

Computational Modeling of Li Diffusion Using Molecular Dynamics

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Xinran Zhang

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Approved by:

Dr. Natalie Holzwarth

Dr. Samuel S. Cho

Dr. Fred Salsbury

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I. Introduction

Lithium batteries are widely used in modern electronic devices, such as portable devices, power tools, and electric vehicles.¹ As the requirements for battery performance increases, the study of lithium batteries continues in order to increase their efficiency and stability. Computational models can be used to analyze the lithium battery materials so that we can have a better understanding of their behaviors, which can help to increase their efficiency and stability.² One way to improve the efficiency of the batteries is to improve the electrolytes, which transport the Li-ions between the anode and the cathode. The higher conductivity of the electrolytes will help to transfer more Li-ions within the batteries and will control the flow of electron in the external circuits; thus will improve the efficiency of the system.

In a previous study by Ong and co-workers, who have used first principles techniques to model battery materials, it was shown that solid electrolytes comprising lithium superionic conductor materials exhibit good safety and stability.³ This group has analyzed the family of compounds related to $Li_{10}GeP_2S_{12}$, which is the highest known conducting electrolytes to date. Their research analyzed Kamaya's experiments,⁴ which successfully increased the conductivity of Li-ion conductors from less than 10^{-4} S/cm by a factor of 100 at room temperature. Ong and colleagues also calculated the diffusion coefficients and activation energies of electrolytes.³

Their research motivated our group to also simulate the diffusion coefficients for our materials. Specifically, Lepley et al.⁵ used first principles methods to analyze the structural properties and ionic conductivity of solid electrolytes Li_3PO_4 and Li_3PS_4 . The first principles methods are based on density functional theory (DFT), which is a computational quantum mechanical method to describe the electronic structure of many body systems. Established by Hohenberg and Kohn⁶ as well as Kohn and Sham⁷ DFT operates under the principle that a scalar function of the ground state electron density as a function of position can represent any property of a many-electron system. The total electron density of the system can be well approximated by summing up individual electron wave functions. Therefore, the system can be treated as independent particles to approximate the electron density of the system. The approximation methods include the approximate local density (LDA) and generalized-gradient approximation (GGA) functions. This independent-particle method provided the key step for further developments in the field of materials, and Kohn and Pople received the 1998 Nobel Prize in Chemistry for their contributions. However, the works of Ong and co-workers and Lepley et al. using strictly first principles methods, while very accurate, detailed, and precise, are typically restricted to about 100 atoms for their calculations due to computational demands.

In the study presented in this thesis, we instead used a classical mechanics approach for computational simulations by performing molecular dynamics (MD) simulations. The approach is well-established and began in the 1950s. Recently, the 2013 Nobel Prize in Chemistry was awarded to Martin Karplus, Michael Levitt, and Arieh

Warshel for their pioneering work in the development of MD simulations. Karplus and Warshel's computer program performed calculations on the π -electron vibrating spectra of carbon based materials.⁸ This program enabled combination of the advantages of classical and quantum methods to a hybrid technique so that complex chemical systems can be described. Warshel also collaborated with Levitt and they speeded up the modeling process through grouping atoms in a classical system and treating them as classical pseudoatoms.⁹ They later developed a general structure to separate the electrons with classical models and quantum models¹⁰ to conduct more accurate calculations. Since then, there are now many different empirical force field MD simulation packages, and the approach is used in many different fields ranging from materials¹¹ to biophysics¹² research.

We initiated our research on using empirical potential molecular dynamics (MD) methods to model lithium battery related materials at larger system sizes. My research is to help the group with classical MD treatments so that we can add some additional results to the *ab initio* studies in future work. We chose LAMMPS,¹³ which is a widely used and convenient MD simulation software package. Through learning to use this LAMMPS code and using it to study lithium battery materials, we have established several different models and analyzed the diffusion processes of pure solid lithium and solid lithium oxide materials. The diffusion coefficients and the activation energies can be further analyzed when examining the ionic conductivity for battery performances in the future. The algorithm and computational potential forms are chosen from the published literature and the results are also compared with the publications in order to make sure we can successfully model the processes, which yield to reliable calculation outcomes.

II. Methods

The pure Lithium solid and Li₂O solid were modeled in this project using empirical potentials calculation methods. The primary tool used for modeling is the LAMMPS Simulator. All of our calculations were done on the DEAC cluster. In order to access the cluster on a Windows system, I installed the Virtual Box and the Ubuntu operating system in order to connect to the cluster through the terminals. XcrySDen¹⁴ and VMD¹⁵ have been used for visualizing the crystal structures and the diffusion processes.

A. Molecular Dynamics

Molecular dynamics is a computer simulation method for examining the physical movements of atoms and molecules, whose phenomena are usually too small to be observed directly, by using a classical approximation to describe chemical systems. The simplified representation, as compared to the quantum mechanical description allows researchers to analyze the motion of complex chemical systems. MD simulation have

been widely used in various academic fields, such as physics, biophysics, chemistry, and materials science.

B. Fundamentals of Molecular Dynamics

In MD simulations, the atoms are assumed to have an empirical interaction function. The motion of the atoms can be calculated by using different numerical methods to solve Newton's equations of motion for a system of interacting particles with possible constraints on ensembles. Here, I describe a general approach for obtaining the positions and velocities of a particle that is acted upon by an effective potential over time. By Newton's equations of motion, the force \mathbf{F} and position \mathbf{r} of the atoms are determined by the interatomic potential U_{eff} . The force is the derivative of potential with respect to displacement \mathbf{r} as Equation 1 shows.

$$\text{Equation 1: } \mathbf{F} = -\frac{dU_{eff}}{d\mathbf{r}}$$

Then, with the constant mass m of the atom, the acceleration \mathbf{a} of the atom can be calculated Equations 2, Newton's second law.

$$\text{Equation 2: } \mathbf{F} = m\mathbf{a}$$

Therefore, in a short time interval Δt , the tiny variation of the acceleration can be neglected. One can then determine the position and the velocity of each atom from the acceleration, initial velocity, and the initial position.

$$\text{Equation 3: } \mathbf{r} = \frac{1}{2}\mathbf{a}\Delta t^2 + \mathbf{V}_0\Delta t + \mathbf{r}_0$$

$$\text{Equation 4: } \mathbf{V} = \mathbf{V}_0 + \mathbf{a}\Delta t$$

\mathbf{V}_0 and \mathbf{r}_0 are the initial velocity and position of the atom.

Different numerical methods are used in MD simulations to find the trajectories of the particles. Besides, the size of the system should be set reasonably so the atoms in the system can perform desired motions without any additional constraints. The initial settings of a simulation also include the dimension of simulation, boundary conditions, and the units of the parameters. Some details are provided below.

a) Verlet's Algorithm

The numerical analysis is applied in the equation of motion when using the small time increment called time step Δt to extrapolate the position of the atoms. The Taylor Series for position as a function of time is:

$$\text{Equation 5: } \mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \frac{d\mathbf{r}(t)}{dt}\Delta t + \frac{1}{2}\frac{d^2\mathbf{r}(t)}{dt^2}\Delta t^2 + \frac{1}{3!}\frac{d^3\mathbf{r}(t)}{dt^3}\Delta t^3 + \dots$$

Rewriting equation 4 from t to $t - \Delta t$ gives:

$$\text{Equation 6: } \mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \frac{d\mathbf{r}(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2\mathbf{r}(t)}{dt^2} \Delta t^2 - \frac{1}{3!} \frac{d^3\mathbf{r}(t)}{dt^3} \Delta t^3 + \dots$$

Adding equation 5 & 6 to eliminate terms, we can obtain the Verlet's algorithm for position, keeping terms larger than Δt^4 :

$$\text{Equation 7: } \mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{d^2\mathbf{r}(t)}{dt^2} \Delta t^2 + \dots$$

The Verlet algorithm uses the position at time t and $t - \Delta t$, as well as the acceleration, which can be obtained from U_{eff} , to extrapolate the position at $t + \Delta t$.

By subtracting equation 5 & 6 and keeping terms larger than Δt^3 , we get:

$$\text{Equation 8: } \mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t) = 2 \frac{d\mathbf{r}(t)}{dt} \Delta t + \dots$$

Therefore, the velocity at t can be obtained

$$\text{Equation 9: } \mathbf{v}(t) = \frac{\mathbf{r}(t+\Delta t) - \mathbf{r}(t-\Delta t)}{2\Delta t}$$

Using these sets of equations, the positions and the velocities of every particle in the system can be updated over time by iteratively using the old positions and velocities to obtain new positions and velocities over a long period of time until a complete trajectory is obtained.

LAMMPS uses an algorithm that has the similar idea to this Verlet Algorithm. Thus, LAMMPS can conduct MD simulations to track the trajectories of atoms' movements. While determining the time step, one must make sure it is short enough to describe the motions accurately. Specifically, it must be shorter than the fastest motion or the simulation will not accurately describe the phenomenon. However, the total time should be limited within a reasonable length so that the simulations can be finished for analysis.

b) Nose-Hoover Algorithm

In order to conduct MD simulations, we need to take into account the principles of statistical mechanics, which include temperature T , pressure P , and volume V . This will ensure that our MD simulations are similar to experimental conditions where the temperature, pressure, and volume can be controlled, like a real experiment. In addition to the traditional Hamiltonian way of treating the particle, LAMMPS uses Martyna's paper¹⁶ to include the extra ensemble effect on the motion of the particles. The details of the paper are very complicated and the main ideas are as follows.

We start from the classical Hamiltonian equation:

$$\text{Equation 10: } \mathbf{H}_{classical}(\{\mathbf{r}_i\}, \{P_i\}) = \sum_i \frac{P_i^2}{2m_i} + U_{eff}(\{\mathbf{r}_i\})$$

The Hamiltonian represents a many particle system. The total energy of the system includes the sum of kinetic that summed among all particles, and effective potential energy of the whole system. The kinetic energy depends on the momentum P_i for the i^{th} atom. The potential energy is a function of positions of all \mathbf{r}_i . m_i is the mass of an atom.

The total effective Hamiltonian of the system in MD simulations has an addition statistical term.

$$\text{Equation 11: } \mathbf{H}_{eff} = \mathbf{H}_{classical} + \mathbf{H}_{ensemble}$$

To be more specific,

$$\text{Equation 12: } \mathbf{H}_{eff} = \sum_i \frac{p_i^2}{2m_i} + U_{eff}(\{\mathbf{r}_i\}) + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + (N_f + 1)kT\xi + P_{ext}V$$

Here, V is the volume of the simulation box. P_{ext} is the target equilibration pressure. P_{int} is a function of momentum and forces that varies with time. p_ϵ is the barostat momentum. p_ξ is the thermostat momentum with a thermostat position ξ . Both the barostatic and the thermostatic variables have parameters to control the equilibration time, which are W and Q respectively. These parameters have the units of (*energy · time*²). N is the number of particles, d is the dimension, and N_f is the degrees of freedom. The equations of motion by Hoover are therefore as follows:

$$\text{Equation 13: } \frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{P}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i$$

$$\text{Equation 14: } \frac{dP_i}{dt} = F_i - \frac{p_\epsilon}{W} P_i - \frac{p_\xi}{Q} P_i$$

$$\text{Equation 15: } \frac{dV}{dt} = \frac{dV p_\epsilon}{W}$$

$$\text{Equation 16: } \frac{dp_\epsilon}{dt} = dV(P_{int} - P_{ext}) - \frac{p_\xi p_\epsilon}{Q}$$

$$\text{Equation 17: } \frac{d\xi}{dx} = \frac{p_\xi}{Q}$$

$$\text{Equation 18: } \frac{dp_\xi}{dt} = \sum_{i=q}^N \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{2W} - (N_f + 1)kT$$

As Martyna explains Hoover's equations of motion, the average of the time derivative of both barostat and thermostat momenta go to zero at equilibrium when the internal pressure averages to the external target pressure and the temperature is related to the average kinetic energy as usual. Therefore, LAMMPS uses these equations of motion to control the NPT ensemble, which is numerically evaluated using a modified form of the Verlet integration.

C. Empirical Potential

Unlike first-principles methods, empirical potential methods treat the system from a classical perspective, in terms of the potential $U_{eff}(\{\mathbf{r}_i\})$ in equation 10. The quantum effects are not explicitly represented in this classical perspective; instead, they are embedded in the potential term. However, one of the most challenging difficulties of using empirical potential is to determine the effective interaction potential U , which needs to be constructed. After introducing the general empirical potential, I specifically used Lennard-Jones potential to perform some initial tests, Modified Embedded Atom (2NN) method to analyze pure solid lithium system and the Buckingham potential method to examine the solid lithium oxide system.

a) Lennard-Jones Potential

Lennard-Jones potential was designed to treat noble gases but now describes how any atoms can interact with each other using the following equation:

$$\text{Equation 19: } U_{eff}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

ϵ is a characteristic energy and σ is a characteristic length. The 12th power term is the repulsive term, and the 6th power term is the van der Waals term. Typically the potential is set up to be zero at the cutoff radius. I used this to test the time step, which is discussed in the result section.

b) Modified Embedded Atom Method (2NN) Potential

In our initial pure lithium modeling, we chose this second nearest neighbor (2NN) modified embedded atom method. This method was originated from the Embedded-Atom Method (EAM), which can be represented by the equation 20 below:

$$\text{Equation 20: } U_{eff}(\{\mathbf{r}_i\}) = \sum_i [\mathbf{F}_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \varphi_{ij}(\mathbf{r}_{ij})]$$

Under EAM, the total potential energy consists of two parts: a many-body term potential as a function \mathbf{F}_i of density $\bar{\rho}_i$ and a two-body interatomic energy $\varphi_{ij}(\mathbf{r}_{ij})$. For the many-body term, the main idea was created from Density Functional Theory, which claims that the total energy of a material can be written as a function F of its density $\bar{\rho}_i$. Instead of the using quantum mechanics in first principles calculations, EAM treats the system with empirical function and $\bar{\rho}_i$, which is approximated in terms of an atom-centered shape for each atom summed over the surrounding neighbor atoms. However, EAM simply deals with an isotropic density; therefore, scientists have modified it to include anisotropic density contributions which is the Modified Embedded-Atom Method (MEAM). The parameters are determined by fitting the energy and forces to reproduce structures observed in experiments or modeled by first principles calculations.

The parameters for this study were taken from the work of Cui and his co-workers.¹⁷ According to their paper, previous studies in MEAM¹⁸ predict that body centered cubic is not the most stable structure for lithium. But they suggest that using a second-nearest-neighbor (2NN) expansion of the density function and the interaction potential can model the body-centered cubic structure more successfully than simply using the first-nearest-neighbor expansion. The 2NN MEAM, takes into account the second nearest neighbor when approximating the atom-centered shape for each atom. This method leads us to reliable results that can be further analyzed to obtain the diffusion and activation energy. This potential is used to model the pure solid lithium system.

c) Buckingham Potential

The Buckingham potential is defined as

$$\text{Equation 21: } U_{eff}(r) = Ae^{-r/\rho} - \frac{C}{r^6} + \frac{1}{4\pi\epsilon_0} \frac{q_1q_2}{r}$$

A is coefficient of the repulsive term between two particles. C is the coefficient of the van der Waals interaction. The last term, $U_{eff}^{coul}(r_{ij})$, represents the Coulombic interaction between charged particles q_1, q_2 .

For periodic boundary conditions, the Coulombic term cannot be evaluated directly, so an Ewald summation needs to be used to help the evaluation:

$$\text{Equation 22: } \sum_{i,j} U_{eff}^{coul}(r_{ij}) = \frac{1}{8\pi\epsilon_0} \left\{ \sum_{i,j} q_1 q_2 \left[\sum_T' \frac{\text{erfc}\left(\frac{1}{2}\sqrt{\eta}|r_i-r_j+T|\right)}{|r_i-r_j+T|} + \frac{4\pi}{V} \sum_{G \neq 0} \frac{e^{-iG(r_i-r_j)} - \frac{G^2}{\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}} \delta_{ij} \right] - \frac{4\pi Q^2}{V\eta} \right\}$$

In this expression, T represents the translations between periodic simulation cells. Similarly, G denotes the reciprocal lattice translation vectors. η is the parameter to control the real space and reciprocal space summation. The prime in the summation over T implies that we exclude the term in which the denominator vanishes. Q represents the total charge in the simulation cell. V is the volume of the simulation cell. The reciprocal space term is evaluated in LAMMPS with the “Kspace_style” command and the remaining contributions are evaluated in real space with the other terms in the Buckingham potential. We used the Buckingham potential and the Ewald summation to simulate Li_2O systems.

D. Diffusion and Activation Energy Calculations

The ions in an electrolyte diffuse due to the small changes in the system, such as space and temperature. Through modeling the process of movement, we output the Mean Squared Displacement (MSD) through LAMMPS. The MSD demonstrates the average displacement of all particles' movement summation, which is adjusted in the system by every time step. According to equation 23, N is the total number of particles in the

simulation cell. The diffusion coefficient D is the slope of plotting the total MSD of the system as a function of time.

$$\text{Equation 23: } D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle$$

The activation energy E_A is the characteristic energy required for diffusion to occur. It can be calculated using the diffusion coefficient by equation 24:

$$\text{Equation 24: } D = D_0 e^{-E_A/(k_B T)}$$

This method is used to analyze both pure solid lithium and Li_2O systems. The diffusion coefficient is proportional to the ionic conductivity of electrolyte. Therefore, a better understanding of diffusion processes will help to improve the ionic conductivity, which can enhance the performance of the batteries.

III. Results

A. Time Step Test

Due to the importance of the time integration in MD simulations, we first want to test how small the time step would be efficient enough to give the correct results using Lennard-Jones potential. We followed Meier's paper¹⁹ and his Ph.D dissertation²⁰ to construct the simulation system. All units are in Lennard-Jones units, which has sigma as the length, epsilon as the energy, and $\{\sigma / [(\epsilon / \text{mass})^{1/2}]\}$ as time. The system consisted of 1372 atoms of Lennard-Jones model fluid in a square box of length 11.757 (sigma), setting density to be 0.8442 (σ^{-3}). These parameters are set to run in the program "makelammmpsinputforperiodic.f90" in order to form the structure called "XXX" that could be read by LAMMPS command "read_data" later. After the system is set, our LAMMPS input file reads:

```
# 3d LJ test
units          lj
dimension      3
atom_style     atomic

boundary       p p p

lattice        sc 11.757
read_data      XXX

pair_style     lj/cut 2.5
pair_coeff     * * 1 1
neighbor       1 bin
```

```

timestep      1.0e-3
thermo        2
thermo_style  custom step temp ke pe press etail

velocity      all create 0.722 43454 dist gaussian mom yes rot yes
fix           1 all nve

run 200

```

The boundary condition is periodic. The lattice *sc* indicates a simple cubic structure. The *pair_style* of “lj/cut 2.5” indicates a standard 12/6 Lennard-Jones potential with a length cutoff of 2.5 sigma. The keyword “*pair_coeff*” sets the pairwise force field coefficients for one or more pairs of atom types. An asterisk is used in conjunction with the I,J types and means all types from 1 to N. Here, we set the coefficients to the default value in epsilon and sigma. The “*neighbor*” command sets the extra distance beyond force cutoff with a bin style to create an operation that scales linearly with the number of atoms per processor. The time step was set to be 10^{-3} , 10^{-4} , 2×10^{-3} , and 2×10^{-4} to compare their differences. The output was recorded at every time step. The initial velocity was created under a temperature of 0.722 (Boltzmann constant / epsilon), according to Meier’s paper and dissertation, with values random generated by a Gaussian distribution and both linear and angular momentum are zeroed. The process was performed under micro-canonical ensemble. The total time was set to be $0.2 \{ \sigma / [(\epsilon / \text{mass})^{1/2}] \}$.

The plots of time step vs. temperature are shown below:

Figure 1: Time step vs. Temperature in Lennard-Jones Fluid. Simulation of 1×10^{-3} compared with 2×10^{-3} .

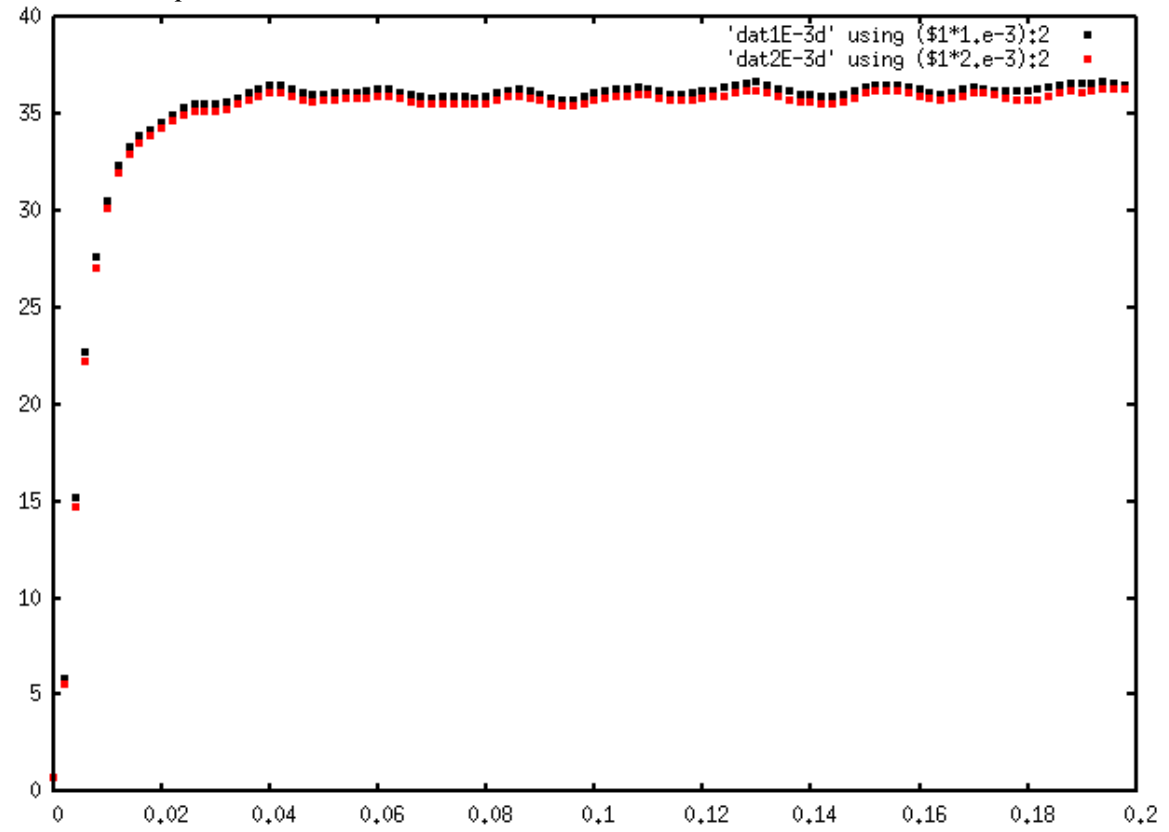
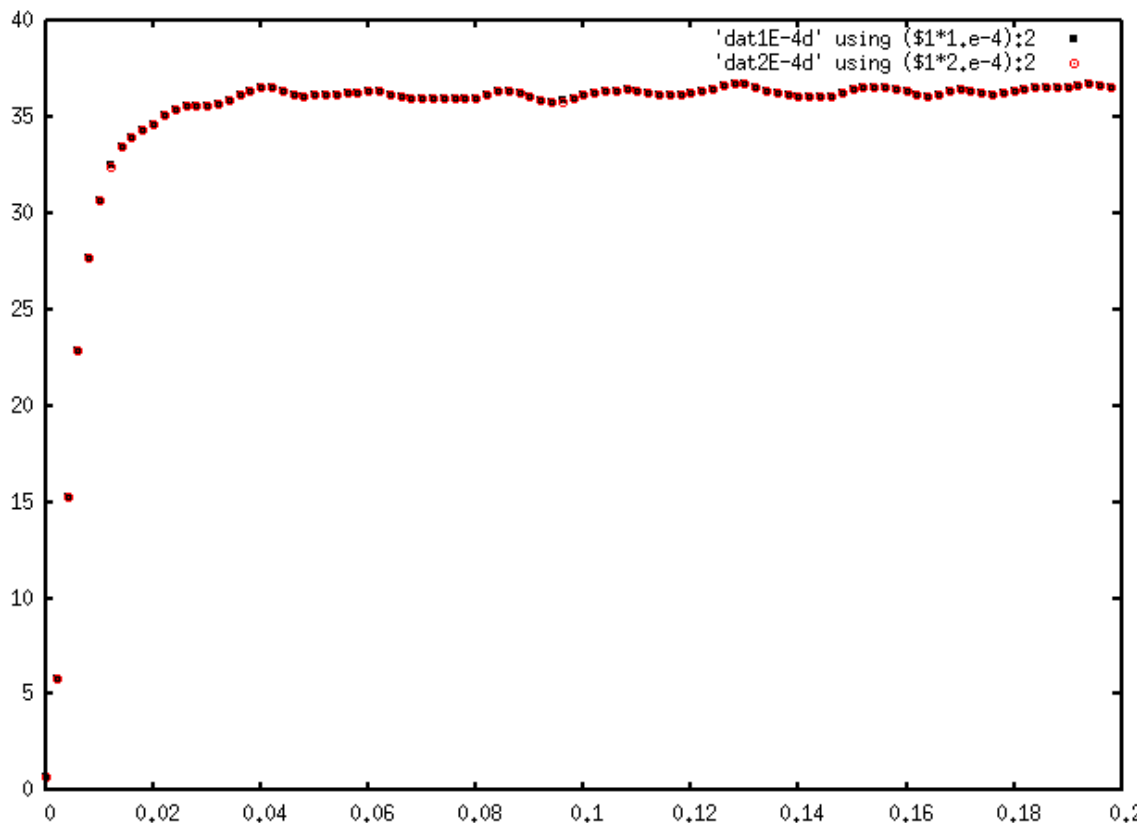


Figure 2: Time step vs. Temperature in Lennard-Jones Fluid. Simulation of 1×10^{-4} compared with 2×10^{-4} .



According to the two figures above, we can see that the pairs under 10^{-4} matches better with each other compared to 10^{-3} , which shows that 10^{-4} is more sufficient to conduct such simulations. Therefore, in the later research of MD simulations, we tried to use 10^{-4} for every time step, if allowed by the total time of the simulation.

B. Pure Lithium Solid

1. LAMMPS input command

In order to use the 2NN MEAM potential, two fundamental files need to be created in order to set the parameters of the system: library.meam and Li.meam. The library.meam file contains the original results from MEAM developer Baskes.¹⁸ The Li.meam file is auxiliary file that contains additional parameters for atoms of your interest. In our case, following Cui's paper, we created a 'Li1' entry to the library.meam file and used the Li.meam file. The 'Li1' entry is created by substituting Cui's parameters into the original Li in the library.meam file. Our data read in this entry is as the following structure:

'Li1'	'bcc'	8	3	6.939			
3.00	1.03	4.88	4.15	5.27	3.45255	1.65	0.64
1.0	-1.46	4.13	-0.57	1	3		

This structure is at a format shown below:

Elt	lat	z	ielement	atwt			
Alpha	B0	B1	B2	B3	alat	esub	asub
T0	T1	T2	T3	rozero	ibar		

The meaning of each parameter is:

Elt: element lat: lattice structure of reference configuration

z: number of nearest neighbors in the reference structure

ielement: atomic number atwt: atomic weigh alat: lattice constant

esub: energy per atom asub: "A" parameter for MEAM by Baskes¹⁸

rozero: element-dependent density scaling that weights the reference background density

The rest of the parameter are standard MEAM values according to Baskes¹⁸. The lattice constant (alat) here is determined from the nearest-neighbor distance r_e , which equals 2.99 in the paper.

Other parameters are in Li.meam file. When writing this file, it is important that every parameter can be read by LAMMPS.

Our Li.meam file, obtained from Cui, reads (explanation from the manual¹³):

rc = 4.8 (cutoff radius for cutoff function)

delr = 0.2 (length of smoothing distance for cutoff function)

augt1=0 (integer flag for whether to augment t1 parameter by $3/5*t3$ to account for old vs. new MEAM formulations, 0= don't augment t1, 1 = augment t1)

ialloy=2 (integer flag to use alternative averaging rule for t parameters, for comparison with the code, 0=standard, 1=alternative, 2=no averaging)

mixture_ref_t=0 (integer flag to use mixture average of t to compute the background reference density for alloys, instead of the single-element values 0= do not use mixture, 1 = use mixture)

erose_form=2 (integer value to select the form of the Rose energy function)
 zbl(1,1) = 0 (blend the MEAM I-J pair potential with the ZBL potential for small atom separations)
 nn2(1,1) = 1 (turn on second-nearest neighbor MEAM formulation for I-J pair
 0 = turn off, 1= turn on)
 Cmax(1,1,1) = 1.91 (Cmax screening parameter when I-J pair is screened by K (I<=J))
 Cmin(1,1,1) = 0.31 (Cmin screening parameter when I-J pair is screened by K (I<=J))
 attrac(1,1) = 0.14 (additional cubic attraction term in Rose energy I-J pair potential)
 repuls(1,1) = 0.14 (additional cubic repulsive term in Rose energy I-J pair potential)

We then constructed a system with desired atoms and their initial positions. Dr. Holzwarth helped me to write a program “makelammpsinputforcubic” so that I am able to create a system with solid lithium atoms. The program includes the inputs of structure, lattice constant, units per each side, and the mass of the atom. After this system is generated, I created a vacancy by manually removing an atom from the structure.

Then, the input file to run LAMMPS simulation can be created. The file reads:

```

Unit          metal
Boundary      p p p
Atom_style    atomic

Read_data     Li_bcc_data

Pair_style    meam
Pair_coeff    * * library.meam Li1 Li.meam Li1

Fix           1 all box/relax iso 0.0 vmax 0.001

Thermo        1
Thermo_style  custom step press etotal lx ly lz xlo xhi ylo yhi zlo zhi

Dump          1 all xyz 1 file.xyz

Minimize      1.0e-20 1.0de-19 1000 10000
  
```

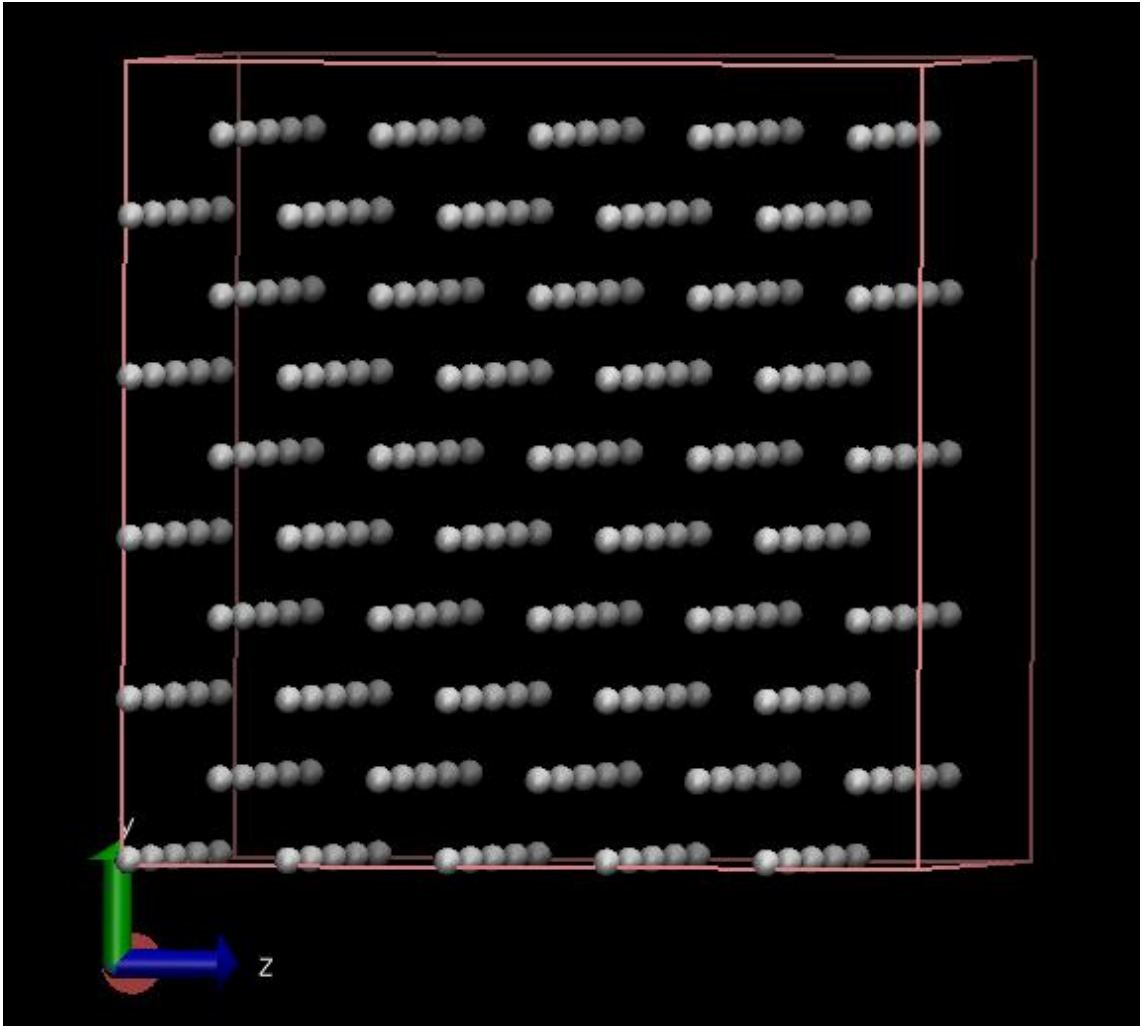
“Units” sets the style of units used for this simulation. Under “metal” units, mass is in grams/mole; distance is in Angstroms; time is in picoseconds; energy and torque are in eV; temperature is in Kelvin; pressure is in bars. “Boundary” sets the style of boundaries of a simulation box in each dimension. In this case, p means periodic boundary condition. “Atomic_style” is used to set the atoms with an atomic style in a simulation. “Read_data” indicates to the initial position file that just generated. “Pair_style” sets the formulas that

are used to compute pairwise interaction. Here, we used the 2NN MEAM as mentioned in the previous section. “Pair-coeff” refers to the parameters of the potential used, which is in the library.meam and Li.meam file. “Fix” commend set a fixed parameter or any ensemble to a specified group of atoms. Here an external pressure is applied to all atoms in the simulation box through “box/relax”. The “iso” parameter means couple all three diagonal components together when pressure is computed. The “vmax” is used to upper limit of the fractional change in the volume of the simulation system. “Thermo” means the number of time steps between each output thermodynamics information is outputted. “Thermo_style” suggests which thermodynamics will be printed. “Dump” is a snapshot of atom quantities to a certain number of time steps under a specific image style. Finally, an energy minimization of the system is performed to start the process.

2. Energies at Different Structures

In the output file, log.lammps, we can find the total energy calculated by the “minimize” command. In order to calculate the energy per atom, I divided the number by the number of atoms; that is, in a case with 5 units per each side, 250 for bcc, 500 for fcc, and 249 for bcc with a vacancy. An example of this is shown as Figure 3.

Figure 3: A bcc structure of solid lithium atoms with 5 units per each side and a vacancy on the top right corner. Visualization is performed with VMD.¹⁵



BCC: Total Energy = -411.8245 (for 250 atoms)

Energy/atom = 1.647298

FCC: Total Energy = -817.45483 (for 500 atoms)

Energy/atom = 1.6349

Difference bcc → fcc = 0.012398

BCCVAC: Total Energy = -409.51321

Energy/atom = 0.663992

The results are the same to those in Cui's paper¹⁷ in terms of the first three significant digits given in the paper. Therefore, it proved that we are able to successfully run LAMMPS for a pure solid lithium system.

3. Diffusion Coefficients and Activation Energies

After our successful simulations in calculating energies, we expanded the method to calculate diffusion coefficients. The basic mechanics are the theory introduced above in equation 3 and equation 4. Some additional commands are added to the input file in order to have the atoms move so we can obtain the MSD. The new input reads:

```

Unit            metal
Boundary        p p p

Atom_style      atomic
Read_data       Li_bccvac_data

Pair_style      meam
Pair_coeff       * * library.meam Li1 Li.meam Li1

Velocity        all create 350 43454 dist uniform mom yes rot yes
Fix             1 all nve
Timestep        1E-3

Thermo          1
Thermo_style    custom step time temp press ke pee total
Run             500

Velocity        all scale 350
Run             500

Velocity        all scale 350
Compute         2 all msd com yes
Compute         3 all vacf
Compute         4 all temp
Fix             5 all ave/time 1 1 1 c_4 c_2[4] c_3[4] file out.msd

Dump            1 all xyz 1 file.xyz

Run 1000000

```

Instead of minimizing the energy, we used “Velocity” command to initiate the movement. This command helps to set the velocities of a group of atoms. Here, we used the “create” argument to apply a temperature under a random number of seed to the

system. The random numbers of seed are generated with a uniform distribution. The linear momentum “mom” and the angular momentum “rot” of the newly created velocities are both set to be zero. By heating the system to the desired temperature with a vacancy inside, the atoms would move away from their original positions according to the forces and velocities. We noticed that depending on the random numbers generated, the final average temperatures did not always match the temperatures applied through the “velocity” command. Then a micro-canonical ensemble is fixed. We use this ensemble because it seems to be the most reliable ensemble for modeling MSD. “Timestep” set the time step size for MD simulations. Sometime it is better to use 1E-3 as one timestep for longer equilibrated runs. Other times, 1E-4 might give better results, such as in the case of a slab geometry. The system has been reset to the desired temperature several times to obtain an equilibrium situation after a set of runs. Then we “compute” the “msd” as mean-squared displacement, the “vacf” as the velocity-autocorrelation function of group of atoms, and the “temp” as temperature. Again, a fix command with “ave/time” is used to output the result to an out.msd file.

We set the temperature at three different scales: high temp. =400K, mid temp. =350K, and low temp. =300K. Temperatures of all atoms are scaled twice with 500 time steps each. The final run is 10^6 time steps after two scaling procedures.

After obtaining the msd results from running LAMMPS, we can use gnuplot to fit the slope of time vs msd using the following steps:

```
F(x)=a*x+b
Fit f(x) './out.msd' u 1:3 via a,b
Plot './out.msd', f(x)
```

The fitting results will be automatically saved under fit.log.

From the slope, by transferring the units to m^2/s , we have our diffusion coefficients at each temperature. With these coefficients, we plotted graphs of $\ln D$ vs. $1000/T$. The results are shown in the Tables and Charts below.

Table 1: Diffusion Coefficients and Activation Energy Calculation for 5x5x5 box

5x5x5 bcc box with 1 vacancy on the top right corner				
T	1000/T	D	log D	Activation E
356.0303	2.80875	7.88E-11	-23.2643	0.054338802
403.5054	2.478281	9.61E-11	-23.0656	
451.123	2.21669	1.15E-10	-22.884	

Chart 1: 5x5x5 bcc box with 1 vacancy on top right corner. Log D vs. 1000/T plot.

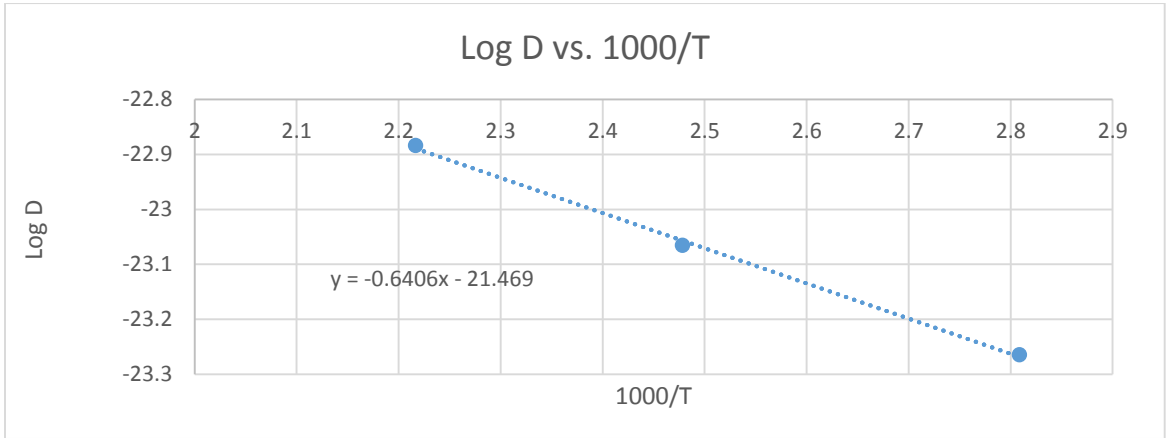


Table 2: Diffusion Coefficients and Activation Energy Calculation for 7x7x7 box

7x7x7 bcc box with 1 vacancy in the middle				
T	1000/T	D	log D	Activation E
351.7828	2.842663	2.75E-11	-24.316	0.074985134
399.298	2.504395	3.68E-11	-24.0257	
446.1802	2.241247	4.65E-11	-23.7923	

Chart 2: 7x7x7 bcc box with 1 vacancy in the middle. Log D vs. 1000/T plot.

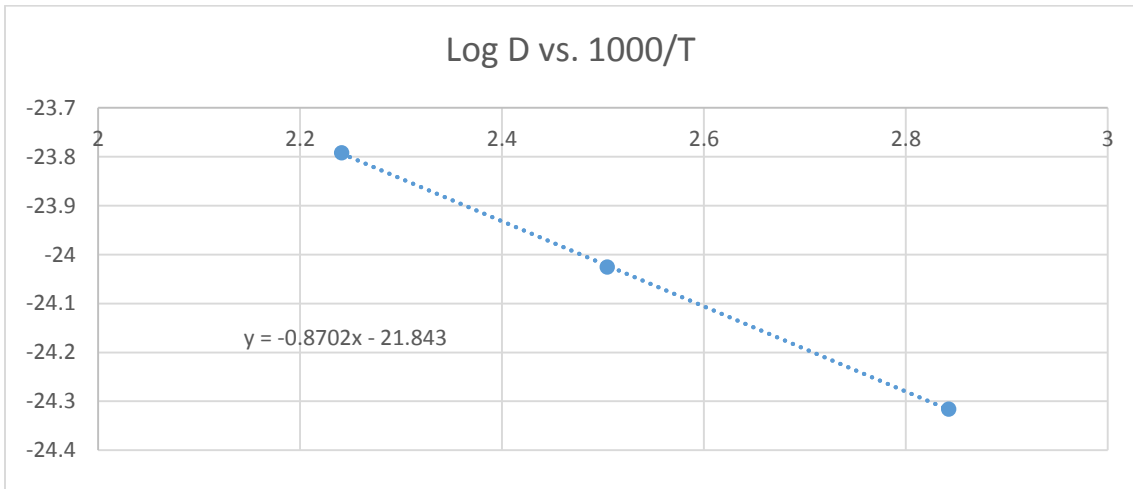
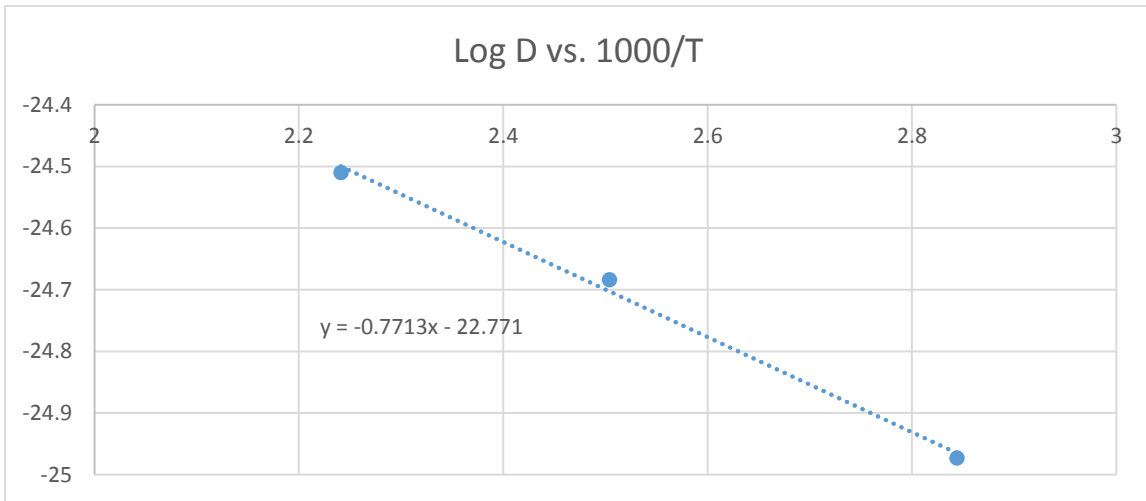


Table 3: Diffusion Coefficients and Activation Energy Calculation for 9x9x9 box

9x9x9 bcc box with 1 in the middle				
T	1000/T	D	log D	Activation E
351.6148	2.844022	1.43E-11	-24.9729	0.066462921
399.3764	2.503904	1.90E-11	-24.6841	
446.1847	2.241225	2.27E-11	-24.5103	

Chart 3: 9x9x9 bcc box with 1 vacancy on top right corner. Log D vs. 1000/T plot.



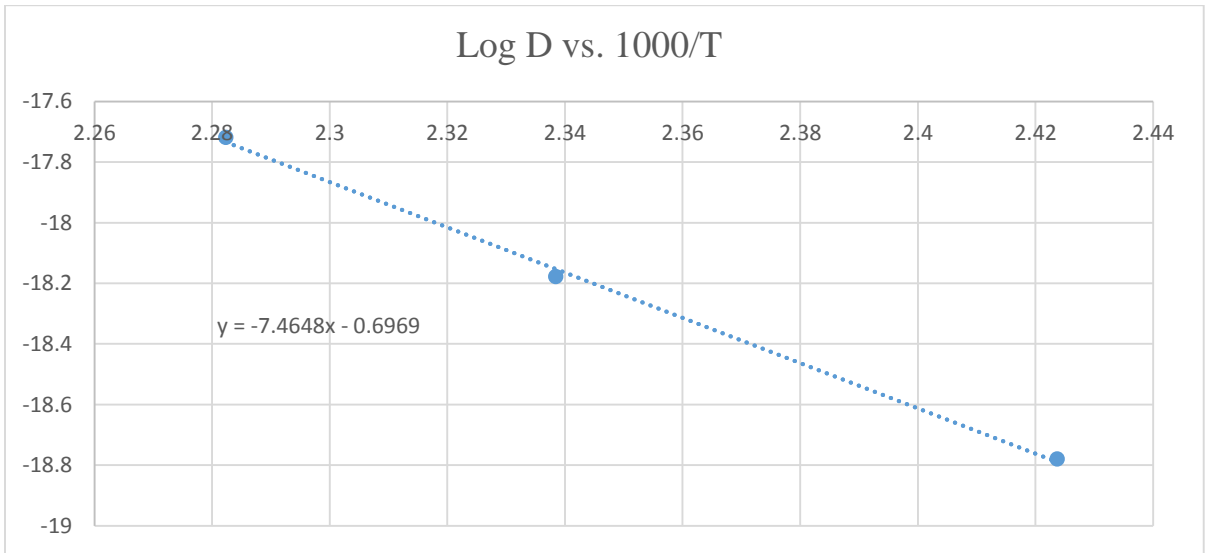
From 3 different simulation results above, we can conclude that our simulation results are significantly smaller than the 0.561eV suggest by the experiments²¹. But the activation energy is the energy needed to overcome to main bottle neck in the process. Although the experiments had shown that the energy to create a vacancy in bcc lithium solid is about 0.5 or 0.6 eV and this is approximately the activation energy for the diffusion coefficient found in the experiment. In our simulations, we started with a vacancy, so lithium atoms moving near that vacancy dominate the diffusion process. Therefore, we do not need to form a new vacancy for the diffusion to take place. Our activation energy is dominated by the energy needed for the vacancy to move, which is proximately 0.05-0.07 eV.

To prove this, we created slab on the top of the box, without any vacancy inside. So a larger activation is required to put one atom in the slab in order to create a vacancy for surrounding atoms to move. One of the example is in Table 4 and Chart 4. The example has the activation energy in the range of what the publication²¹ is suggested, which proves the explanation of our small activation energies in previous runs.

Table 4: Diffusion Coefficients and Activation Energy Calculation for 9x9x9 box

9x9x9 bcc box with no vacancy but with a slab on top					
Set Temp	Avg Temp	1000/T	D	log D	Activation Energy
800	412.5927	2.423698	6.98E-09	-18.7796	0.643241816
850	427.6331	2.338453	1.28E-08	-18.1776	
900	438.1517	2.282315	2.02E-08	-17.7191	

Chart 4: 9x9x9 bcc box with no vacancy but a slab on top. Log D vs. 1000/T plot.



Therefore, our simulations for pure solid lithium were successful. With this ability, we moved to model a more complex system, Li_2O

C. Li_2O Crystal

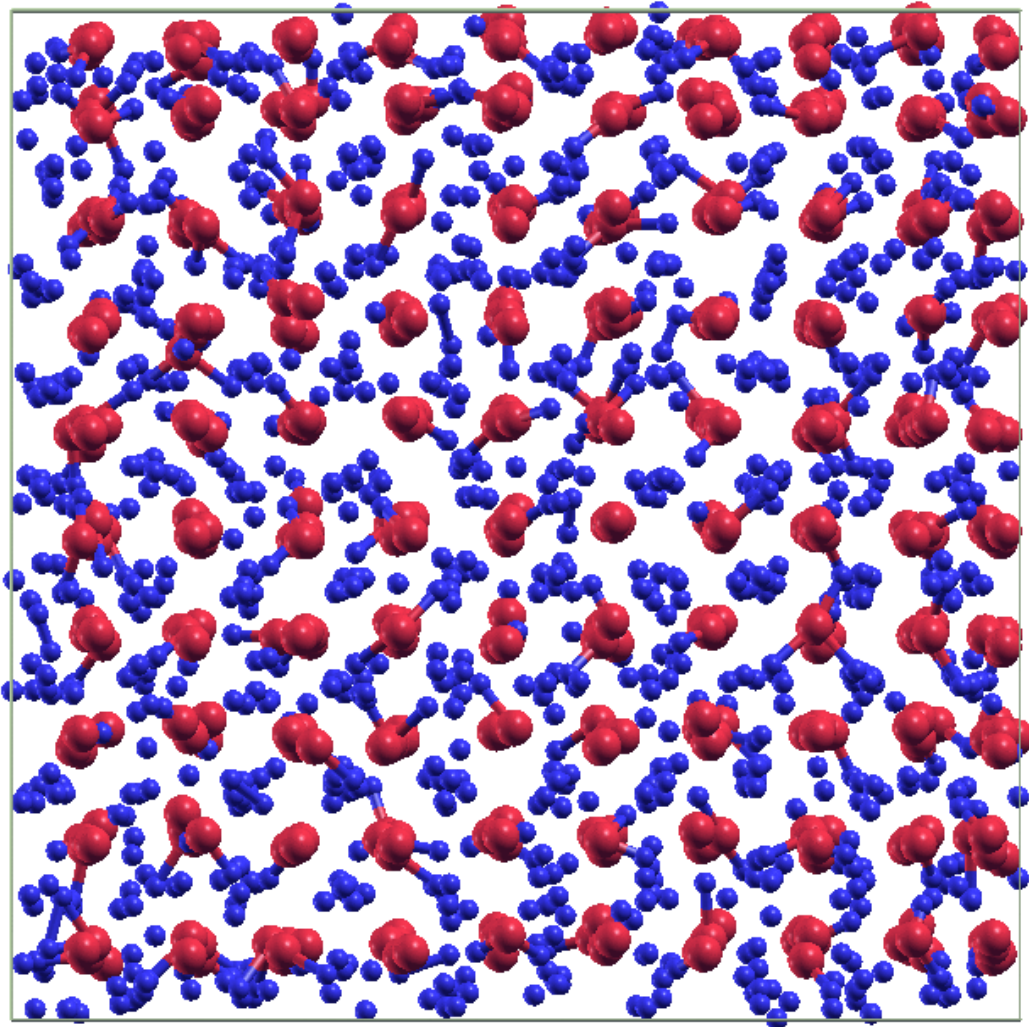
1. LAMMPS input command

Lithium oxide has a fluorite structure. We created a 5x5x5 box with 1500 atoms including 1000 lithium atoms and 500 oxygen atoms under a face-centered cubic structure. The melting temperature is way higher for Li_2O than for pure lithium. Thus, we decided not create any vacancy and heat the atoms to let it move freely. The input file to run the “mksupercellforlmps” program written by Dr. Holzwarth, so that we can create the structure is:

5x5x5	Li_2O	(name and content)
4.3	4.3 4.3	(lattice constant)
CHARGE		(atom type)
12	2	(number of atoms in the conventional cell, number of types)
1	-2 0 0 0	(coordinates of each atom in the box
1	-2 0.5 0.5 0	1 = oxygen with -2 electron charges
1	-2 0 0.5 0.5	2 = lithium with 1 electron charges)
1	-2 0.5 0 0.5	
2	1 0.25 0.25 0.25	
2	1 0.75 0.75 0.25	
2	1 0.25 0.75 0.75	
2	1 0.75 0.25 0.75	
2	1 0.75 0.75 0.75	
2	1 0.25 0.25 0.75	
2	1 0.75 0.25 0.25	
2	1 0.25 0.75 0.25	
5	5 5	(number of units per each side)
0	0	(number of vacancy and interstitial)
15.999	6.94	(masses of the elements)

After running the program with the parameters in the above file, we can create desired lithium oxide system. Figure 4 shows the graphic representation of this system.

Figure 4: A fcc structure of solid lithium oxide system with 5 units per each side. Blue represents Lithium; red represents Oxygen. Visualization is performed by XcrySDen.¹⁴



After the system has been set up, we are able to establish input command to run LAMMPS. One of the difficulties in MD method is choosing the right potential for each system. Different from pure solid lithium atom, we chose the FIT-EMP potential form, which is one of Buckingham-type pairwise potential models to model Li_2O systems. The Buckingham potential describes the Pauli repulsion energy and van der Waals energy for the interatomic interactions²². The parameters was taken from Dr. Oda and his colleagues' work²³. This potential needs no special parameter files. All parameters are indicated in the input file of LAMMPS. The input file reads:

```
Dimension      3
Boundary       p p p
Unit           metal
```



```

Atom_style      charge
Read_data      5x5x5

Group          O   type 1
Group          Li  type 2

Velocity        all create 3000 45454 dist uniform mom yes rot yes
Fix            1 all npt temp 1500 1500 100 iso 0 0 100
Timestep       1E-3

Thermo_style   custom step time temp press vole total ecol
Thermo        100

Pair_style     buck/coul/long      10      10
Pair_coeff    1 1 0                1        0
Pair_coeff    1 2 465.54           0.2939   0
Pair_coeff    2 2 0                1        0

Neigh_modify   one 20000
Neigh_modify   page 200000

Kspace_style   ewald 1.e-9
Pair_modify    table 0

Run 400000

Unfix          1
Fix           14 all nve

Compute        2 Li msd com yes
Compute        3 Li vacf
Compute        4 Li temp
Fix           5 Li ave/time 1 1 1 c_4 c_2[4] c_3[4] file Li.msd

Compute        10 Li msd com yes
Compute        11 Li vacf
Compute        12 Li temp
Fix           13 Li ave/time 1 1 1 c_4 c_2[4] c_3[4] file O.msd

Dump           9 all custom 1000 XXX.txt element xu yu zu
Dump_modify    9 element O Li

Run 200000

```

In this system, we used charged atoms at a 3-D dimension. The atoms are grouped by elements, so there are two groups: oxygen and lithium. During the initial trial runs, we found that the box we created are too small for 1500 atoms to move freely. Thus, we first

used fixed the system with an isothermal-isobaric (NPT) ensemble so that the system can expand to reach the equilibrium (Figure 3 and 4 below represent this process in terms of volume and pressure). The potential is set by “Pair_style” and its related parameters are set by “Pair_coeff.” The “buck/coul/long” means that we are using a Buckingham potential with a long range Coulombic term added, which is partially computed in Fourier Transform space and controlled with the “Kspace_style” command. This is followed by Buckingham cutoff and the Coulombic cutoff, which we both set to be 10. Then the interatomic potential coefficients is inputted according to the numbers Dr. Oda’s paper²³. “Page” and “one” options for “neighbor_modify” affect how memory is allocated for the neighbor lists. “Kspace_style” defines a long-range solver to use with each timestep so that long-range Coulombic interactions can be computed. Here, we asked it to perform a standard Ewald summation at a 10^{-9} relative error in forces. “Table” command controls the efficiency of the calculation. After the equilibrium process, we relieve the previous fixed constraints and fix the micro-canonical ensemble to have a free-movement calculation of lithium atoms. The position of each atom at certain number of time step is save under a txt file, which we can later transform to a xsf file for XcrySDen visualization. The process should be run long enough in order to receive a complete analysis of atoms’ movements.

Figure 3: A fcc structure of solid lithium oxide system with 5 units per each side.

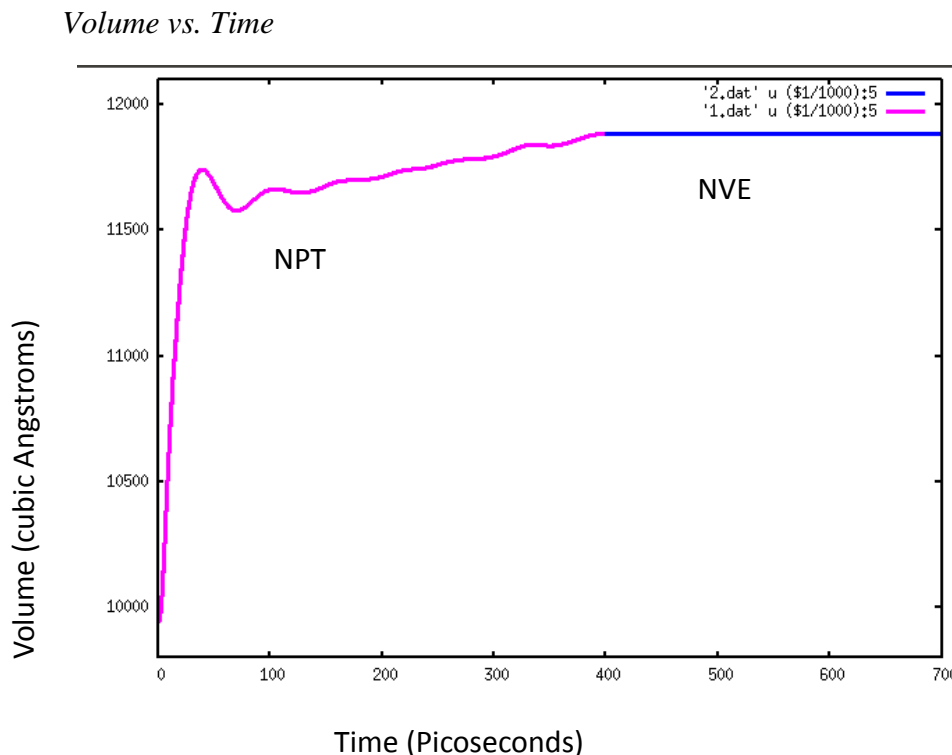
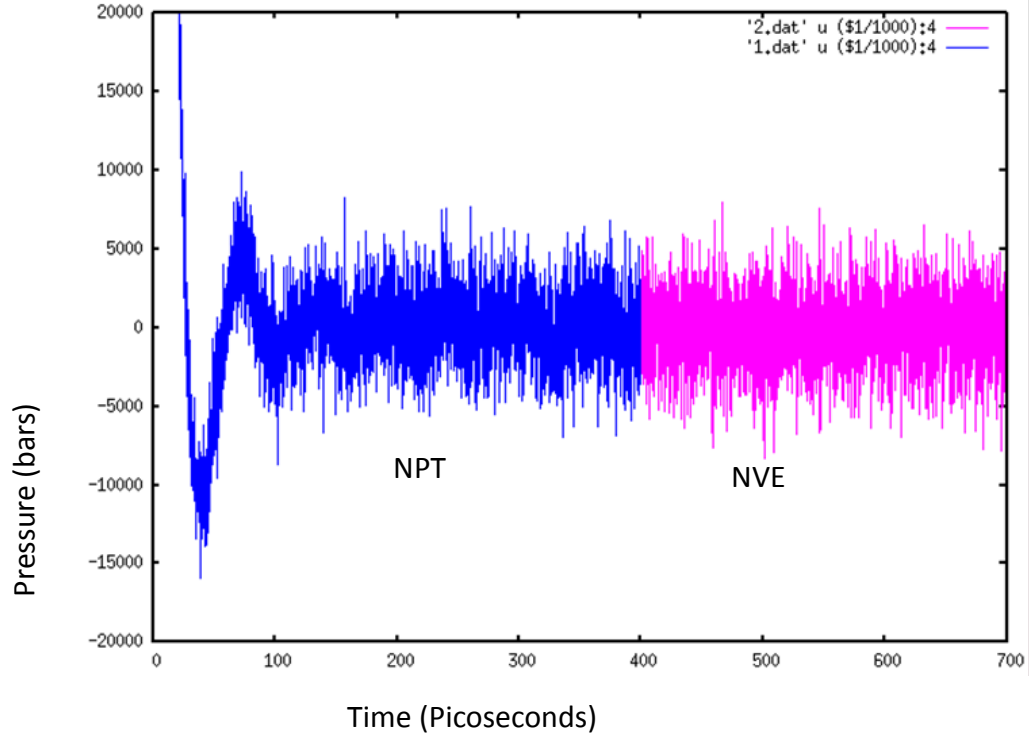


Figure 4: A fcc structure of solid lithium oxide system with 5 units per each side.

Pressure vs. Time



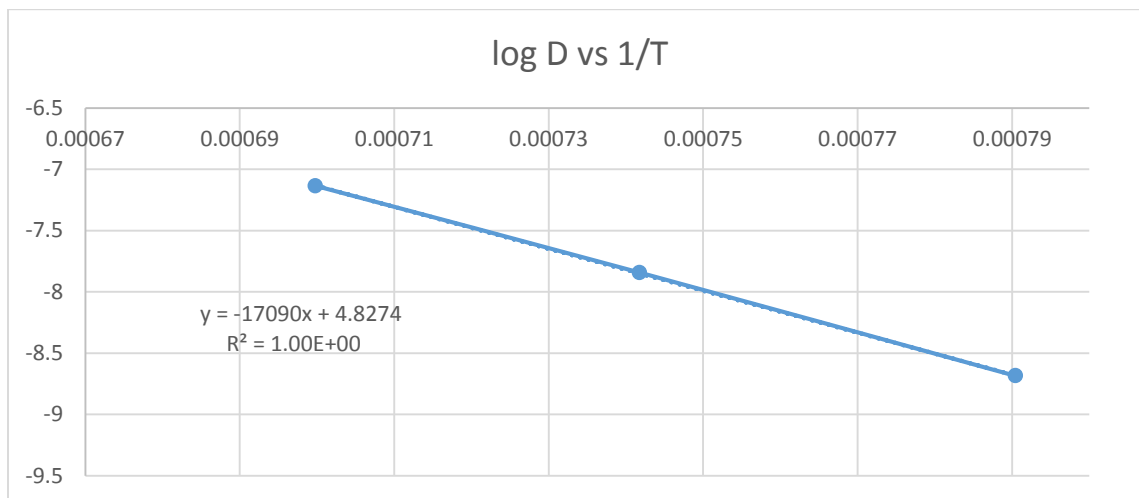
2. Diffusion Coefficients and Activation Energies

Using previous equation 3 and 4 again, we can calculate the diffusion coefficients and activation energy. The results are as the table 5 and chart 5 shown below:

Table 5: Diffusion Coefficients and Activation Energy Calculation for 5x5x5 Li2O

5x5x5 Li2O				
T	1/T	D	log D	Activation Energy:
1265.142	0.00079	0.000169	-8.68397	1.4726453
1348.165	0.000742	3.93E-04	-7.842	Error est. in calculation:
1429.05	0.0007	7.97E-04	-7.13514	1.57%

Chart 4: 5x5x5 Li2O. Log D vs. 1000/T plot.



The result has a small percentage error, especially compared with the pure lithium system. This shows that the noise does not affect our calculation as much as it does previously. In addition, the result is similar to Dr. Oda's paper²⁴, which models several different diffusion processes for this material.

IV. Summary

In conclusion, the pure solid lithium system shows that the atoms' motions are very small. Thus, the diffusion can be highly affected by the noise. Therefore, the outcomes contains a relatively large error. However, when it comes to the study of lithium oxide, the movements are observed to be larger and quicker near the melting point. The small percentage error leads us to the conclusion that the noise in the system does not influence the results as much.

After this learning process, our group is able to use LAMMPS code to simulate some simple solid lithium battery materials. The study of more complicated materials are still pending.

After all, we have successfully modeled some relative simple structured materials and are able to do some helpful calculations from the simulations. We are looking forward to make full use of LAMMPS to help our studies in the future.

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