

JOINT INSTITUTE FOR NUCLEAR RESEARCH Frank laboratory of Neutron Physics

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

PROJECT REPORT ON THE INTEREST PROGRAM Participation period: March 4 – April 3 2025 (wave 12)



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# Contents

Abstract	
Project aim	2
Introduction	2
Equations used for calculations	3
1. Basic equations of the force field.	3
2. Temperature and pressure controls	6
3. Treating electrostatics and Ewald's summation	
4. The Lennard-jones potential	
MD simulation softwares	
Functionality and applications of DL_POLY	
Project	
Acknowledgement	
References	

### Abstract

Molecular dynamics (MD) simulates the collective behavior of atoms or molecules by following their classical equations of motion. It allows the study of the statistical and thermodynamic properties of physical, chemical or biological systems. Molecular dynamics (MD) simulation acts as the bridge between the microscopic length and time scales and the macroscopic world of the laboratory. It is useful when actual life experiments are too expensive to be done in a laboratory. This technique is largely used in chemical physics, materials science, and biophysics. In this report, MD simulation will be generally discussed, there are discussion of equations, force fields, and numerical calculation methods. Nowadays, there are a lot of MD simulation force fields such as GROMACS, CHARMM, DL\_POLY, AMBER and others. In this Interest program, we have mainly focused on and studied DL\_POLY and AMBER force fields.

## **Project aim**

Throughout the INTEREST program, the following tasks were discussed:

1. the basic equations, potentials and simulation techniques.

2. the computer code description for simulation of liquid model (Lenard-Jones potential).

3. the use of selected general-purpose code for the simulation of ionic, polymeric and biochemical molecular systems.

4. the theory of the basics of hybrid MD approach (classical quantum-chemistry potentials simulation methods).

5. MD test modeling.

### Introduction

Molecular dynamics (MD) simulation, first developed in the late 70s, has advanced from simulating several hundreds of atoms to systems with biological relevance, including entire proteins in solution with explicit solvent representations, membrane embedded proteins, or large macromolecular complexes like nucleosomes or ribosomes. Simulation of systems having ~50,000–100,000 atoms are now routine, and simulations of approximately 500,000 atoms are common

when the appropriate computer facilities are available. This remarkable improvement is in large part a consequence of the use of high-performance computing (HPC), and the simplicity of the basic MD algorithm. An initial model of the system is obtained from either experimental structures or comparative modeling data. The simulated system could be represented at different levels of detail. Atomistic representation is the one that leads to the best reproduction of the actual systems. Once the system is built, forces acting on every atom are obtained by deriving equations, the force-fields, where potential energy is deduced from the molecular structure. Force-fields are complex equations, but they are easy to calculate. The simplicity of the force-field representation of molecular features: springs for bond length and angles, periodic functions for bond rotations and Lennard–Jones potentials, and the Coulomb's law for van der Waals and electrostatic interactions, respectively, assures that energy and force calculations are extremely fast even for large systems. (1)

#### **Equations used for calculations**

#### 1. Basic equations of the force field.

#### Molecular dynamics simulation is based on II Newton's law:

$$Fi = mi^*ai, Fi(r) = mi \frac{d^2 * ri(t)}{dt^2}$$

Where m*i* is the atom's mass,  $ai = \frac{d^2 * ri(t)}{dt^2}$  is its acceleration, *r* is constant and *Fi* is the force acting upon it due to the interaction with other atoms.



Figure 1 Molecular dynamics simulation model. Force computation and motion update of the atoms are repeated for millions of iterations. (2)

Total potential energy action between atoms:



Where each energy in the total summation represents the following: Valence length potential:

$$U_b = \frac{1}{2} \sum_{b} K_b \, (r - b_0)^2$$

Valence angle potential:

$$U_{\theta} = \frac{1}{2} \sum_{\theta} K_{\theta} \left(\theta - \theta_{0}\right)^{2}$$

Torsion dihedral potential:

$$U_{\varphi} = \frac{1}{2} \sum_{\varphi} K_{\varphi} [\cos(n\varphi - \delta) + 1]$$

Van-der-Waals interaction potential (12-6 or Lennard-Jones (lj)):

$$U_{LJ} = \sum_{i,j} \left[ \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}} \right]$$

Electrostatics potential:

$$U_{el} = \sum_{i,j} \frac{q_i q_j}{\varepsilon r_{ij}}$$

(3)

Hydrogen bonding potential:

$$U_{HB} = \sum_{i,j} \left[ \frac{A'}{r_{ij}^{12}} - \frac{B'}{r_{ij}^{10}} \right]$$

The atoms in a system have many interaction among each other. Those can be classified in to bonded and non-bonded interactions. The bonded interactions are the acts between atoms that are linked by covalent bonds. As shown in Fig.2, stretching, angle, torsion, etc are due to bonded-forces among atoms. Bonded forces only affect a few neighboring atoms, and can be computed in O(N)time for Natoms. Non-bonded interactions are the acts between atoms which are not linked by covalent bonds. These are caused by the electro- static potential, Lennard-Jones potential due to vander waals forces, etc. The forces that cause such interactions are called non-bonded forces. (2)



Figure 2

### 2. Temperature and pressure controls

Berendsen thermostat:

The **Berendsen thermostat** is an algorithm to re-scale the velocities of particles in molecular dynamics simulations to control the simulation temperature. In this scheme, the system is weakly coupled to a heat bath with some temperature. The thermostat suppresses fluctuations of the kinetic energy of the system and therefore cannot produce trajectories consistent with the canonical ensemble. The temperature of the system is corrected such that the deviation exponentially decays with some time constant tao. (4)

$$rac{dT}{dt} = rac{T_0 - T}{ au}$$

In the Berendsen algorithm the equation of motion with a heat exchanges (dissipation, friction):

$$\sigma = \left[ 1 + \frac{\Delta t}{\tau_T} \left( \frac{T}{T_{ext}} - 1 \right) \right]^{1/2}$$
$$v \left( t + \frac{1}{2} \Delta t \right) = \left[ v \left( t - \frac{1}{2} \Delta t \right) + \Delta t \frac{f(t)}{m} \right] \sigma$$
$$v(t) = \frac{1}{2} \left[ v \left( t - \frac{1}{2} \Delta t \right) + v \left( t + \frac{1}{2} \Delta t \right) \right]$$
$$r(t + \Delta t) = r(t) + \Delta t v \left( t + \frac{1}{2} \Delta t \right)$$

The Nose-Hoover thermostat:

In the approach by Nosé and Hoover, an extra degree of freedom is introduced in the Hamiltonian. The heat bath is considered as an integral part of the system and has a fictious coordinate S which is introduced into the Lagrangian of the system. This Lagrangian for a N particle system is written as the following, which is too complex for our scope in this course. (5)

$${\cal L} = \sum_{i=1}^N rac{m_i}{2} s^2 \dot{f r}_i^2 - U({f r}) + rac{Q}{2} \dot{s}^2 - g k_B T {
m ln}\, s$$

So therefore, the equations used within our courses scope was the following:

$$\sigma\left(t + \frac{1}{2}\Delta t\right) = \sigma\left(t - \frac{1}{2}\Delta t\right) + \frac{\Delta t}{\tau_T^2} \left(\frac{T}{T_{ext}} - 1\right)$$
$$\sigma(t) = \frac{1}{2} \left[ \sigma\left(t - \frac{1}{2}\Delta t\right) + \sigma\left(t + \frac{1}{2}\Delta t\right) \right]$$
$$v\left(t + \frac{1}{2}\Delta t\right) = v\left(t - \frac{1}{2}\Delta t\right) + \Delta t \left[ \frac{f(t)}{m} - \sigma(t)v(t) \right]$$
$$v(t) = \frac{1}{2} \left[ v\left(t - \frac{1}{2}\Delta t\right) + v\left(t + \frac{1}{2}\Delta t\right) \right]$$
$$r(t + \Delta t) = r(t) + \Delta t v\left(t + \frac{1}{2}\Delta t\right)$$

### 3. Treating electrostatics and Ewald's summation

In some cases, the electrostatics could be calculated easily, introducing the "cutoff" where cutoff radius is introduced for the force and potential estimation, shown in figure 3&4. (2)



Figure 3

Electrostatics potential	Distance dependence	Coulomb force
$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon(r_{ij})} \frac{q_i q_j}{r_{ij}}$	$\epsilon(r) = \epsilon r$	$\boldsymbol{f}_{j} = \frac{1}{2\pi\epsilon_{0}\epsilon(r_{ij})} \frac{\boldsymbol{q}_{i}\boldsymbol{q}_{j}}{\boldsymbol{r}_{ij}^{4}} \boldsymbol{r}_{ij}$
$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$	$\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$	$\boldsymbol{f}_{j} = \frac{1}{2\pi\epsilon_{0}} \frac{\boldsymbol{q}_{i}\boldsymbol{q}_{j}}{r_{ij}^{3}} \boldsymbol{r}_{ij}$
$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \left\{ \frac{1}{r_{ij}} - \frac{1}{r_{cut}} \right\}$	$0 < r_{cut} < r_{max}$	$\boldsymbol{f}_{j} = \frac{1}{2\pi\epsilon_{0}} \frac{\boldsymbol{q}_{i}\boldsymbol{q}_{j}}{r_{ij}^{3}} \boldsymbol{r}_{ij}$

#### Figure 4

The Ewald's summation for n for Coulomb interaction is a correct approach taking into account periodicity, shown in figure 5. (3)



$$\frac{1}{4\pi\epsilon_0} \sum_{n< j}^N \frac{q_j q_n}{r_{nj}}$$

is divided into two sums, -(1) in wave-number space, (2) in real space,

$$\frac{1}{2V_{0}\epsilon_{0}}\sum_{k\neq0}^{\infty}\frac{exp(-k^{2}/4\alpha^{2})}{k^{2}}\left|\sum_{j}^{N}q_{j}exp(-i\boldsymbol{k}\boldsymbol{r}_{j})\right|^{2}$$
$$\frac{1}{4\pi\epsilon_{0}}\sum_{n< j}^{N^{*}}\frac{q_{j}q_{n}}{r_{nj}}erfc(\alpha r_{nj})$$

as well as a correction sums for the intermolecular (chemical bonds) interactions:

$$-\frac{1}{4\pi\epsilon_0}\sum_{molecules}\sum_{l\leq m}^{M^-}q_lq_m\left\{\delta_{lm}\frac{\alpha}{\sqrt{\pi}}+\frac{erf(\alpha r_{lm})}{r_{lm}^{1-\delta_{lm}}}\right\}$$

## Figure 5

#### 4. The Lennard-jones potential

The Lennard-Jones potential is a simple model that still manages to describe the essential features of interactions between simple atoms and molecules: Two interacting particles repel each other at very close distance, attract each other at moderate distance, and eventually stop interacting at infinite distance. The Lennard-Jones potential is a pair potential, i.e. no three- or multi-body interactions are covered by the potential. In the table below it is shown different lj parameters for different atoms. (3)(6)

Table 1

атом	$\epsilon/k_{B}(K)$	σ (nm)
н	8.6	0.281
He	10.2	0.228
C	51.2	0.335
N	37.3	0.331
0	61.6	0.295
F	52.8	0.283
Ne	47.0	0.272
S	183.0	0.352
Cl	173.5	0.335
Ar	119.8	0.341
Br	257.5	0.354
Kr	164.0	0.383

**Table 1.** The LJ (Lennard-Jones)-parameters of  $\mathcal{E}$  and  $\sigma$  for different atoms.

$$\sigma_{CS} = \frac{\sigma_{CC} + \sigma_{SS}}{2}, \quad \mathcal{E}_{CS} = [\mathcal{E}_{CC} * \mathcal{E}_{SS}]^{1/2}$$

The Lorentz-Berthelot mixing rule



### **MD** simulation softwares

AMBER: Assisted Model Building with Energy Refinement (AMBER) is the name of a widely-used molecular dynamics software package. The AMBER software suite provides a set of programs to apply the AMBER forcefields to simulations of biomolecules.

DL\_POLY: DL\_POLY is a general purpose classical molecular dynamics (MD) simulation software. It provides scalable performance from a single processor workstation to a high-performance parallel computer.

LAMMPS: Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a molecular dynamics program from Sandia National Laboratories.

CHARMM: Chemistry at Harvard Macromolecular Mechanics (CHARMM) is the name of a widely used set of force fields for molecular dynamics, and the name for the molecular dynamic's simulation and analysis computer software package associated with them.

# Functionality and applications of DL\_POLY

DL\_POLY has an extremely wide range of applications. These are possible through a comprehensive functionality with many levels of complexity.

1. **Molecular Structures.** The simplest entities recognized by DL\_POLY are atoms, which are regarded as point particles interacting with neighboring particles via a Centro symmetric potential function. Simple atomic ions are also represented in this way. Their dynamics are described by translational motion as in a classical Newtonian treatment. Also possible are rigid molecules, which are point atoms maintained in a fixed geometry. These entities possess both translational (Newtonian) motion and rotational (Eulerian) motion and are useful for describing small molecules, such as water. For larger and more flexible structures, such as polymers, point atoms may be connected by rigid bonds allied with some intramolecular interactions, such as bond angle and dihedral angle potentials, which maintain the basic molecular geometry but permit intramolecular

conformational changes, which are an essential feature of the dynamics (and chemistry) of chains.

- 2. Force Field. The DL\_POLY package does not support a unique force field, as is common in other packages (e.g GROMOS, AMBER etc) where specialization of the applications makes such a feature sensible.
- 3. **Integration algorithms**. The DL\_POLY integration algorithms were originally based on the Verlet leapfrog algorithm. This is a simple and economic algorithm possessed of great stability and is highly suitable for simulations of long duration. The leapfrog algorithm integrates the translational equations of motion. The rotational motion is handled by an algorithm that updates the angular velocity through Euler's equations, and updates the molecular orientation by means of quaternion equations.
- 4. **Boundary Conditions.** The specification of the boundary conditions is an essential aspect of any finite simulation. DL\_POLY provides for the specification of the following boundary conditions, all of which replicate an infinite system: cubic periodic boundaries; orthorhombic periodic boundaries; and parallelepiped (or triclinic) periodic boundaries. Systems with no boundaries at all (e.g. an isolated biopolymer in space) are also permitted.

### Applications most suitable for DL\_POLY:

- 1. **Radiation Damage.** Highly energetic particles progressing through a crystal structure produce cascades of ions within the matrix, giving rise to structural changes and defect formation. Specific materials such as zircon (ZSiO4), which have potential for immobilization of nuclear waste, have been studied with DL\_POLY.
- 2. Contact forces in ceramics. For some years we have been studying the origins of friction between crystal surfaces of MgO, TiO2 and NaCl. Contact between surfaces was modelled as a probe making contact with a surface of the same material. The approach and withdrawal of the probe was done in a series of discrete steps, which allowed for re-establishment of equilibrium at each stage. A thermal bath maintained the temperature of the system. Several significant phenomena were observed, the most important of which was the `jump-to-contact' in which the probe made a discontinuous advance towards

the surface to form a contiguous material. After the jump, the probe could not in general be withdrawn without strong hysteresis, which was manifested in damage to the probe or surface, in some instances leading to drawn out wires of material between the probe and surface.

3. Ion transport and the mixed alkali effect in silicate glasses. DL\_POLY has recently been employed to provide the ionic trajectories in a virtual reality study of alkali ion diffusion in silicate glasses. With the aid of isosurfaces and traced particle trajectories in immersive videos it has been possible to reveal clearly the coupling that exists between the diffusing ions and the low frequency modes of the glass network. Ions were shown to hop cooperatively between sites in the glass. These novel observations shed new light on the mixed alkali effect in these materials. (7)

#### Project

In this research that particularly spiked my interest, Dl\_poly was used for simulation of radiation damage effects to monitor the effect of radiation effects of encapsulated waste materials as well as in fusion reactors. modeling these effects using molecular dynamics (MD) simulations. In these simulations, an atom is given high initial velocity, and displaces atoms on its path which, in turn, displace other atoms in the system. A collection of these atoms is often referred to as "collision cascade". Since this is very close to my master's thesis, this course gave me a great insight to a tool that would be rather powerful and helpful in the radiation damage detection and mitigation field.



Figure 7

### Acknowledgement

I would like to humbly express my deepest gratitude to INTEREST and Prof Kholmirzo Kholmurodov for this fruitful and eye-opening journey of immersive learning, I can't thank professor enough for his understanding and cooperation, and I certainly can't wait to learn more and join INTEREST for more and new experiences which broaden my knowledge horizons and mould me into a better nuclear engineer. Thank you to everyone who was and is involved in such an esteemed program.

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