{12}} - \frac{B}{\|q_i - q_j\|^6} + C \sum_{M_1 \neq M_2 \in \mathcal{M}} \sum_{\substack{i \in M_1 \\ j \in M_2}} \frac{c_1 c_2}{\|q_i - q_j\|}.$$

Hereby $m_i > 0$ and $c_i \in \mathbb{R}$ denote the atomic masses and charges respectively. Furthermore C is the Coloumb constant, $k_\theta > 0$ denotes the stiffness of the covalent bonds and $k_\theta > 0$ the stiffness of the angle between both covalent bonds. A and B are the constants which determine the shape of the Lennard-Jones potential terms.

3. TASKS

3.1. Preliminaries. Familiarize with the given dynamical system and discuss the properties.

- Explain the dynamics induced by each of the terms of the potential energy V .
- Determine the equations of motion for this Hamiltonian system.
- Choose an appropriate numerical integration method to compute trajectories of the resulting system of ordinary differential equations.
- Discuss the computational restrictions raised by the individual terms in the potential energy function.

3.2. Direct Simulation. To check your findings, simulate water molecules on the whole space \mathbb{R}^3 .

- Implement the numerical integration scheme of your choice and compute trajectories of an ensemble of water molecules. For this purpose find a compatible, but nontrivial initial state.
- Visualize output of the simulation.

3.3. Periodic Boundary Conditions. In many cases one would like to consider a microscopic box of water taken from a (much) larger medium. Therefore periodic boundary conditions seem a to be good assumption.

- Not all of the terms in the potential energy function are local. What are the implications for your algorithm.
- Use a cut off for all short range interactions and implement periodic boundary conditions on a box which has edges at least as long as the cut off radius.
- Approximate the far field interaction by the Ewald Summation.
- Explain the computational complexity of your algorithm and validate by benchmarks.
- Improve the far field evaluation by using the particle Ewald Summation.

REFERENCES

- [1] G.-S.-I. e.V. für Üternationale Bildung und Europäische Zusammenarbeit, J. von Neumann-Institut für Computing, J. G.-U. Mainz, M.-P.-I. für Biophysikalische Chemie, and M.-P.-I. für Polymerforschung, eds., *Computational soft matter: from synthetic polymers to proteins; Winter School, 29 February - 6 March 2004, Gustav-Stresemann-Institut, Bonn, Germany. 2: Lecture notes*. No. 23 in NIC series, Jülich: NIC, 2004. OCLC: 253989746.