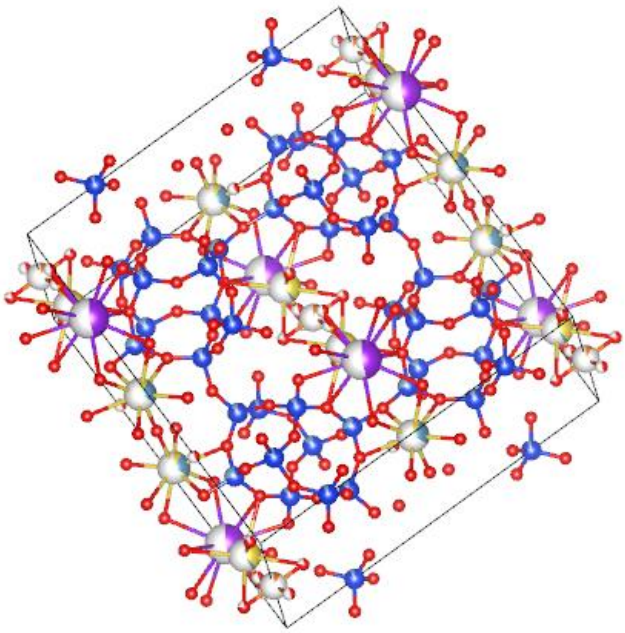
"MD-SIMULATION RESEARCH (FROM ATOMIC FRAGMENTS TO MOLECULAR COMPOUND)" INTRODUCTORY COURSE REPORT

WAVE 4 (May 24, 2021 – July 2, 2021)



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1. Introduction

MD-simulation was originally developed in early 1950s, USA and since then several of methods and techniques developed till the present. Molecular dynamic simulation (MD-simulation) has wide range of application in the interdisciplinary fields such as molecular biology, material chemistry, biophysics and nanotechnology.

What does it do?

MD-simulation is computational modelling method for analyzing the interaction between atom and molecules based on Newton's law. We can do simulation and modelling on various type of surface interactions such as biomolecules with inorganic surfaces, minerals, polymers, nanoparticles, and carbon allotropes [1].

Why MD-simulation?

The simulation techniques can be divided to Quantum mechanics, DFT methods, MD-simulations (All-atom (AA), Coarse grain (CG), Implicit solvent (IS), and Brownian dynamics (BD) as shown in Figure 1.
Usually, biomolecules have thousands and thousands of atom in their structure and MD-simulation gives us the possibility to calculate their interaction parameters despite 10000-30000 atom numbers. For example, atom number is limited up 100-200 atoms in DFT method. Moreover, we can simulate the bonds, electrostatic forces and potentials by MD-simulation while DFT method calculates only the electronic state of atom or molecules.

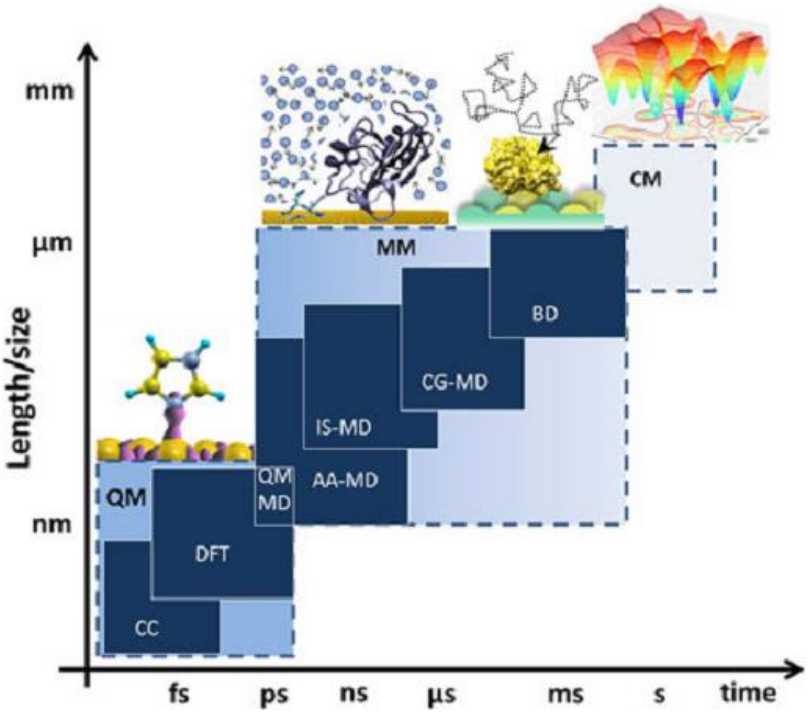

Fig 1. Typical time and length scales of different simulation techniques [1]

2. Theoretical background on MD-simulation

In quantum simulation, *Kohn-Sham theorem* is used which is describes single particle. In MD simulation, *Hohenberg–Kohn theorem* is used which states that the ground state of any interacting many particle systems with a given fixed interparticle interaction is a unique functional of the electron density.

The simulation process is depend on 2 factor: size (modelling atom or molecule numbers) and simulation time (dynamic). If simulating atom or molecules are too big, it takes long time to complete the simulation process. Therefore, CG or Cut-off methods can be used for reducing simulation duration.

CG: CG part should contain the atom or molecules can represent the characteristics of the calculating system as shown in Figure 2.

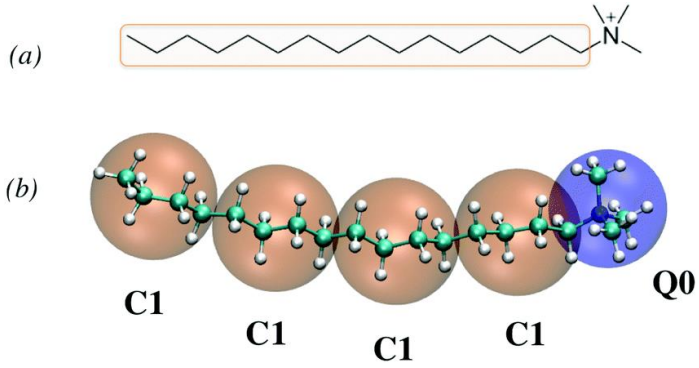

Fig 2. a) Coarse grained molecules, b) original molecular structure [2]

Cut-off: Only cut-off part is used for the calculation. But this method can give a damage to sensitive biomolecules and it may causes the artificial energy fluctuation.

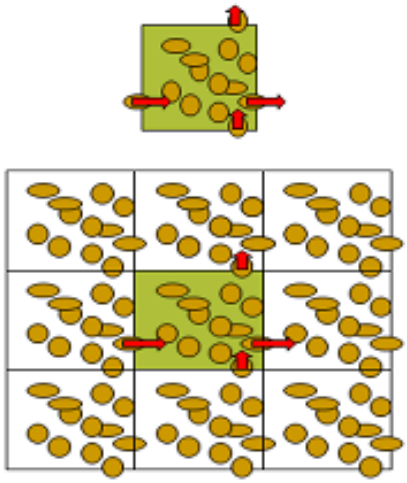

Fig 3. Cut-off area [3]

In MD-simulation, we calculate 3 main potentials and forces in the systems:

1. Intramolecular interactions for chemical bonds
2. Intermolecular interactions for Van der Waals forces
3. Coulomb electrostatic forces

Inter-atomic Potential

Inter-atomic interaction means atoms interacting with each other and this is expressed by Lennard-Jones potential. Lennard-Jones potential describes Van der Waals non-bonding interaction between two atoms. Lennard-Jones potential expressed by following equation:

$$V(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

In which *V(r)* represents the Lennard-Jones potential, ε is unit of energy, and *r* is the distance between centers of two atoms and σ is the average atomic density.

Intra-molecular Forces

Intra-molecular forces are the forces that hold atoms together within a molecule. Following forces will be calculated in MD-simulations:

1. Bond potentials

Bond force shows the contribution of chemical bonds to the system configuration energy.

2. Valence angle bond

When angle defined by two bonds, it is called valence angle. It shows the contribution of valence angle to the system configuration energy.

3. Dihedral Angle potentials

Dihedral angles are defined by the locations of four atoms, j, k, l and m, which are connected via three bond vectors.

3. Simulation techniques on some materials

During these course, we explored about the simulation methods on various kind of materials such as proteins, lipid membranes, metallic nanoparticles into carbon nanotube, and nanosystems combined with neutron scattering experiments.

Simulation methods and techniques could depend on what material characterization you have. Before you start the simulation process, the preparation of the right input data is essential. Depends on the simulation software, input data might have different requirement. Also, web source of input data is available for many kind of materials. For example:

1. For proteins: https://www.ebi.ac.uk/pdbe/
2. For minerals: http://database.iem.ac.ru/mincryst/links.html
   http://rruff.geo.arizona.edu/AMS/amcsd.php

4. Simulation packages

MD can be performed using several program packages, among them followings are most popular MD-simulation programs:

1. Amber:
2. CHARMM
3. GROMACS
4. NAMD
5. DL_POLY

Codes available at:

- WIENK
- VASP

DL_POLY

DL_POLY is classical molecular dynamics (MD) simulation software developed at Daresbury Laboratory by I.T. Todorov, W. Smith, A.M. Elena and others [4]. The advantage of DL_POLY software is possible to do simulation on many kind of materials such as:

1. Simple atomic systems and mixtures e.g. Ne, Ar, Kr, etc.
2. Simple unpolarisable point ions e.g. NaCl, KCl, etc.
3. Polarisable point ions and molecules e.g. MgO, H2O etc.D
4. Simple rigid molecules e.g. CCl4, SF6, Benzene, etc.
5. Rigid molecular ions with point charges e.g. KNO3, (NH4)2SO4, etc.
6. Polymers with rigid bonds e.g. CnH2n+2
7. Polymers with rigid bonds and point charges e.g. proteins
8. Macromolecules and biological systems

9. Molecules with flexible bonds
10. Silicate glasses and **zeolites**
11. Simple metals and alloys e.g. Al, Ni, Cu etc.
12. Covalent systems e.g. C, Si, Ge, SiC, SiGe etc.

I chose this simulation packages for my simulation because it can work n zeolite minerals.

5. MD-simulation for zeolite and heavy metal interaction

Zeolite is one of the promising adsorbent materials due to its multi-functional property with simple treatment methods, provided easy availability of low-cost adsorbent can be found locally. The application of zeolite includes a wide range in various fields such as heavy metal adsorption, fuel cell technology, and storage of radioactive wastes. The source of natural zeolite in Mongolia has been estimated at 4.8 million tons. Several researchers studied the removal of heavy metals in wastewater by Mongolian natural zeolite. Moreover, our previous research was focused on the adsorption ability of anionic and cationic pollutants such as Pb(II), Cd(II), Zn(II) by raw natural zeolite and As(V) by Magnesium oxide modified zeolite. The result showed that Mongolian natural zeolite has higher efficiency to adsorb Pb(II) at acidic condition than Cd(II) and Zn(II) cations and As(V) anion adsorption ability of modified zeolite was increased [5].

The aim of studying for this course is to do simulation on natural and synthetic zeolite calculation with some heavy ions.

In DL_POLY method, CONFIG, CONTROL, FIELD, TAB/EAM, and REVOLD will be calculated. The some input files of zeolite is from Mincryst as follow:

Monoclinic, C 2/m Z = 1

Lattice parameters (cub. angs.,degr.):

a = 17.6589 alpha = 90.0
b = 17.9241 beta = 116.24
c = 7.4034 gamma = 90.0

Co-ordinates, thermal parameters, occupation for atomic positions:

NoP	x/a	y/b	z/c	B(j)	atom / occupation
1	0.1795	0.1713	0.099	0.0	Al = 0.13, Si = 0.87
2	0.2103	0.4119	0.5035	0.0	Al = 0.13, Si = 0.87
3	0.2074	0.1892	0.7067	0.0	Al = 0.13, Si = 0.87
4	0.0682	0.2993	0.4188	0.0	Al = 0.13, Si = 0.87
5	0.0	0.217	0.0	0.0	Al = 0.13, Si = 0.87
6	0.1872	0.5	0.4726	0.0	O = 1.00
7	0.2367	0.124	0.6081	0.0	O = 1.00

8 0.1917 0.153 0.8916 0.0 O = 1.00
9 0.2349 0.1059 0.2535 0.0 O = 1.00
10 0.0 0.3282 0.5 0.0 O = 1.00
11 0.0799 0.1595 0.0569 0.0 O = 1.00
12 0.1275 0.2347 0.5541 0.0 O = 1.00
13 0.0168 0.2771 0.1818 0.0 O = 1.00
14 0.2139 0.2532 0.1927 0.0 O = 1.00
15 0.1169 0.3764 0.4214 0.0 O = 1.00
16 0.157 0.0 0.59 0.0 Na = 0.13, Na = 0.0
17 0.043 0.5 0.179 0.0 Ca = 0.37, Ca = 0.0
18 0.234 0.5 0.038 0.0 K = 0.61, K = 0.0
19 0.0 0.0 0.5 0.0 Mg = 0.09, Mg = 0.0
20 0.335 0.0 0.092 0.0 H(2)O = 0.38, H(2)O = 0.0
21 0.118 0.0 0.864 0.0 H(2)O = 0.44, H(2)O = 0.0
22 0.082 0.408 0.964 0.0 H(2)O = 1.00
23 0.5 0.0 0.5 0.0 H(2)O = 1.00
24 0.027 0.108 0.396 0.0 H(2)O = 0.51, H(2)O = 0.0
25 0.125 0.0 0.357 0.0 H(2)O = 0.37, H(2)O = 0.0
26 0.072 0.0 0.683 0.0 H(2)O = 0.69, H(2)O = 0.0
27 0.055 0.0 0.154 0.0 H(2)O = 0.94, H(2)O = 0.0
28 0.149 0.0 0.682 0.0 H(2)O = 0.73, H(2)O = 0.0

Same type of zeolite configuration is showed in below figure, illustrated by VESTA:

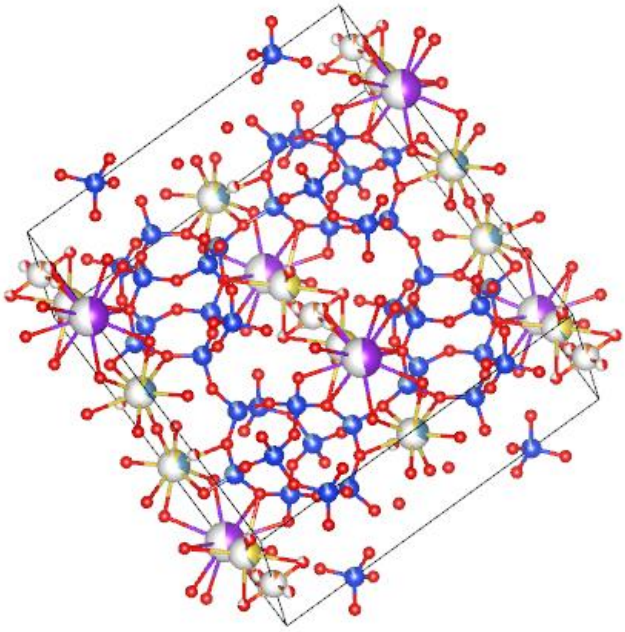

Fig 4. Zeolite configuration structure

6. Further study

In future studies, I would like to run above zeolite sample with Pb^{2+} and As^{3+} ions. Also some radioactive element gave good adsorption efficiency with zeolite and that might give interesting result. The expected data from MD simulation gives us the information about the most active adsorption site on zeolite.

Another point is, not only zeolite adsorption, but also another materials could be tested in my further study with the collaboration of international colleagues.

Acknowledgement

I appreciate Prof. Kholmirzo Kholmurodov to give us valuable knowledge on MD-simulation introduction course. I would like to acknowledge INTEREST program team, JINR University Centre for giving us the opportunity to join this course.

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