JOINT INSTITUTE FOR NUCLEAR RESEARCH

Frank Laboratory for Neutron Physics

INTEREST PROGRAMME (WAVE-9)

FINAL REPORT

MOLECULAR DYNAMICS SIMULATION RESEARCH

(FROM ATOMIC FRAGMENTS TO MOLECULAR COMPOUND)

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Acknowledgement

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Abstract

The primary goal of materials science is to improve existing materials and to design new materials. In computational materials science, we aim to achieve this goal by modeling and simulation. MD Simulation first started simulating just a bucketful of hard spheres to see the liquid–solid phase transition (Alder and Wainwright 1957). Since then, efficient algorithms and powerful codes along with the ever-upgrading computing power have greatly accelerated the progress. A drastic demonstration is the simulation of 320 billion atoms (Kadau). Molecular dynamics is a process of numerically simulating the intricate time dependent kinetics, bonding and thermodynamic behavior of atoms and molecule. It involves computer modelling from atomic point of view to molecular level. In molecular dynamic (MD) conformational ensemble can be explored for any given molecule.It has broad prospects in almost all fields ranging from engineering and technology till medicine. In this report the fundamental process for molecular dynamics simulation will be examined and the case of "Rational Approaches toward the Design and Synthesis of Zeolitic Inorganic Open-Framework Materials" will be discussed.

Project Goals

The goal of this project is to explore MD research Simulation and design of physical and biochemical nanostructures, systems and compound. Extension of MD simulation to the innovation of material science and zeolites for useful application in the Oil and Gas Industries to enhance the productivity of the Billion dollar Industry.

Scope of Work

The Scope of this study will be as follows.

i. The fundamental equations, potentials fields and simulation techniques.
ii. Numerical code explanation for simulation of liquid model (Lenard-Jones potential).
iii. Introduction to the fundamental steps for simulating molecular dynamics in systems, atomic structures, ionic structures, macromolecules, polymers, and biological moleculessuch as Protein
iv. Material Science and Oil and Gas Industry

Introduction[8]

MD is an integration of Newton's equations of motion over time to obtain the time evolution of the system and thus the properties of our interests.

- Given the initial positions and velocities of every atom, and using the provided interatomic potential, the forces on each atom are calculated.
- Using this information, the initial positions are advanced toward lower energy states through a small time interval (called a timestep, Δt), resulting in new positions, velocities, and so on.
- With these new data as inputs, the above steps are repeated, typically for more than thousands of such timesteps until an equilibrium is reached, and the system properties do not change with time.

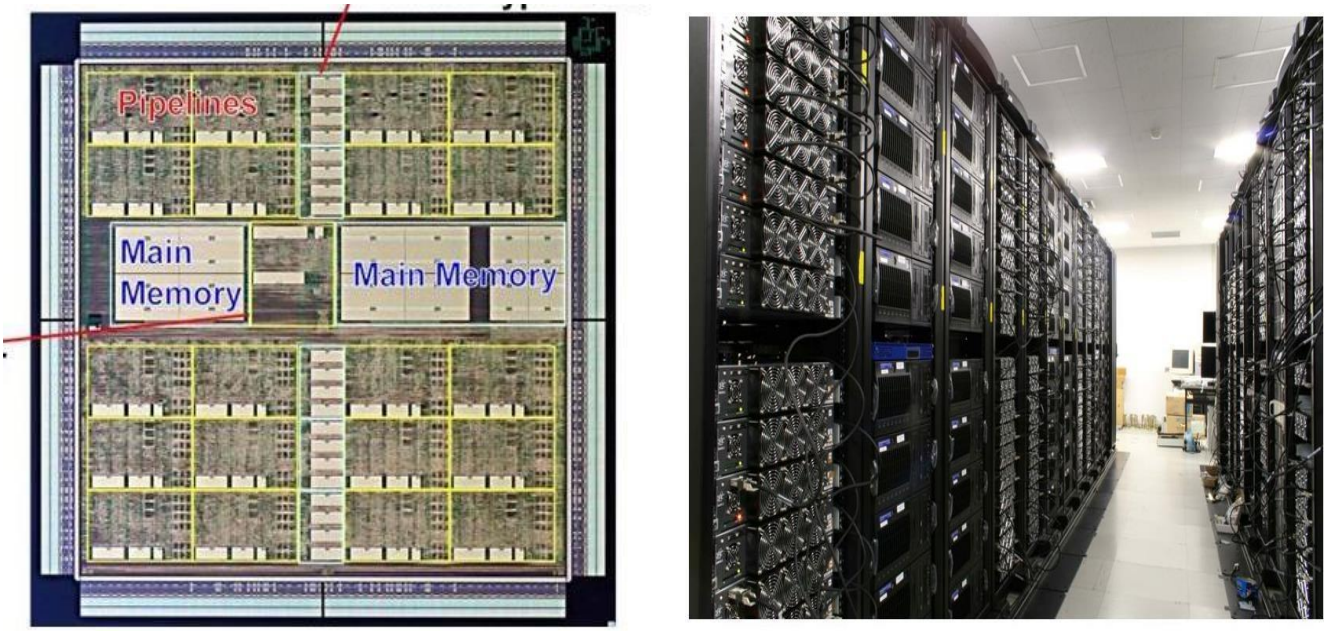
During and after equilibration, various raw data are stored for each or some timesteps that include atomic positions and momenta, energies, forces, and so on. Properties that can be calculated directly or via statistical analysis from these data are as follows:

- Basic energetics, structural and mechanical properties. (note that some of these data were used to fit the potentials empirically.)
- Thermal expansion coefficient, melting point, and phase diagram in terms of pressure and volume.
- Defect structure and diffusion, grain boundary structure, and sliding.
- Heat capacity, free energy differences between phases, and thermal conductivity.
- Radial distribution function and diffusion coefficient for liquids.
- Descriptions for processes and phenomena such as sputtering, vapor deposition, fast

plastic flow, crack growth and fast fracture, nanoindentation, propagation of shock wave, detonation, irradiation, ion bombardment, cluster impact, and operation of nanogear.[8],[4],[5],[12],[13]

Some common software used for molecular dynamics simulation are Amber (Assisted Model Building with Energy Refinement), DL_Poly, Desmond CHARMM (Chemistry at Harvard Macromolecular Mechanics), NAMD (Nano-scale Molecular Dynamics), OpenMM, GROMACS (Groningen Machine for Chemical Simulation), GROMOS (Groningen Molecular Simulation), AIMD (Ab Initio Molecular Dynamics), DFT (Density function Theory), Martini, WEIN2K, VASP (Vienna Ab Initio Simulation) and LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [6], [9], [10].

The Popular Software package used for visualizing MD simulation results is VMD (Visual Molecular Dynamics).



(a) (b)

Figure 1. Structure of MDGRAPE-3 Accelerator (a) Memory-Chip and (b) Systems

Methodology[8],[13],[15]

Generally, the steps involved in carrying out molecular dynamic simulation are:

i. Selection of an interaction models (either pairs, triplet, or quadruplet of particles).
ii. Selection of boundary conditions (configuration or position, forces, velocities).
iii. Select the conformational ensemble (canonical ensemble (NPT), isothermal-isobaric ensemble or the micro canonical ensemble (NVE), NAMD, AMBER, …).

iv. Select the target temperature, density or pressure.

v. Select the integrator, thermostat, barostat to be utilized.

vi. Perform the simulation.

vii. Analyze the result using post-processing.

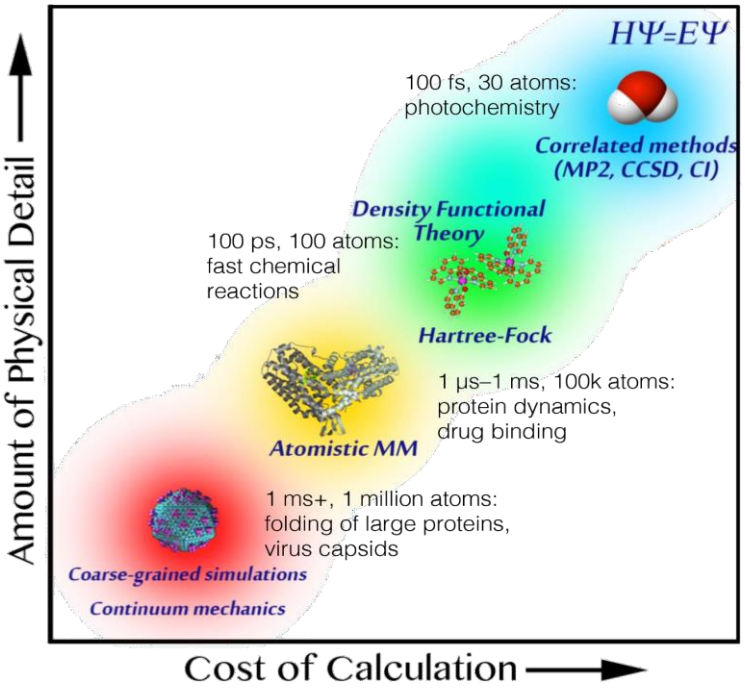


Figure 2. Typical Computational Cost for some common MD-Simulation

Fundamental Equations and Simulation Technique[15]

In molecular dynamics, the conventional Newton's law of motion is used to study the energysurface of each atoms/molecule by resolving the interatomic motion of the systems.

$$\vec{F} = m\vec{a}$$

Where, m is the mass of the atom, $\vec{F}$ is the atomic force and $\vec{a}$ acceleration of the atom. It is vital to recollect that atom are always in continuous motion and that this motion tends to affect their energy surface. The ordinary differential equation form of the Newton's equation numerically solved in molecular dynamics simulation is as follows.

$$m_i \frac{d^2 r_i(t)}{dt^2} = F_i(r),\ i - 1,2,\dots,n$$

$$\{r_i, m_i, F_i\}$$

$$r = \{r_i, r_{2,\dots}, r_n\};$$

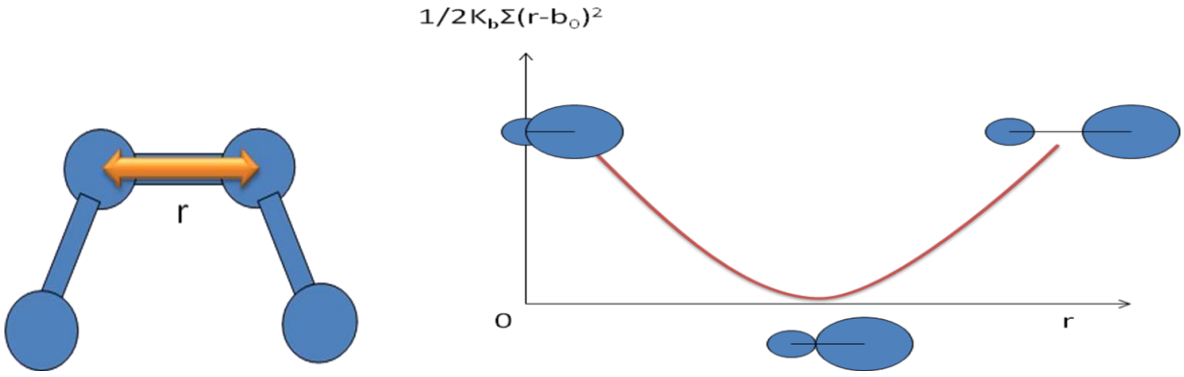
$$\frac{d^2 r_i(t)}{dt^2} = F_i(r_i(t)) - \gamma_i m_i \frac{dr_i(t)}{dt} + R_i(t)$$

Force Field Potential and Velocity Distribution[15]

$$U(\boldsymbol{r}) = U_b + U_\theta + U_\varphi + U_\omega + U_{LJ} + U_{el} + U_{HB} + \dots$$

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

$$U_\theta = \frac{1}{2} \sum_\theta K_\theta (\theta - \theta_0)^2$$



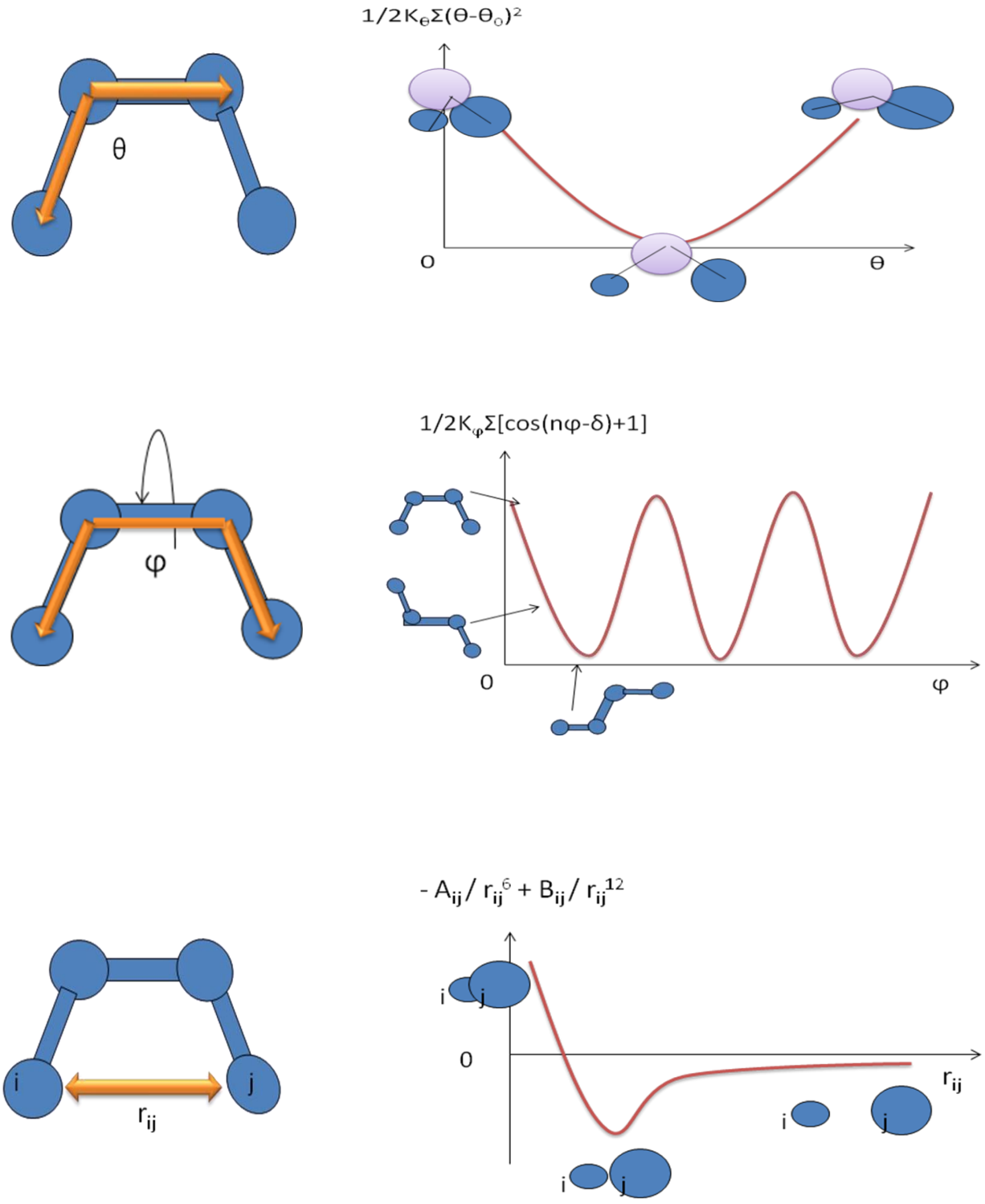


Fig. 3. Graphs of chemical potentials.

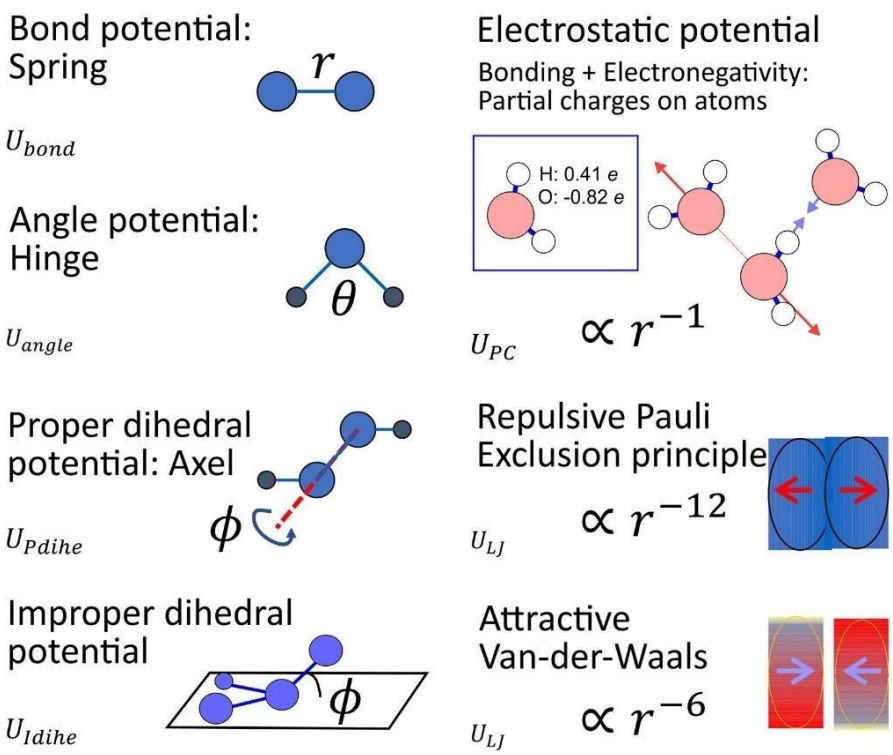


Figure 4. Force Field Potentials Functions and Schematics

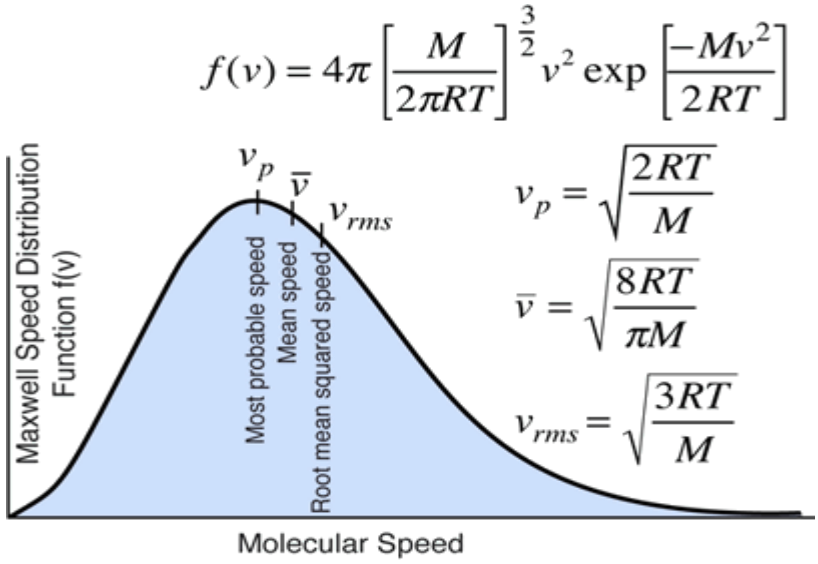


Figure 5. Maxwell-Boltzmann Distribution Function Plot

Lennard-Jones potential [15]

The Lennard-Jones ((lj) or (12-6)) potential looks is as follows

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

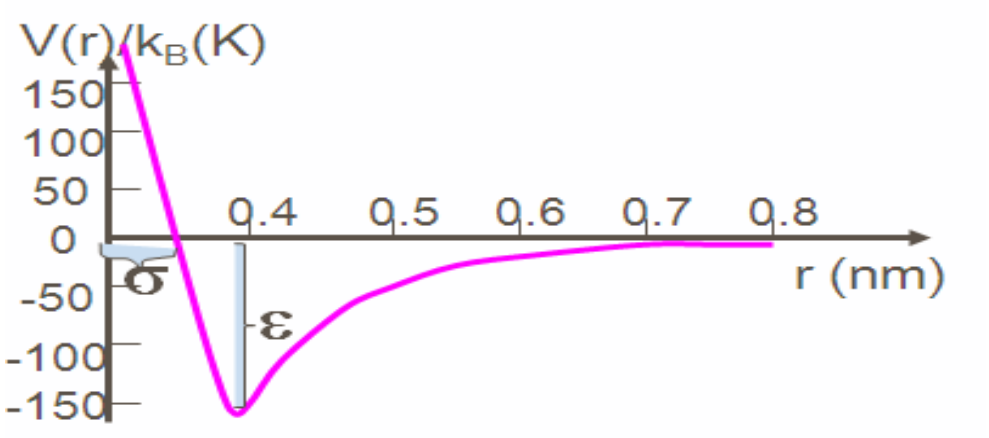


Fig. 6. The Lennard-Jones potential energy dependence on the atom-atomic distance.

Table 1. The LJ (Lennard-Jones)-parameters for different atoms.

атом	ε/k_B (K)	σ (nm)
H	**8.6**	**0.281**
He	**10.2**	**0.228**
C	**51.2**	**0.335**
N	**37.3**	**0.331**
O	**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**

The Lorentz-Berthelot mixing rule: $\sigma_{cs} = \frac{\sigma_{cc} + \sigma_{ss}}{2}$, $\varepsilon_{cs} = \left[\varepsilon_{cc} * \varepsilon_{ss}\right]^{1/2}$

Case Study

Molecular dynamics simulations of valinomycin interactions with potassium and sodium ions in water solvent[14]

Valinomycin was first isolated from the bacterium Streptomyces fulvissimus in 1955. In 1967, it was confirmed that valinomycin as a carrier catalyses the exchange of K+ and H+ across the mitochondrial membrane without causing a change in Na+ concentration. Biological membranes have several types of ion pumps that work due to the free energy of ATP hydrolysis, a special Na + / K + -ATPase system of integral proteins, known as sodium potassium pumps. Valinomycin is an example of a protein that transports potassium ions. Valinomycin has a macrocyclic (ring) structure as shown in FIG. 7 (a) and (b).

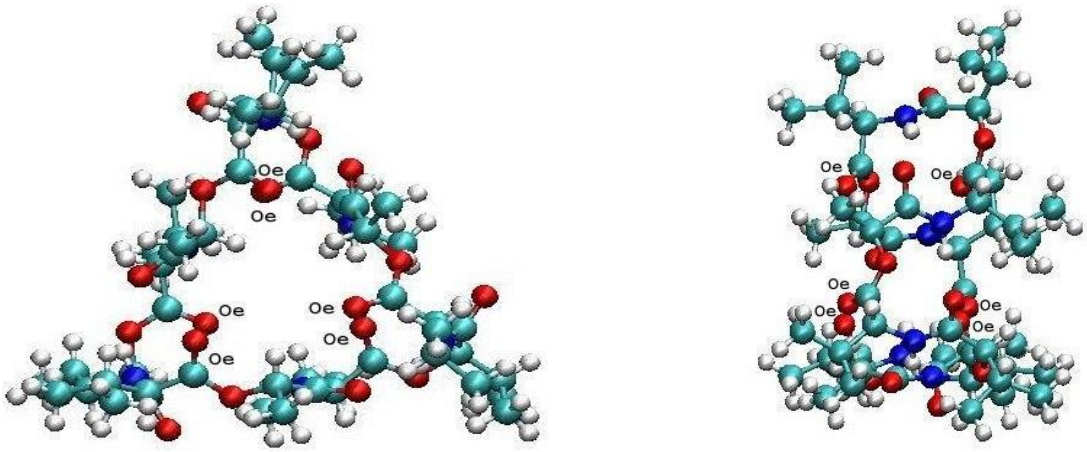


Fig 7: ***a) Molecular view*** ***b) Side view***

Due to its chemical structure, valinomycin can form complexes with potassium ions trapped by molecules within the ring. On the other hand, valinomycin is readily soluble in the lipid phase of the membrane. The outer part is non-polar. Thus, valinomycin molecules located on the membrane surface capture potassium ions from the surrounding solvent. Potassium ions are then transported by valinomycin by diffusion across the membrane, and finally the ions are released from the solvent against the cell membrane. This creates an ion concentration gradient in the cell membrane. The potential relative to the cell perimeter varies from -70 mV to +50 mV. Translocations stimulate synaptic signalling required for biological function.

In this work, we aimed to measure the electric field strength (potential gradient) of a model system describing valinomycin as potassium (K+) and sodium (Na+) ions based on molecular dynamics (MD) simulations. The reaction field algorithm was used to calculate electrostatic interactions.

Molecular dynamics (MD) simulations have been performed using the DL_POLY code, which was developed by the molecular simulation group at the Daresbury Laboratory (England) with the support of the Research Council for Engineering and Physical Sciences.

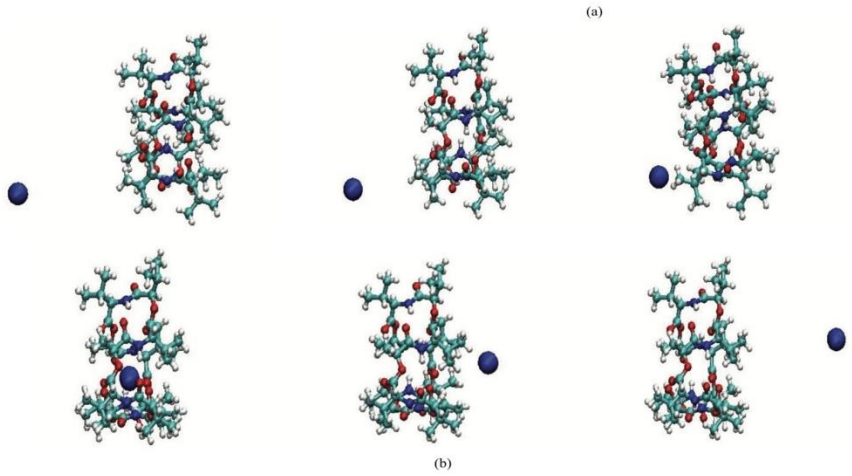
The valinomycin molecule consists of 168 atoms; the number of K^+(Na^+) ions was 109. The water molecules were simulated as 3-site rigid bodies; the total number of water atoms was 3339 (1113 × 3).

Computer simulations were performed for a constant temperature of 300 K using the Nose – Hoover algorithm with the thermostat relaxation constant of 2 ps. For the van der Waalsinter- actions, we have used the Lennard – Jones (LJ) potential. The interaction potential parameters and atomic masses and charges are shown in Tables 1 and 2. The integra- tion of the equations of motion was performed using the Verle integration scheme in quaternion. Theintegration step was 2 fs (femtoseconds). The intermolecular che- mical bonds were estimatedon the basis of the Shake algorithm to an accuracy of 10^{-8}.

Table 2. The Lennard – Jones (LJ) potential parameters for different atomic pairs.

Atomic pair	Potential	Functional form	Parameters	ε, kcal/mol	σ, Å
C-C	*LJ*	$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$	**ε, σ**	0.12	3.30
H-H	…	…	…	0.02	1.78
N-N	…	…	…	0.16	3.12
O-O	…	…	…	0.20	2.85
OS-OS	…	…	…	0.15	2.94
Oe-Oe	…	…	…	0.20	2.85
OW-OW	…	…	…	0.16	3.17
HW-HW	…	…	…	0.02	1.78
K-K	…	…	…	0.32	3.13
Na-Na	…	…	…	0.08	2.73

Result:



A valinomycin molecule (a triangular shape chain is in the center)surrounded by potassium ions (green spheres) and water molecules (red and white are oxygens and hydrogens, respectively).

Figure 8.Six consequent configurations of valinomycin and a sodium ion penetrating into the cavity are shown (b). The snapshots correspond to the time moments of t = 0, 1, 2, 3,5 and 10 ps (the electric field is directed from left to right)

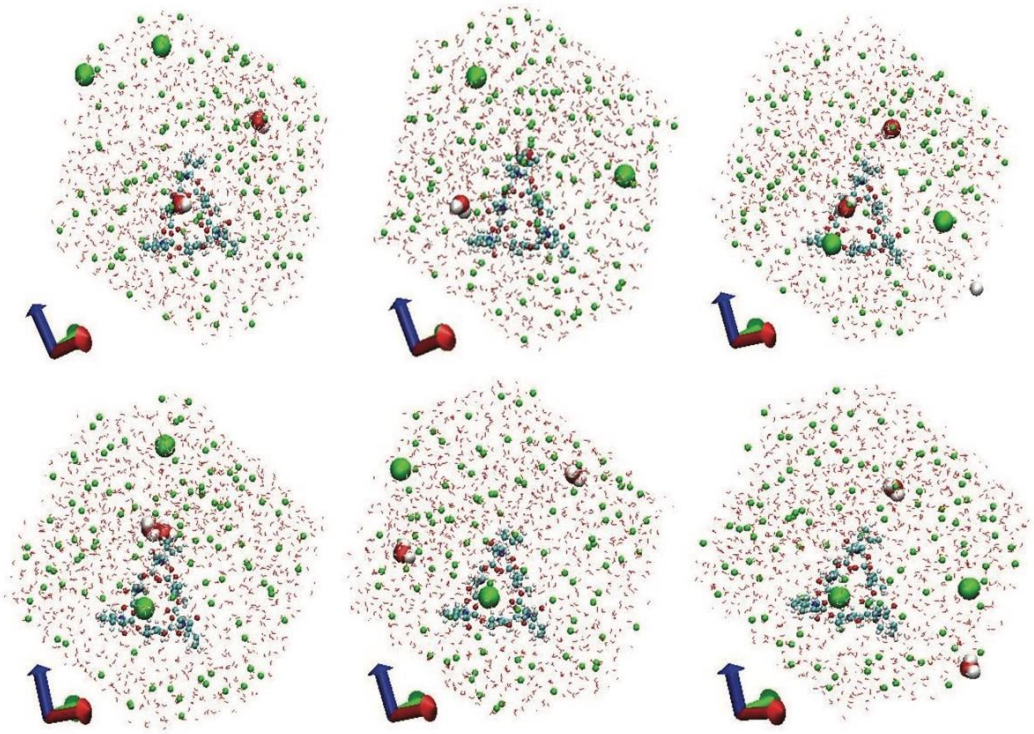


Figure 9. Six consequent configurations of valinomycin with potassium ions (green spheres). The snapshots correspond to the time moments of t = 0,1, 2, 3, 5 and 10 ps (views from left to right and from top to bottom).

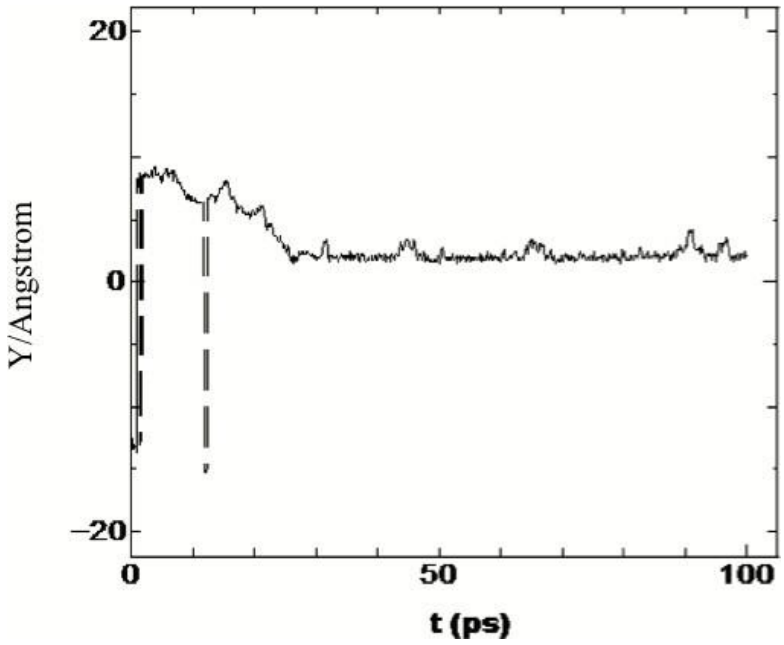


Figure 10. A trajectory diagram of a potassium ion captured by a valinomycin molecule

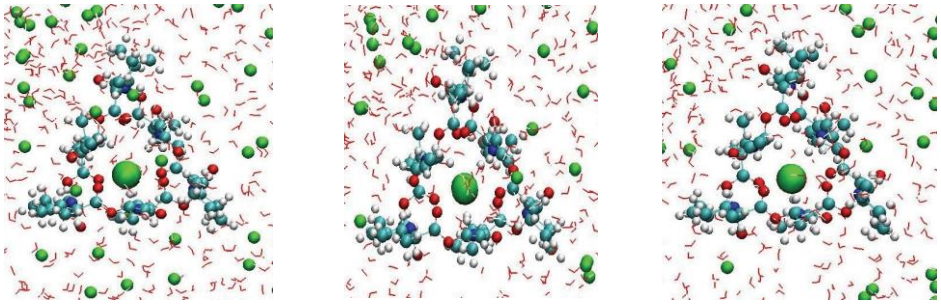


Figure 11. Three consequent configurations (b) show the ion position inside the valinomycinlocalization cavity.

Future Research Prospect

Rational Approaches toward the Design and Synthesis of Zeolitic Inorganic Open-Framework Materials[1]

Zeolites and related inorganic open-framework materials are nanoporous crystalline materials that have widespread applications in catalysis, adsorption, and ion-exchange and are one of the most important catalysts in oil refining, petroleum industry, and fine chemical industry.Their excellent performance is essentially determined by their structural characteristics, such as the size of the pore window, the accessible void space, the dimensionality of the channel system, the numbers and sites of cations, etc. In addition, their properties (e.g., diffusion and catalysis) can be also manipulated through variations in morphology

Rationalization of the synthesis of zeolitic materials with desirable structures is one of the most fundamental challenges in zeolite science. In this Account, we will illustrate the state of art in this area, mainly highlighting aspects of our research on the rational design and synthesis of zeolitic inorganic openframework materials

Computational simulation has proven to be a powerful tool for designing interesting but not yet discovered zeolite structures. However, how to access the target zeolite structures synthetically is one of the most formidable issues in zeolite and materials science. Although zeolite synthesis has been extensively studied during the last six decades, the rational synthesis is still far behind the empirical trial-and-error synthesis. This identifies the challenges and problems that remain in this area. Zeolite crystallization represents one of the most complex chemical problems in crystallization phenomena, such as polymerization-depolymerization, solution-gelation, and nucleation-crystallization.

Until now, however, there is no sufficient understanding of the formation mechanism of zeolites by which amorphous gels are converted to the porous crystalline solids at the molecular level. Especially, there is no understanding on how to control the self-assembly of reaction species that determines the formation of a specific zeolite structure under a given set of synthesis conditions. This significantly limits the synthesis of zeolites in a predictable way

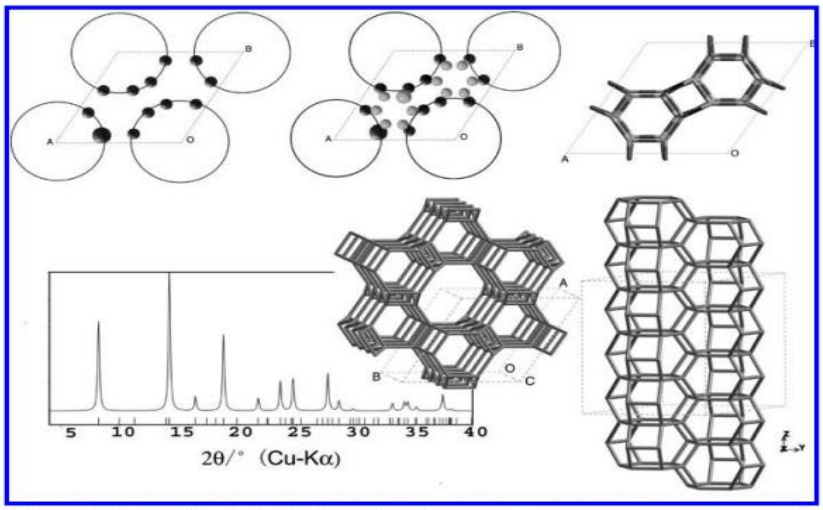


FIGURE 2. Illustration of the generation process for a hypothetical framework H1, assuming the space group of $P6_3/mmc$ ($a = b = c = 15$ Å). The pore radius is set at 6.0 Å. The first unique atom represented by a larger black ball is confined to the pore wall followed by the generation of 23 equivalent atoms using symmetry operation *I* (top left). The second unique atom represented as a larger grey ball is randomly placed outside of the forbidden zones, followed by the generation of 11 equivalent atoms by symmetry operation *j* (top middle). Bridging atoms are added (top right). Framework structure containing 12-ring channels enclosed by columns of can cages along the c axis and the simulated XRD pattern (bottom).

Synthesis Guided by the Structure-Directing Effect of SDAs.[1],[2]

Zeolite synthesis is typically driven by templates or SDAs.However, the specific role of SDAs in complex assembly to highly ordered open frameworks remains unclear at the molecular level. Although a direct analogy between the SDA and the resultant channel space cannot be clearly established, there is ample evidence that the SDA does have an influence on defining the channel geometry.Specifically, computer modeling has proven to be useful for examining the structure directing effects of known molecules, as well as predicting suitable SDAs for a given structure in terms of the host-guest interaction

Synthesis Guided by Data Mining[1].

Taking account of the chemical and physical problems on way to the rational synthesis of zeolitic inorganic open-framework materials, we have been attempting to explore another route to guide the synthesis of zeolitic materials through data mining. Since open-framework aluminophosphates (AlPOs) constitute an important family of zeolites and related microporous materials and show rich structure chemistry,we take AlPOs as an example to explore the basic mode for the designed synthesis of zeolitic materials through data mining

TABLE 1. Sets of Input Template Parameters Exhibiting Highest Accuracy

N^a	template parameters											training accuracy (%)	testing accuracy (%)
1	F12											80.54	78.08
2	F12	F16										84.31	81.75
3	F12	F16	F21									85.74	82.06
4	F12	F15	F16	F17								86.94	82.31
5	F12	F15	F16	F17	F18							87.51	82.44
6	F12	F13	F14	F15	F18	F19						87.86	82.36
7	F12	F13	F14	F15	F17	F19	F21					87.94	82.36
8	F12	F13	F14	F15	F17	F18	F19	F21				87.97	82.17
9	F12	F13	F14	F15	F16	F17	F18	F19	F21			87.97	82.08
10	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21		87.99	81.97
11	F11	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21	87.98	81.64

[a] *N* is the number of input template parameters.

Currently, various computation techniques have been used to retrieve knowledge from the data analysis,such as neural networks, support vector machines, classification trees, clustering analysis, principal component analysis, control theory, etc. For example, Baumes et al. showed how data mining techniques offer a solution for detecting a potential new structure from a synthesis that produces a mixture of zeolitic structures.

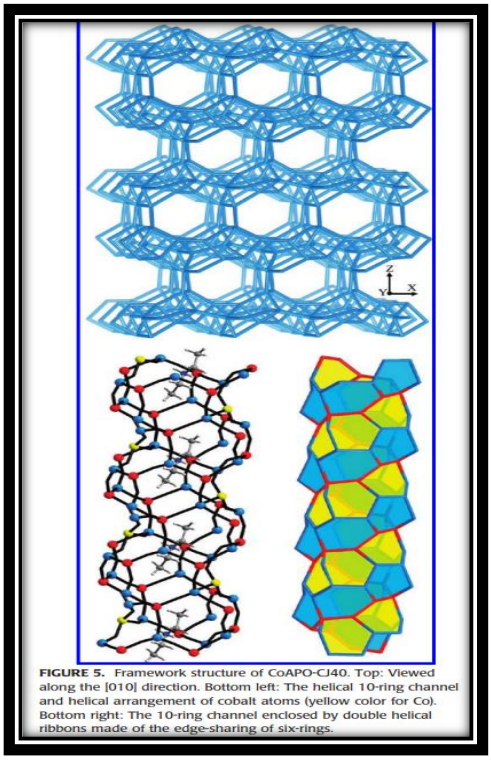


FIGURE 5. Framework structure of CoAPO-CJ40. Top: Viewed along the [010] direction. Bottom left: The helical 10-ring channel and helical arrangement of cobalt atoms (yellow color for Co). Bottom right: The 10-ring channel enclosed by double helical ribbons made of the edge-sharing of six-rings.

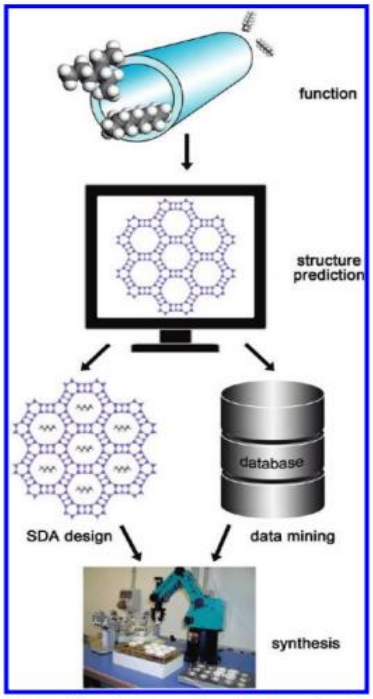


FIGURE 6. Future blueprint for engineering the rational synthesis of zeolitic materials with desired functionalities and structures.

It is worth noting that there are a number of challenges ahead in the path toward the rational zeolite synthesis. Although great strides have been made in this area, future advances in understanding the formation mechanism of zeolitic materials at the molecular level are essential before the promise is fulfilled.

Conclusion

The scope of MD simulation has extended its boundaries across various domains making it an inevitable tool in any field in this modern world.Advancements in MD simulation would not only benefit the research community but also would definitely be a major boost for industries and product based companies.

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