Bulk Modulus of Solid Argon Crystal

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Abstract

This study used molecular dynamics to explore the bulk modulus of solid argon. By employing the Lennard-Jones potential, the interatomic interactions and the compression. This helped to model the interatomic interactions. Using the NpT ensemble, the study determined the equilibrium volume (V_0) at constant temperature and pressure. The pressure-volume relationship was also examined over two ranges of deformation with the aid of the NVT ensemble. With the corresponding pressure and volumes obtained, the slope of the bulk modulus was determined, which aided in the derivation of the Murnaghan and Birch-Murnaghan equations, providing information about the mechanical response of solid argon to compression. The results show that the Birch-Murnaghan equation provides superior accuracy at higher deformations compared to the Murnaghan model making it a more suitable equation of state model to describe the mechanical response of solid argon under extreme conditions.

Keywords: *Compression, Bulk modulus, equation of state*

1 Introduction

Studying the mechanical properties of materials such as the bulk modulus (B) is crucial to understanding their behavior under stress and strain. The bulk modulus measures the resis-

tance of materials to compression and helps to determine their elastic behavior. It is defined as the negative ratio of the pressure change to the relative volume change under isothermal conditions (T = constant) and the ratio of the pressure change to the relative entropy change under isentropic conditions (S = constant) [1].

By simulating the behavior of solid argon under different pressures and volumes, we are able to explore the elastic properties of the material, which is important for designing materials with specific mechanical characteristics.

This study utilized molecular dynamics (MD) simulations to calculate the bulk modulus of solid argon with the aid of LAMMPS and Python. The Lennard-Jones (LJ) potential was also used to examine the interatomic interactions because of its effectiveness in simulating noble gas crystals. In addition, the study used two equations of state (EOS): the Murnaghan and Birch-Murnaghan models to analyze the pressure-volume ($P(V)$) relationship [1].

2 Theory

2.1 Lennard-Jones Potential

The Lennard-Jones potential describes the interaction between chemically inert and neutral atoms and is mathematically represented as:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{1}$$

where:

- ϵ: Depth of the potential well,
- σ: Zero-potential distance,
- r: Distance between particles.

$\left(\frac{\sigma}{r}\right)^{12}$ describes the short-range repulsive forces, originating from the Pauli exclusion principle and the overlap of the electron cloud. The $\left(\frac{\sigma}{r}\right)^{6}$ describes the attractive forces which describe the long-range vander Waals forces, which is an attractive force between atoms that is usually weak. Both the attractive force and repulsive forces are present in Lennard-Jones potential. The image below shows the Lennard-Jones potential and indicates the repulsive and attractive force region.

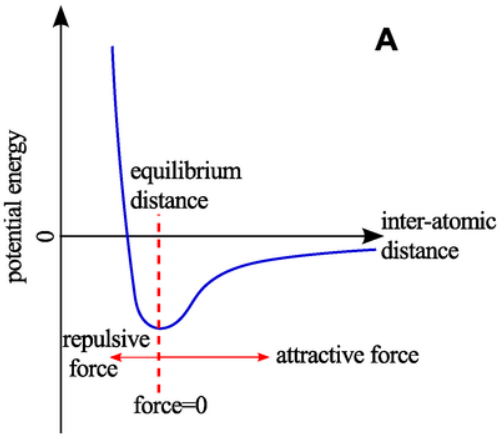

Figure 1. Lennard-Jones Potential

2.2 Definition of Bulk Modulus

The bulk modulus is a measure of a material's resistance to uniform compression and is represented mathematically as:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T \tag{2}$$

where:

- B: Bulk modulus,
- V: Volume,
- P: Pressure,
- T: Temperature.

There are two types of bulk modulus which are the isothermal bulk modulus and the isentropic bulk modulus. In the isothermal bulk modulus, the temperature (T) is kept constant. Where as in the isentropic bulk modulus, the entropy is kept constant. Below equation describes the isentropic bulk modulus:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_S \tag{3}$$

The variables are the same just like the case of the isothermal just that S stands for entropy which is kept constant as opposed to the temperature.

2.3 Murnaghan Equation of State

The Murnaghan EOS models the relationship between pressure and volume. It was proposed in the year 1944 by Francis D.Murnaghan and has been extensively used over the years in the scientific world. The model draws on the fact that as you compress a solid, it becomes extremely difficult to compress it further. It is mathematically represented below as:

$$P(V) = \frac{B_0}{B_0'} \left[\left(\frac{V}{V_0} \right)^{-B_0'} - 1 \right] \tag{4}$$

where B_0 is the bulk modulus at equilibrium volume (V_0), and $B_0' = \frac{\partial B}{\partial P}$ is the derivative of pressure. pressure derivative. It is important to note that this model lacks accuracy at larger deformations and is well suited for small volume changes [1].

Equally important is the fact that while the bulk modulus is reliant on the volume of the material, as it is denoted by the relationship $B = B(V)$, attention is usually drawn to the zero bulk modulus, which is denoted as $B_0 = B(V_0) = B(V(p = 0))$.

2.4 Birch-Murnaghan Equation of State

The Birch-Murnaghan equation models the pressure-volume relationship and is given by:

$$P(V) = \frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right] \times \left[1 + \frac{3}{4}(B_0' - 4)\left(\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right)\right] \tag{5}$$

where:

- B_0: Bulk modulus at equilibrium volume,
- V_0: Equilibrium volume,
- B_0': Pressure derivative of the bulk modulus,
- V: Current volume.

Compared to the Murnaghan EOS, the Birch-Murnaghan EOS provides more accurate results and is suitable for describing material behavior under higher order deformations [2]. Nevertheless, both equations emerge from thermodynamic principles and provide a framework for examining how materials respond to compression.

3 Methodology

3.1 Simulation Setup

In this study, the simulations were performed using the LAMMPS software, GNU plot and Python 3.12:

- **NpT Ensemble:** The equilibrium volume (V_0) was calculated at $T = 30\,\mathrm{K}$ and $P = 0\,\mathrm{atm}$.
- **NVT Ensemble:** The pressure-volume relationship was analyzed over two deformation ranges: $0.95V_0 \leq V \leq 1.05V_0$ and $0.85V_0 \leq V \leq 1.15V_0$ respectively.

The **NpT ensemble** was used to determine V_0. The 'log.lammps' file was obtained and cleaned to extract relevant parameters such as volume, energy, and pressure. From the NpT ensemble, the 'stat' command was used to obtain the equilibrium volume $V_0 = 19147.778$, which was then used to calculate the lattice constant and the respective volume for the two volume ranges. The lattice constant was calculated using the formula below for the respective volumes obtained from the respective ranges:

$$a = \left(\frac{V}{125}\right)^{\frac{1}{3}}$$

where v is the respective volumes obtained

from the NVT ensemble and 125 represents the number of atoms in the solid argon's unit cell.

3.2 Calculation of Bulk Modulus B_0 at Zero Pressure

$$B_0 = -V_0 \left(\frac{\partial p}{\partial V} \right)_T \tag{6}$$

where V_0 is the equilibrium volume, and $\frac{\partial p}{\partial V}$ is the derivative of pressure with respect to volume at constant temperature.

Finite differencing was used to approximate this derivative based on the equilibrium volume. The computed value for B_0 was:

$$B_0 = 2.02638249 \text{ GPa}$$

where: ∂p is the change in pressure between two volumes. and ∂V is the corresponding change in volume. The volumes obtained from the NVT ensemble and the equilibrium volume V_0 were used to compute pressure values for 11 equally spaced volumes ($0.95V_0 \leq V \leq 1.05V_0$) and 8 additional volumes in the range $0.85V_0 \leq V \leq 1.15V_0$, using Python, GNU Plot, and LAMMPS. The following table was obtained:

Vo_values	a	Volume	pressure	P1 (bar)	P2 (bar)	std
0.95	5.259898	18190.389	1317.926	1316.13989	1298.03145	76.6452
0.96	5.278289	18381.867	1009.765	996.779707	988.019276	77.7428
0.97	5.296554	18573.345	711.6778	708.622606	705.126684	78.647
0.98	5.314693	18764.822	450.4702	448.344099	447.362769	79.5864
0.99	5.332709	18956.3	209.4482	213.002712	212.886541	79.5839
1	5.350604	19147.778	-7.9491	-0.0073999	-0.0052061	80.1081
1.01	5.36838	19339.256	-195.828	-192.99757	-192.88895	81.2661
1.02	5.386039	19530.734	-378.764	-368.02039	-367.22455	82.3191
1.03	5.403583	19722.211	-547.794	-526.90078	-524.36445	82.9565
1.04	5.421015	19913.689	-689.464	-671.26315	-665.56214	84.6877
1.05	5.438334	20105.167	-820.843	-802.55505	-791.97985	84.3672

Figure 2. Table of Volumes and Pressures

The table above presents the respective volumes and pressures obtained, where a is the lattice parameter. P (bar) represents the simulated pressure without fit, P_1 (bar) represents the pressure calculated using the Murnaghan equation of state, while P_2 (bar) corresponds to the pressure from the Birch-Murnaghan equation of state which will be explained better in the latter section of the study.

3.3 Calculation of Derivative of Bulk Modulus

To obtain the derivative of the bulk modulus denoted as B_0', it is important to calculate B_0^+ and B_0^- using the following formula:

$$B_0^+ = -V_0 \left(\frac{\Delta p^+}{\Delta V^+} \right)$$

$$B_0^- = -V_0 \left(\frac{\Delta p^-}{\Delta V^-} \right)$$

where: Δp^+ and Δp^- are the changes in pressure in line with small increment and decrement in volume. The ΔV^+ and ΔV^- are the changes in the volume.

$$B_0' = \frac{B_0^+ - B_0^-}{p^+ - p^-}$$

By making a plot of B_0^+, B_0, and B_0^-, p^+, p^-, and p at equilibrium, which is zero, we obtained

a plot describing the correlation between bulk modulus and pressure, as described and presented in the later section of the study. Importantly, by fitting these values, we obtained the value $B_0' = 8.86906$.

4 Results and Findings

This section of the study presents the calculated values of the volume, pressure and the standard deviation as the y error bars which were obtained using LAMMPS, Python and GNU Plot under the two varying volume ranges.

4.1 Dependence of Pressure on Volume

Using the equilibrium volume value obtained from the NpT, 11 different equispaced volumes were obtained in the range $0.95V_0 \leq V \leq 1.05V_0$. This was done by multiplying these ranges with the equilibrium volume, providing the volume column in Figure 1. This was followed by the calculation of the lattice parameter as the cube root of (Volume / 125) by making changes to the `simulation.in` file and running the `run_simulation.bat` file to obtain the thermodynamic parameters. From these parameters, our pressure and standard deviations were obtained using the stat command in GNU for values within the sampling range (after the equilibration range between 1 and 1000). We used the sampling range [10001:30000]. Below is a graph of the obtained result from the plot of the pressure against volume showing the dependence.

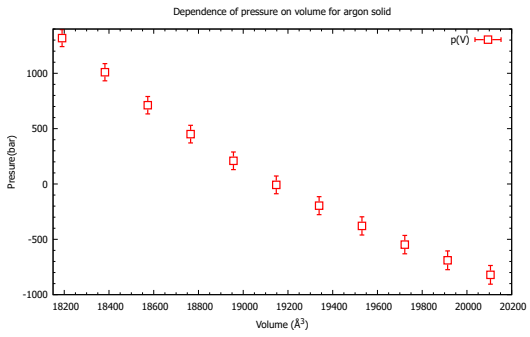

Figure 2. Dependence of pressure on volume

From the above plot, it can be seen that as the volume increases, the pressure decreases, which is an expected behavior for a compressible solid. When the volume is reduced (compression), the pressure increases, and when the volume increases (expansion), the pressure decreases. The negative pressure values indicate a tensile state, which shows that the material is under expansion beyond its equilibrium state in some cases.

4.2 Correlation between Bulk Modulus and Pressure

The correlation between the bulk modulus and pressure was explored through the use of finite differences to analyze the pressure above and below equilibrium, from which bulk modulus values were obtained. This was essential in obtaining the derivative of bulk modulus B_0' using gnu plot which was used to fit the equations of state. The graph below shows this relationship between the bulk modulus and the pressure.

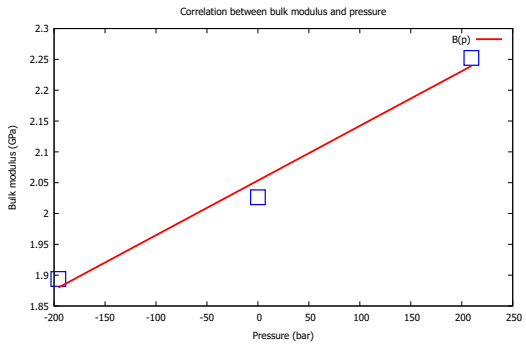

Figure 3. Correlation between bulk modulus and pressure

The above graph portrays that bulk modulus increases with pressure. It can be seen from the graph that bulk modulus increases as pressure increases, indicating that as compression (higher pressure) occurs, material resists further compression more strongly. Positive pressure indicates a compressive state, while negative pressure indicates a tensile state.

4.3 Equation of State Calculations

The Murnaghan and Birch-Murnaghan equations of state were obtained using these parameters: V_0 (Equilibrium volume), B_0, and B_0' (Derivative of Bulk Modulus).

4.4 Murnaghan Equation of State Result starting at 0.95

Using the Murnaghan equation, we performed a fit to obtain the pressure for the Murnaghan equation which was compared against the volume for the ranges $0.95V_0 \leq V \leq 1.05V_0$. The graph presented below offers insight into the behavior of pressure against volume for the Murnaghan equation of state.

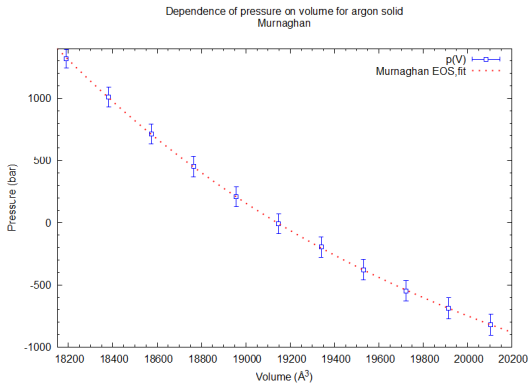

Figure 4. Dependence of Pressure on Volume with Magnaghan

In the above presented graph, the red dotted lines indicates the Murnaghan EOS fit used to

model the pressure-volume relationship of the solid argon under compression and expansion. It can be seen that as the volume increases, the pressure decreases which is expected of compressible materials. The pressure is high at lower volumes which connotes that solid is highly compressed. On the other hand, at higher volumes, the pressure becomes negative showing tensile stress or expansion. This graph has ascertained that the Murnaghan equation of state can be beneficial in effectively describing the elastic response of solid argon to compression and expansion. When compared with the simulated result of the pressure against volume in the previous section, it can be seen that the Murnaghan fit graph corresponds with the pressure-volume result. Both graphs show a negative correlation between pressure and volume which is in tandem with expected compressibility behavior of solid argon.

4.5 Birch-Murnaghan Equation of State Starting at 0.95

Using the Birch-Murnaghan equation, we performed a fit to obtain the pressure for the Birch-Murnaghan equation which was compared against the volume for the ranges $0.95V_0 \leq V \leq 1.05V_0$. The graph presented below offers insight into the behavior of pressure against volume for the EOS.

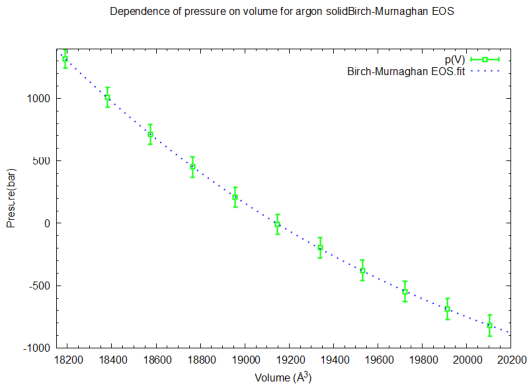

Figure 5. Dependence of Pressure on Volume with Birch-Magnaghan

In the above presented graph, the blue dotted lines indicates the Birch-Murnaghan EOS fit used to model the pressure-volume relationship. Similar to the Murnaghan result obtained earlier, It can be seen that as the volume increases, the pressure decreases which is expected of compressible materials. The pressure is high at lower volumes which connotes that solid is highly compressed. On the other hand, at higher volumes, the pressure becomes negative showing tensile stress or expansion. This graph has ascertained that the Murnaghan equation of state can be beneficial in effectively describing the elastic response of solid argon to compression and expansion. When compared with the raw simulated result of the pressure against volume in the previous section, it can be seen that the Murnaghan fit graph corresponds with the raw-pressure volume re-

sult. Both graphs show a negative correlation between pressure and volume which is in tandem with expected compressibility behavior of solid argon. Also, there is little to no differences in the Murnaghan and Birch Murnaghan equations of state. They both performed similarly and there is little to know difference in the way they describe the behavior of solid argon.

4.6 Dependence of pressure on Volume Starting at 0.85

This section of the study describes the simulated volume against the pressure in the range $0.85V_0 \leq V \leq 1.15V_0$ obtained using the stat command in GNU plot. Below graph shows the behavior of pressure against volume.

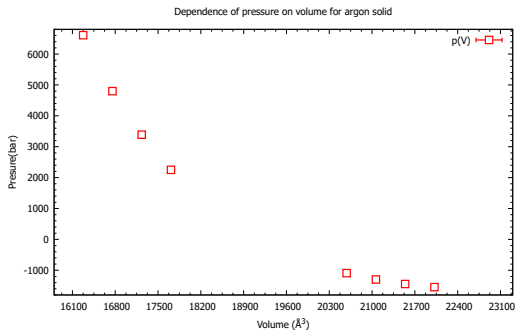

Figure 6. Dependence of pressure on volume

From the above plot, it can be seen that as the volume increases, the pressure decreases, which is an expected behavior for a compressible solid. When the volume is reduced (compression), the pressure increases, and when the volume increases (expansion), the pressure decreases. This is similar to the trend observed in the range between 0.95 to 1.05. In addition, this trend aligns with the fundamental equation of state (EOS) principles where pressure and volume are inversely related.

4.7 Murnaghan and Birch-Murnaghan Equation of State Analysis at 0.85

This section of the study analyzes the equation of state for both the Murnaghan and Birch-Murnaghan equation of state for the volume range $0.85V_0 \leq V \leq 1.15V_0$. The graph below shows the behavior of the two equation of state which are values of the fit of the Murnaghan and Birch-Murnaghan against volume.

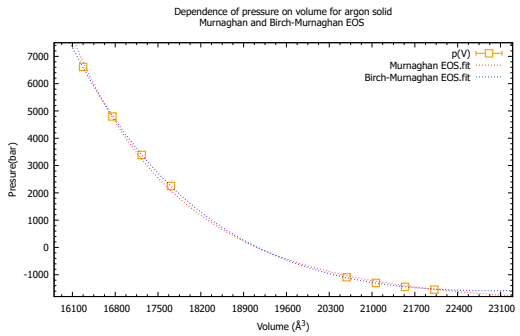

Figure 7. Dependence of pressure on volume Murnaghan and Birch

From the above presented graph, it can be seen that as the volume decreases, both fits capture the observed trend observed in the pressure against volume dependent seen

earlier that as pressure decreases, volume increases. Both equation of states meaningfully captured the behavior of the solid argon under compression. However, the Birch-Murnaghan seems to fit the data more closely especially at higher compressions (smaller volumes). The Murnaghan shows observable deviations which are visible at extreme pressures. In addition, the Birch-Murnaghan follows a slighly non-linear path compared to the Murnaghan EOS, which assumes a simpler functional form for the pressure-volume relationship. This indicates that the Birch-Murnaghan EOS accounts for higher-order elastic effects better than the Murnaghan EOS. Nonetheless, since both models follow the same trend, they validate the numerical results obtained without the fit used to determine the bulk modulus (B_0). We can posit that the Birch-Murnaghan equation appears to be a more accurate representation of the material's behavior especially at higher pressures. In addition, since the behavior of the material at higher volume when compared with the lower volume range of 0

4.8 Dependence of error e on the volume V

This section of the examines the error e on the volume V and sheds the light on the state which is better between the two equations of state at higher deformations. Below graph offers insight into the dependence of error e on the volume.

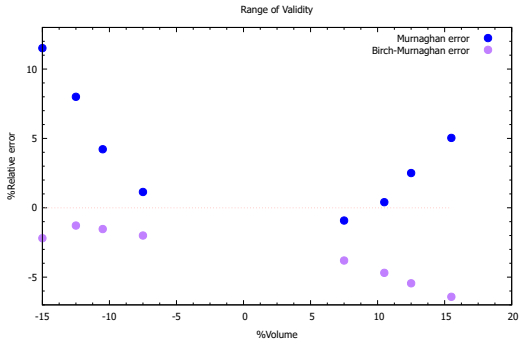

Figure 8. Dependence of Error on Volume

From the above presented graph of the relative error against volume. There are two errors which are the Murnaghan equation and Birch-Murnaghan equation of state errors. The Birch-Murnaghan shows a lower relative error across the range of volumes observed indicating a better fit of the behavior of the material. The Murnaghan equation on the other hand shows a more significant deviation especially at higher deformations. Notably, at low deformations (close to equilibrium volume) they both show reletaively low errors. However, as the volume moves away from equilibrium, the Murnaghan equation accumulates more error. It can also be seen that Birch-Murnaghan equation maintains more accuracy across a broader range of volume. Therefore, we can infer that the Birch-Murnaghan equation of state better describes the material behavior at higher deformations

and the Murnaghan equation is less accurate as the volume shifts away from equilibrium. This is due to the fact that he Birch-Murnaghan includes higher order terms, which makes it more capable of capturing possible non-linearity in material compression.

5 Conclusion

This study carried out the molecular dynamics simulations of argon solid. Using the Lennard-Jones potential, the effectiveness of the equations of state in determining solid argon's bulk modulus and compression examined. Between the two equations of state, the Birch-Murnaghan equation provided the most accurate representation of $P(V)$ relationship between pressure and volume, making it more preferred for analyzing compressive behavior in solids. From the results of the study in the volume range $0.95V_0 \leq V \leq 1.05V_0$ both the EOS models exhibited similar behaviors and there was little to no difference in how they described the behavior of the solid argon. However, in the broader range of volume $0.85V_0 \leq V \leq 1.15V_0$, the Birch-Murnaghan's performance outweigh that of the Murnaghan as it accounts for higher order elastic effects while the Murnaghan tends to diverge more at extreme pressures.This makes the Birch-Murnaghan a better model especially as it showcases better fit at extreme pressures which might be attributed to sophisticated treatment of compressibility. This study findings thus shows that the Birch-Murnaghan should be utilized at a wide pressure range (broad volume range) while the Murnaghan should be reasonably utilized at smaller ranges.

6 References

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