

## Investigation of Chemical Phenomena using Molecular Dynamics Simulations

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### Abstract

The B1-B2 crystal phase transition of potassium chloride is investigated using molecular dynamic simulation. The simulations are started with rock structure phase (B1) contained 216 pairs of potassium and chloride ions and carried out on the Buckingham potential. The phase transition into CsCl structure is occurred at 1 GPa using Nose-Hoover ensemble. A good agreement is achieved between the obtained volume from the study and the obtained volume from the theoretical and experimental studies with an error between 11.22 % and  $\pm 12.14\%$  respectively.

**Keywords:** (Simulations, dynamics, structure, phase, particles, molecular, potential, ions )

### 1. Introduction.

Computer simulations are a modern tool of research to find out the properties and structure of various materials. They are aimed to investigate the macroscopic characteristics of a molecular system from the microscopic interactions because they are based on the reproducing the experiments results to interpret invisible microscopic details (eg. particle coordinates and velocities). Computer simulations are considered as complementing to experimental as well as theoretical method due to their contribution to the understanding of laboratory results and also their capability to extrapolate the experimental data in the regions which are not achievable or easy in the laboratory. On the other hand, simulation can be employed as a predictive devise according to the flexibility of the user in controlling the simulation parameters and measuring every conceivable property (involving the correlation property) of a system through a numerical experiment. The most common computer simulations are Monte-Carlo, and Molecular dynamics.

Monte-Carlo method (MC) is a stochastic technique that depends on the probability statistics and random numbers to investigate the microscopic properties of the system. This method extends easily to simulate various ensembles, satisfy the principle of microscopic reversibility and the time saving as the potential energy is desired as result of its flexibility in choosing of sampling functions and underlying matrix. Hence, it is used to study the process of crystal growth, atomic ordering-disordering, glide of dislocations over a system of obstacles, ect [1,2].

Rapaport (1995) defines the molecular dynamic method (MD) as a statistic method to calculate equilibrium and transport properties of a system that contains a large interacting particle by solving the classical equations of motions. The energy, temperature and pressure represent the equilibrium properties of a system. Whereas, diffusion coefficient, thermal conductivity, and viscosity represent the transport properties. Molecular dynamic simulation is a most detailed molecular simulation method

because it is able to express all the details of individual particle motions in a system as a function of time. The MD direct measurement of equilibrium and transport properties of the system (macroscopic properties) requires to be expressed as a function of the position and momenta of a particle in that system which can be obtained using the Newton equation. The Newton equation solves for each particle after choosing a model system of MD simulation which defines the potential energy interaction function of N particles [3].

Therefore, when the MD simulation performs, the first step is initializing the system by selecting the initial positions and velocities of the particles in the system. Second, the description of the potential energy interactions between the particles is specified by choosing the model system. Third, calculation of the total force of each particle by differentiating the potential energy between two particles with taking into account the distance between them. The following equation represents the expression of the force with potential energy:

$$f(r_{ij}) = -\partial U(r_{ij}) / \partial r_{ij} \dots\dots\dots (1)$$

Where  $f$  is force,  $U(r_{ij})$  is potential energy between  $i$  and  $j$  and  $r_{ij}$  is the distance between them. Fourth, Newton's law ( $F = ma = m \ddot{r}$ ) which provides the particle's acceleration is numerically integrated to obtain a new velocity of each particle; a second integration gives a new position of each practical. Practically, there are various numerical integration methods to calculate the velocity and the position accurately such as the common Verlet and predictor-corrector algorithms. The new configuration of the system at the desired range time is determined after carrying out these calculations and the trajectories are generated for each particle by repeating this process. Hence, the averages of measured quantities are obtained [4].

Van Gunsteren and Berendsen (1990) mentioned that the MD results depend on initial positions and velocities of the particles in the system. From various sources such as X-ray structure, model buildings, distance geometry calculations and random search techniques the initial configuration for the particles (such position and coordinates) can be obtained. While the initial velocity can be chosen zero or obtained from a Maxwellian or Gaussian distributions.

Equilibration of the system must be set up before the measurements are taken. At this stage many properties are monitored such as pressure, temperature and energy which means running the simulation until one of these properties becomes stable with time. The required time of equilibration depends on the relaxation time of the properties. Some properties need a short equilibration time (picoseconds) such as kinetic energy. On the other hand, others need a long equilibration time (ten of picoseconds) such as dielectric properties [5].

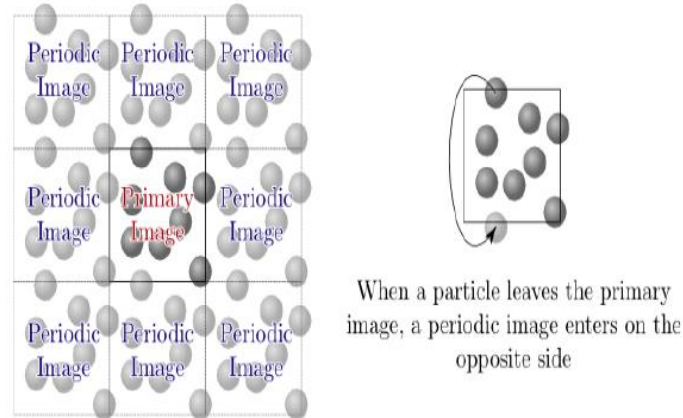
Molecular dynamics simulations are facilitated on memory parallel computer through a designed package of data files and subroutines programs called DL-POLY. There are two forms of DL-POLY: DL-POLY2 and DL-POLY4. CONTROL, CONFIG and FIELD are the three required input files to run a simulation in DL-POLY. All the required variables for running the simulation such as temperature, pressure, and number of steps ect are showed in the CONTROL file. Whereas, the dimensions of the unit, the atomic labels (coordinates, velocities and forces) as well as the periodic boundary condition are indicated in CONFIG file and the force field information of the molecular are showed in FIELD file. The most important output file in DL-POLY is REVCON file which shows the final configuration (coordinates of the system, KCl) at the end of the simulation to conclude the changes in the system during the simulation. DL-POLY4 was used in this study which grants all the required functionalities

for the crystal phase transition such as fore field, periodic boundary condition as well as the constant pressure ensembles such as Nose-Hoover algorithm which is a combination of Nose-Hoover barostat and thermostat.

### 1.1 Boundary condition.

The Molecular dynamics provide the microscopes properties of whole system by simulating only a small sample which contains a finite number of atoms (a few hundred or thousand) because a system with infinite number of atoms would be impossible to simulate accurately. The most common choice of boundary conditions is periodic boundary condition which is used to simulate the infinite bulk surrounding sample to minimize the surface effect according to the classical mechanism [3,6]. Periodic boundary condition is implemented in two ways. First, it is implemented in the particles trajectories. Second, it is implemented in the minimum images conversion.

The primary cell is a volume where the sample's particles are generated. By assuming that the bulk is surrounded by its identical copies in the primary cell. The periodic cells have the same size, shape as the primary cell and contain the images of the particles that in the primary cell surround the primary cell without separated boundary between them. As a result, the particles can move inside and outside the cell freely and when the particles leave the cell, at the same time their images follow the trajectories and meddle through the opposite side as shown in figure(1). The images will replace the particle to keep the number of particles constant. Minimum images conversion is aimed to ensure that the particles and their images have the same potential energy thus the same energy conversion. In short ranges interactions means only the images of cells that correspond to primary cells are desired for minimum energy conversion.



**Figure (1):** shows the periodic boundary condition in two dimensions with the primary cell surrounded by eight of its images.

### 1.2 Ewald sum.

The interaction between a charge and its periodic images can be computed by the Ewald summation technique which is routinely employed to simulate ionic systems. An infinite collection of point charges in the system called the charge distribution  $Q(r)$  is given in the following equation:

$$Q(r) = q_i \delta(r - r_i) \dots\dots\dots (2)$$

Based on Gaussian charge distribution (Eq. 3), the charged cloud which has the equal magnitude and opposite sign is centered in each point charge ( $q_i$ ) at long ranged?

$$Q^G(r) = -q_i \left( \alpha / \sqrt{\pi} \right)^3 \exp - a^2 |r - r_i| \dots\dots\dots (3)$$

Therefore, each ion is neutralized and shielded from the point charge interactions which can be calculated using screened charge distribution ( Eq. 4)

$$Q_i^s(r) = Q_i(r) + Q_i^G(r) \dots\dots\dots (4)$$

At this point the interaction becomes short-ranged (real space part of Ewald sum) and treated approximately using a finite summation of following equation:

$$E^s = (4\pi\epsilon_0)^{-1} \frac{1}{2} \sum_{n=0}^{\infty} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{r_{ij} + n} \operatorname{erfc}(\alpha r_{ij} + n) \dots\dots\dots (5)$$

Where  $\operatorname{erfc}$  (error function) =  $2\pi^{-1/2} \int_x^{\infty} \exp - y^2 dy$

Using equation (4) the original charge distribution  $Q_i(r)$  can be recovered by adding a negative Gaussian charge distribution -  $Q_i^G(r)$  to  $Q_i^s(r)$  .these Gaussian interactions in reciprocal space is expressed:

$$E^G = (4\pi\epsilon_0)^{-1} 2\pi L^{-3} \sum_{k \neq 0}^{\infty} k^{-2} \exp - k^{-2} / 4\pi^2 \left( \sum_{j=1}^N q_j \exp - ikr_j \right)^2 = (4\pi\epsilon_0)^{-1} \pi^{-1/2} \alpha \sum_{j=1}^N q_j^2 \dots\dots (6)$$

It is clear from equation 6 that the infinite sum can be approximated by a finite one due to the presence of the exponential factor [6].

In short, Ewald summation plays a significant role in MD simulation by replacement a potential infinite sum in real space through two finite sums one in real space and another in reciprocal space [7].

Molecular dynamic simulation has been widely used in several of application. For example, the study of liquids, biomolecular, crystal defects, polymers as well as its use recently to investigate phase transition due to development of MD modifications which cause changes in the size and shape of the MD cell, hence changes in structure of the system [2].

### 1.3 The Buckingham potential.

The intermolecular potential functions are considered as the core of any molecular dynamics simulation. They are describing equations for the interactions of the particle's system in the simulation. The Constituent potential energy of the system, forces and the electron cloud to act upon each atom. This contributes the determination of atom's motion as well as its kinetic energy can be described when the intermolecular potential functions are combined with the electrostatic interactions. For short range interactions, the Buckingham potential function was employed in this study which describes the

potential repulsion between the particle ( $U_{rij}$ ) and an attraction term ( $r^{-6}$ ) as shown in the following equation;

$$U_{rij} = A \exp\left(\frac{rij}{P}\right) - \frac{C}{rij}$$

Where A, p and C are constant. Table (1) shows the constant values of Buckingham potential function that used in this study [7].

Atoms	A	P	C
$k^+/k^+$	3796.9	0.2603	124.98
$Cl/Cl$	1227.2	0.3214	124.98
$k^+/Cl$	4117.9	0.3048	0

**Table (1):** The Buckingham potential function constants

#### 1.4 Ensembles.

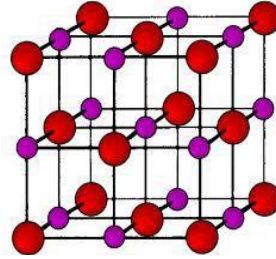
For a system of N particles in a phase space, the microscopic state can be represented by a point (position p, momenta r) for individual particle of the system. A collection of points which have the identical microscopic state (such as volume, pressure or temperature) is represented as an ensemble. In molecular dynamic simulations the generated points as function with time are belonging to the same ensemble which has different microscopic state and same identical macroscopic state.

The most common used ensembles in molecular dynamic simulation are canonical, grand canonical and isothermal isobaric ensembles. In the canonical ensemble (NVT) the volume and number of particles are the same and the total energy can be fluctuated using thermostat such as Berendsen thermostat which obtains the exponential relaxation of temperature by measuring the velocities of the particles in the system and Nose-Hover thermostat creates an additional freedom into the system and control the temperature by reducing the reservoir heat impact to the additional freedom.

The isothermal isobaric ensembles (NPT) the system has the same number of molecules as well as thermostat, the volume can be fluctuated and regulated by barostat. The grand canonical ensemble ( $\mu$ VT) is similar to conical ensemble which the system has the same volume and temperature, but they are open which means the particle will exchange with a surrounded bath. Hence, the number of instantaneous particle number may fluctuated, but the chemical potential is the same [8].

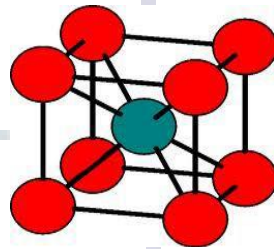
#### 1.5 Crystal structure.

The rock salt structure (also known NaCl) has a cubic close packed (Face Centered Cubic FCC) arrangement. In face- centered cube lattice the atoms are arranged at the centers and the corner of cube face of the cell as shown in figure (2). Each type of ion is surrounded by six opposite charge ions potassium ions. Therefore, each ion has a six coordinate ion.



**Figure (2):** the face centered cube of NaCl. Red spherical and purple spherical represent  $\text{Cl}^-$  and  $\text{Na}^+$  ions respectively.

Cesium chloride structure also has a cubic close packed (Body Centered Cubic BCC) arrangement. In body centered cubic lattice the atoms are arranged at the corners of the cube with another atom at the center of the cube as shown in figure (3). In CsCl structure each ion has an eight coordinates number due to each ion is surrounded by an eight opposite charged ion [9].



**Figure (3):** the body centered cubic of CsCl. Red spherical and green spherical represent  $\text{Cl}^-$  and  $\text{Cs}^+$  respectively.

Potassium chloride at room temperature and atmosphere pressure adopt to the NaCl structure (B1) which is transformed under high pressure into the cesium chloride (B2). For many years the B1-B2 pressure- induced phase transition of KCl has been studied theoretically and experimentally . Froyen & Cohen (1986) found that the B1-B2 phase transition of KCl occur at 2GPa experimentally while Akbarzadeh & Kashavarzi (1996)[10]. theoretically predicted the KCl phase transition to be at 1.5 GPa.

This study is aimed to investigate crystal phase transition of potassium chloride using constant molecular dynamic simulation. This simulation starts with the B1 (KCl-type) structure, encourages the phase transition (CsCl-type) to occur by applying an external pressure.

## 2. Method:-

The simulation system in this study was composed of 216 ions of chloride and potassium. DL-POLY4 package was employed to carry out the molecular dynamic simulation [7]. Periodic boundary conditions (initial box dimensions  $X=Y=Z=18.70 \text{ \AA}$ ) and Ewald summation were applied to electrostatic. For short range interactions the cutoff (rvdwl) was set to be  $7 \text{ \AA}$ . 0.005 ps was the chosen time step. Nose-Hoover barostat and thermostat combination were used as constant pressure ensembles

and temperature at 1 GPa and 300 K° respectively as well as trying different available types of barostat and thermostat combination of ensembles with changing in their values of relaxation time ( $f_1$  and  $f_2$ ).

### 3. Results and Discussion.

The radial distribution function was used to examine the distance between potassium and chlorine ions which was used to investigate of the nearest neighbor coordination of the phase transition.

The radial distribution function (RDF,  $g(r)$ ) is a correlation function that describes the average density of particles at a coordinate ( $r$ ) relative to any particle in the system. The obtained RDF from the molecular dynamic simulation of this study is shown in figure (4). It is clear from this figure that the density of  $Cl^-$  is at about 2.9 Å. This distance is agreed very well with the obtained data by (Singh, Baghel, & Baghel, 2010)[11].

The statistical analysis was employed to determine the change in static properties as a function of time and to examine the equilibration of the system during the simulation by increasing the pressure.

The total energy of the system was stabilized after 2 ps which mean the system reached to equilibration at this time as shown in figure (5).

The temperature at 300 K° and pressure at 100 Katm (1GPa) were also stabilized after 2 ps during the simulation. Due to the used ensemble was Nose Hoover thermostat barostat combination (constant stress and temperature ensemble (nst)), this enabled the pressure and temperature to be constant whereas, the volume of the system was fluctuated and stabilized after 2 ps. The figures (6), (7) and (8) show the plot of the temperature, pressure and the volume of the system as a function of time respectively.

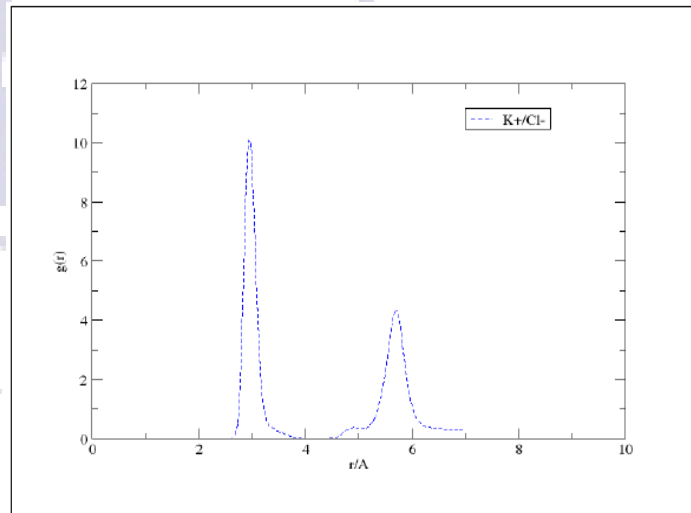


Figure (4):  $K^+$ -  $Cl^-$  radial distribution function obtained from MD simulation.

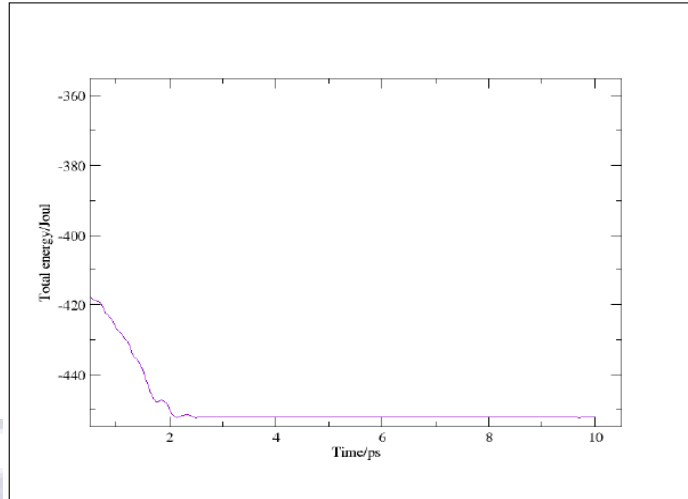


Figure (5): The obtained total energy from the simulation against time

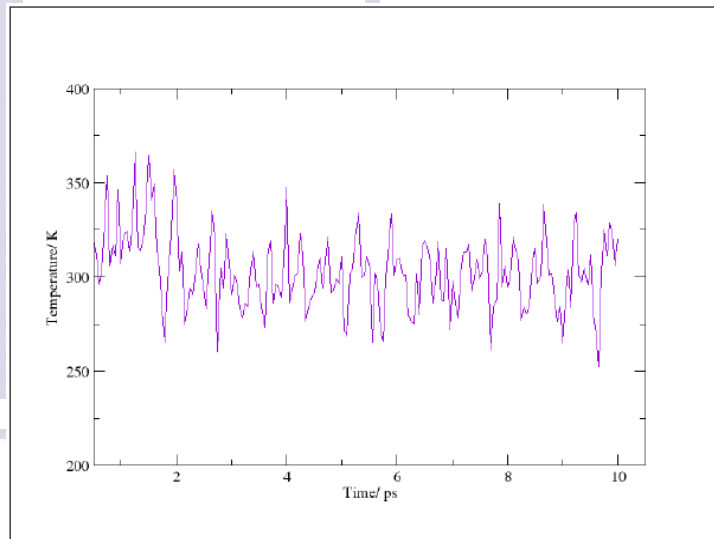
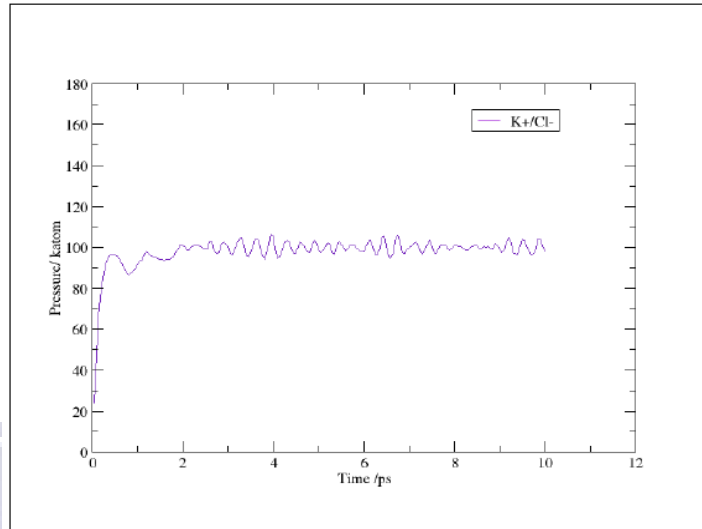


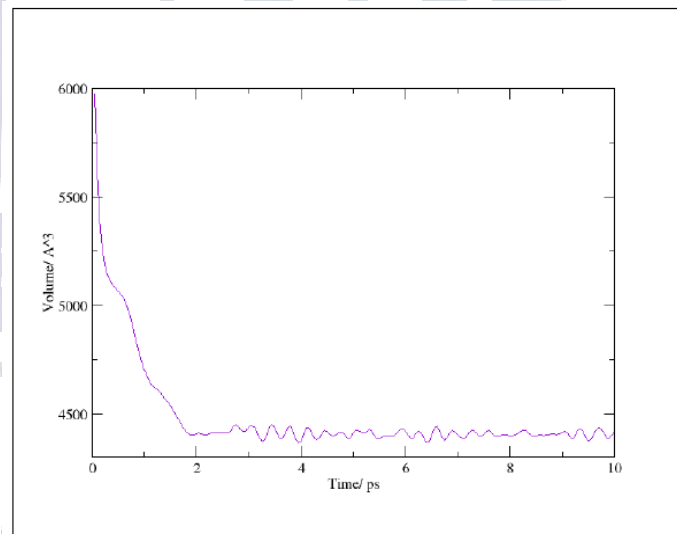
Figure (6): The obtained temperature from the simulation against time

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**Figure (7):** The obtained pressure from the simulation against time.



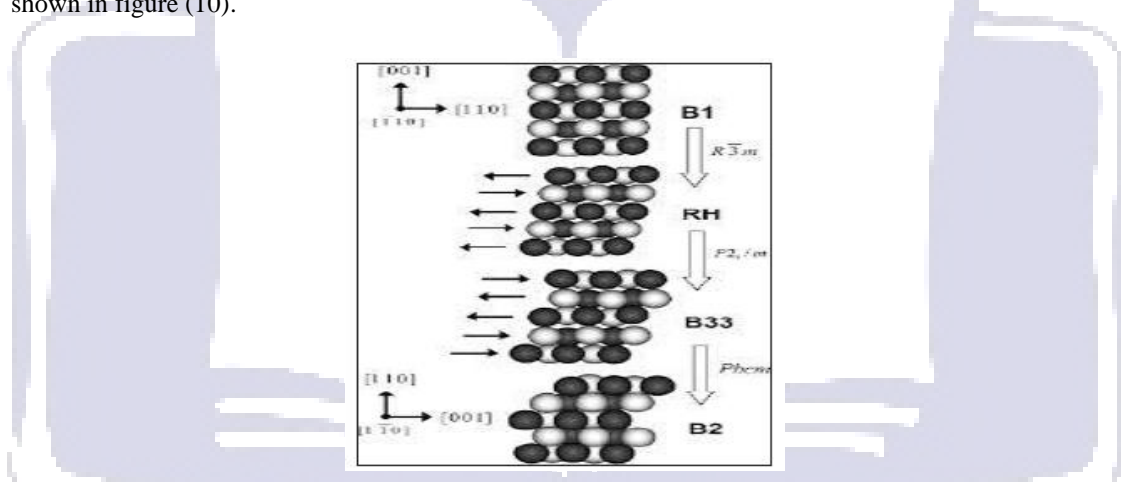
**Figure (8):** The obtained volume from the simulation against time.

The obtained results from applying different (npt) ensembles in the simulation at 300 K<sup>o</sup> , 1GPa and 0.005 ps with different time relaxation of the ensembles was the same as the obtained results using the npt Nose-Hoover ensembles with 0.1-2 ps of  $f_1$  and  $f_2$  respectively.

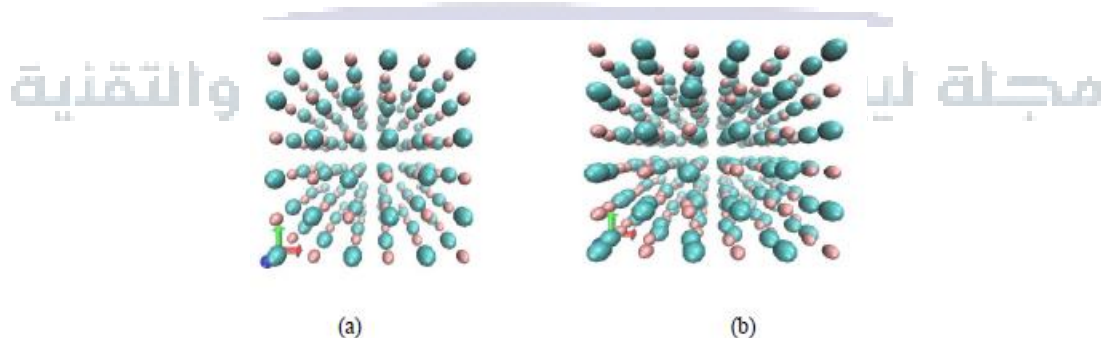
The ensemble (npt)	$f_1$	$f_2$	Unit of $f_1$ and $f_2$
Berendsen	0.1	2	ps
Langevin	0.1	1	ps <sup>-1</sup>
Martyna-Tuckermam-Klein	0.2	1	ps

**Table (2):** The used relaxation time values of the npt ensembles

Experimentally, the shock waves are applied to observe the KCl crystal phase transition from B1 to the B2 structure (Leoni & Nesper, 2000) [12]. Though the dependency of the shock- induced transition kinetics on the wave's direction, the activation energy should assume to be the same and the system is only over the critical point after applying the shock waves when thermodynamic parameters are comparable well. Therefore, the observed experimental results of anti-parallel layer (001) are the same described type of layer by the mechanism of (Hyde & O'Keeffe, 1973) [13]. The Hyde and O'Keeffe mechanism proposes that the unit cell orientation is considered to elucidate the transformation of rock salt structure (B1) into CsCl structure (B2) during the simulation. The atoms in neighboring (001) layer shift in an anti-parallel manner along (110). Therefore, the centric layer shifts first whereas the top and the low layer maintain their position as shown in figure (9). The sliding of the layers leads to change the coordination number from 6 to 8. The obtained snapshots of B1 and B2 structures by this study are shown in figure (10).



**Figure (9):** The unit cell transformation of the B1 structure into the B2 structure. RH and B2 are intermediate structures.



**Figure (10):** Snapshots of the obtained of B1-B2 phase transition from the present study.  
(a) B1 structure, (b) B2 structure.  $K^+$  is represented in brown,  $Cl^-$  in green.

Table (3) shows the obtained volume of the B1-B2 phase transition in KCl from this study, the obtained volumes of experimental (Vaidya & Kennedy, 1971)[14] and the theoretical (Zhang & Chen, 2003)[15] studies. The present study has found the B1-B2 transition pressure ( $P_{tr}$ ) less than the experimental and theoretical  $P_{tr}$ . However, the calculated volume of B1-B2 phase transition by this study is agreed well with theoretical and experimental values with  $\pm 11.22\%$  and  $\pm 12.14\%$  of error respectively.

The study	$P_{tr}$ (GPa)	$V_{B1}$ ( $\text{\AA}^3$ )	$V_{B2}$ ( $\text{\AA}^3$ )
Present study	1	65.39	44.88
Theoretical study of Zhang & Chen	2.58	55.37	49.92
Experimental study of Vaidya & Kennedy	2	57.01	50.33

**Table (3):** B1-B2 phase transition parameters, including pressure ( $P_{tr}$ ) and the volume values of B1 ( $V_{B1}$ ) and B2 ( $V_{B2}$ ).

#### 4. Conclusion.

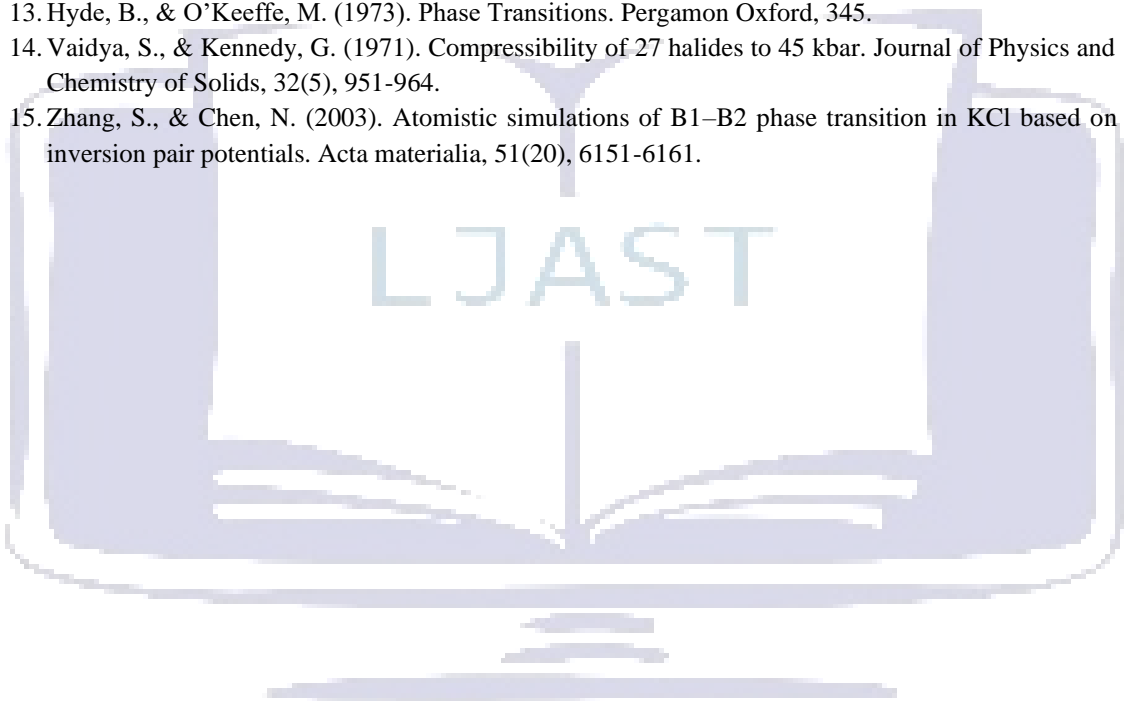
Molecular dynamic simulation has been conducted to investigate the crystal phase transition of potassium chloride at a constant temperature and pressure by applying Nose- Hoover thermostat and barostat combination. The obtained volume was agreed well with the theoretical and experimental studies.

It is hoped that the obtained results from this study will consider to compare with future studies in molecular dynamic simulations to investigate the KCl phase transition using different ensembles and parameters such as time steps and short rang cutoff ect.

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