THE STRUCTURAL PROPERTIES OF LIQUID MOLYBDENUM UNDER HIGH PRESSURE: MOLECULAR DYNAMICS SIMULATIONS STUDY

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Abstract

In this study, the structural properties of liquid molybdenum at high pressure and high temperatures were investigated by using the classical molecular dynamics simulation technique. Finnis-Sinclair type many-body potentials were used to describe interatomic interactions between atoms in the system. The liquid system was simulated under different pressures ranging from 0 to 50 GPa to observe the effect of pressure on structural properties. The pressure dependence of some structural properties such as volume, pair distribution functions, mean square displacement and diffusion coefficient was analyzed in detail. The results showed that the first, second and third nearest neighbor distances vary depending on the pressure and the atomic mobility decreases as the pressure applied to the liquid system increases.

Keywords: Liquid molybdenum, MD simulation, high pressure.

INTRODUCTION

The structural properties of metallic liquids at high temperature and under high pressure have recently attracted the attention of many researchers [1-5]. There is more than one technique for preparing metallic alloys containing two or more components. The most preferred of these techniques is the method of mixing the liquid forms of each element forming the alloy together. The mechanical properties of the solid (crystalline or glassy) material obtained from the melt vary depending on the heterogeneity of the atomic arrangement in the liquid state, the applied pressure and the quenching rate [6-8]. Therefore, it is important to comprehensively analyze the structural properties of liquid metals at high pressure and temperature. The structural properties of these metals can be investigated using both experimental and theoretical methods. In particular, molecular dynamics (MD) simulations among theoretical methods are frequently used to investigate the structural development of liquid metals at high pressure and temperature, since they have the ability to analyze in detail at the atomic scale [9-14]. Molybdenum (Mo), which is used in many fields from increasing the strength of steel at high pressures and temperatures to nuclear energy applications, is an important element in the production of alloys with high heat and corrosion resistance. However, studies on liquid Mo are still very limited [15-18]. With this motivation, we have analyzed in detail the structural properties of liquid molybdenum at high temperature and under high pressure, using the MD simulation technique in this study.

EXPOSITION

In this study, FS type many-body potential was used to describe interactions between atoms in MD simulations. According to the FS potential, the total energy E of a system consisting of N atoms is expressed as [19,20]:

$$E = \frac{1}{2}\sum_i \sum_j V_{ij}(r_{ij}) - A \sum_i \sqrt{\rho_i} \, , \qquad (1)$$

$$V_{ij} = \begin{cases} (r_{ij} - c)^2 (c_o + c_1 r_{ij} + c_2 r_{ij}^2) & (r_{ij} \le c), \\ 0 & (r_{ij} > c), \end{cases} \qquad (2)$$

$$\rho_i = \sum_{j \ne i} \emptyset(r_{ij}), \qquad (3)$$

$$\emptyset_{ij} = \begin{cases} (r_{ij} - d)^2 + \frac{\beta(r_{ij}-d)^3}{d} & (r_{ij} \le d), \\ 0 & (r_{ij} > d), \end{cases} \qquad (4)$$

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where, $V_{ij}(r_{ij})$ is the pairs potential energy and is the repulsive term of the total energy expression. r_{ij} is the distance between atoms i and j. ρ_i is the total electronic charge density at the site of atom i, constructed by superposition of the local atomic charge densities. $\emptyset_{ij}$ is atomic charge density function. A is the embedding energy and forms the attractive term of the total energy expression. c_o, c_1, c_2 and β are adjustable parameters used in the fitting process. c and d are cutoff parameters. FS potential parameters calculated by Finnis *et al.* [19] for Mo element are listed in Table 1 and details are given in Ref. [19,20].

Table. 1. *FS potential parameters for Mo.*

parameter	value	parameter	value
d (Å)	4.114825	c_o	43.4475218
A (eV)	1.887117	c_1	−31.9332978
β	0	c_2	6.080424
c (Å)	3.25		

In this study, all MD simulations were performed using the parallel code DL_POLY 2.0 [21] package. The initial configuration of the liquid Mo system was prepared as follows: first, 6750 Mo atoms were placed in a body-centered cubic (bcc) crystal lattice in a cubic box with periodic boundary conditions. Next, the crystal system was heated using the isothermal- isobaric (NPT) ensemble under 0 pressure from 0 K to 4000 K with a temperature increase of 50 K. Finally, the liquid system at 4000 K was equilibrated with 100000 MD steps using under constant temperature and constant volume (NVT) canonical ensemble. The Liquid Mo was simulated using the NPT ensemble under pressures of 0, 10, 20, 30, 40 and 50 GPa, respectively. In each simulation, a total of 100000 MD steps were used, with 75000 MD steps to equilibrate the system and 25000 MD steps for the production of averages. Nosé-Hoover barostat and thermostat [22] were used to control the pressure and temperature of the system during the simulations. Newton's equations of motion were numerically solved with a 1.0 fs time step using the Velocity Verlet algorithm.

To test the accuracy of the FS potential used in our MD calculations, we determined physical properties such as cohesive energy (E_c), lattice constant (a_0) and melting temperature (T_m) for bulk Mo and compared them with the experimental results [23] in Table 2.

Table. 2. *Some physical properties for bulk Mo.*

Quantity	MD-FS	Experimental [23]
E_c (eV)	6.807	6.820
a_0 (Å)	3.147	3.150
T_m (K)	3450	2895

Except for the melting temperature, the cohesive energy and lattice constant for bulk Mo are in good agreement with the experimental results. The melting temperature obtained from MD-FS Mo is approximately 20% greater than the experimental result. In MD simulations, the melting temperature is usually approximately 10-20% higher than the actual value due to the applied periodic boundary conditions. Ercolessi [24] explained this hysteresis as "waiting for a seed of the liquid phase to emerge with a spontaneous fluctuation". These results show that the FS potential used in the MD simulations accurately describes the interatomic interactions for bulk Mo. The temperature dependent change of the potential energy obtained from MD simulations for bulk Mo under 0 GPa pressure during the heating process is shown in Figure 1.
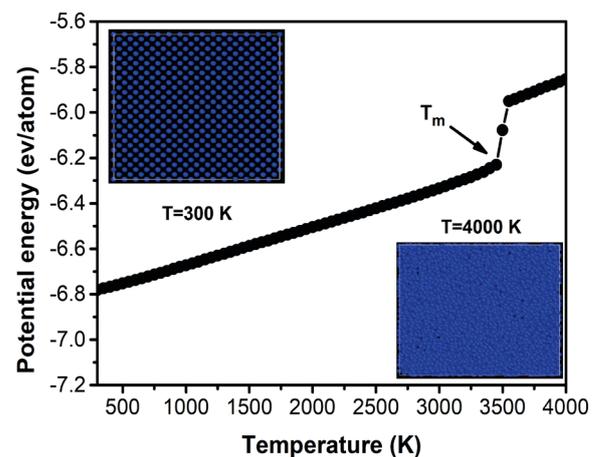

Fig. 1. *Temperature dependence of the potential energy of bulk Mo under 0 GPa during the heating processes.*

Potential energy exhibits a linear increase with temperature from low temperatures to around the melting point, while it shows a sudden increase at the melting. This increase indicates

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that a first-order phase transition occurs in the system. The potential energy continues to increase linearly with temperature from the melting point to 4000 K. Also, the atomic configurations of the system at 300 and 4000 K are presented in the inset of Figure 1. The atomic configuration at 4000 K assures us that bulk Mo is completely in the liquid phase at this temperature.

The variation of the reduced volume and lattice constant of the liquid Mo depending on the pressure at 4000 K is presented in Figure 2.
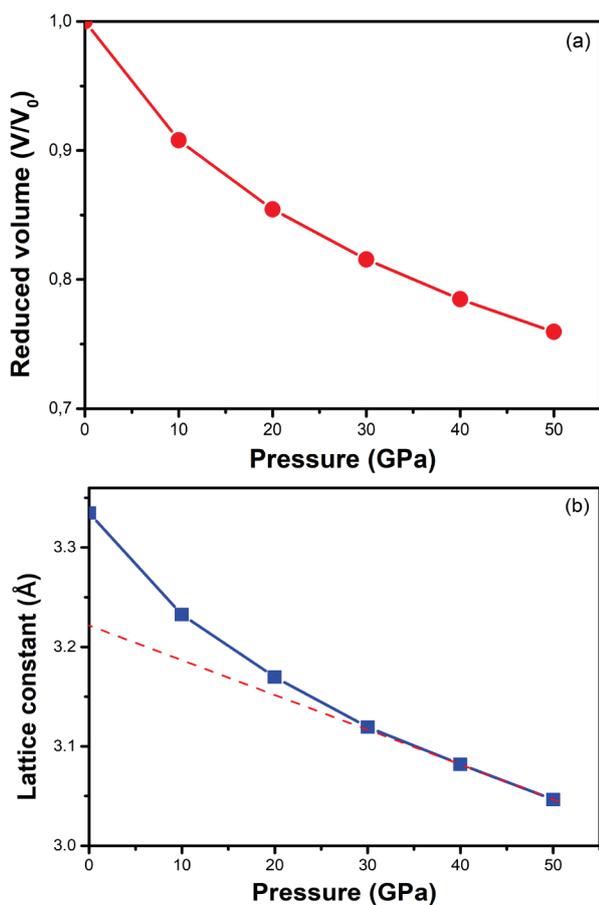
Fig. 2. Pressure dependent change of (a) reduce volume (b) lattice constant of liquid Mo at 4000 K. V_o is the volume under 0 GPa. The red dashed line is the linear fit.

Figure 2a shows that the volume of the system decreases by approximately 25% up to 50 GPa. This behavior can be explained by the knowledge that the liquid volume decreases under an applied external pressure. In Figure 2b, the lattice constant tends to decrease with the increase in pressure. While this decrease is far from linear behavior up to 30 GPa, it shows a linear behavior between 30GPa and 50 GPa.

The simplest and most common way to answer the question of how pressure or temperature acting on a system changes the structural properties is to evaluate the pair distribution function (PDF). The expression of the PDF, $g(r)$, is as follows [25]:

$$g(r) = \frac{\Omega}{N^2} \langle \sum_i^N \sum_{i \neq j}^N \delta(r - r_{ij}) \rangle$$

(5)

where N and Ω represent the number of atoms, and volume of the simulations cell, respectively. Figure 3 shows PDFs of liquid Mo at 4000K under different pressures.
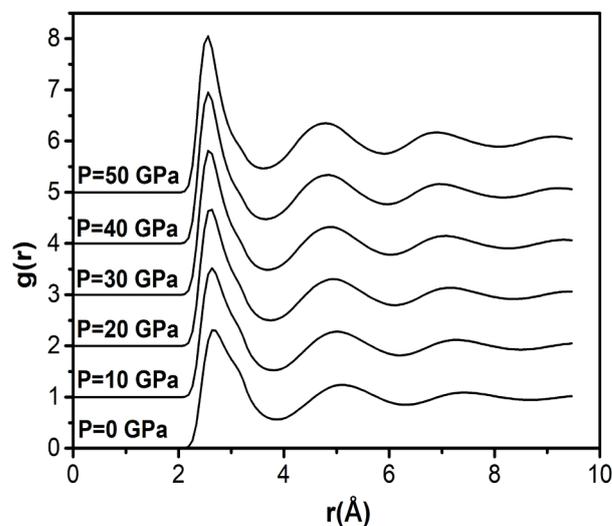

Fig. 3. Pressure dependent change of PDFs of liquid Mo at 4000 K.

For all pressure values, the PDF converges smoothly towards a high r values. This indicates that the atoms in the liquid system are randomly distributed. A slight shoulder occurs at the first peak of the PDF at 0 GPa. This shoulder disappears with the increase in pressure. In addition, with the increase in pressure, the positions of the first, second and third peaks of the PDF shift towards small r values, while the amplitudes of the peaks increase. In Figure 4, the variations of the position and amplitude (peak intensity) of the first, second and third peaks of the PDF are displayed depending on the pressure. In Figure 4(a), the positions of the peaks of the first and second peaks decrease almost linearly with increasing pressure, while the position of the third peak does not decrease linearly. The decrease curve for the third peak has a greater

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slope, up to 30 GPa, while the slope is smaller for pressures greater than 30 GPa. With the increase in pressure, the amounts of decrease in the first, second and third peak positions are ~4.84%, ~6.98% and ~8.24%, respectively. In Figure 4b, the amplitudes of the first three peaks of the PDF increase almost linearly with increasing pressure. The slopes of the amplitude curves for each peak are different from each other. The first peak has the greatest slope. With the increase in pressure, the amount of increase in the amplitudes of the first, second and third peaks is ~23.99%, ~11.77% and ~5.76%, respectively. These results show that increasing pressure causes a decrease in volume by reducing the interatomic distances, thus packing the atoms more densely.

observe the effect of applied pressure on the dynamic structural properties of a liquid system. The diffusion coefficients of the atoms are calculated by using the Einstein equation [25]:

$$D = \lim_{t \to \infty} \frac{\langle \Delta r(t)^2 \rangle}{6t}$$

(6)

where t is the diffusion time, $\langle \Delta r(t)^2 \rangle$ is MSD which can be described as [25]:

$$\langle \Delta r(t)^2 \rangle = \frac{1}{N} \sum_1^N |r_i(t + t_o) - r_i(t_o)|^2. \quad (7)$$

In the last equation, $r_i(t_o)$ is the position vector of the ith atom for the system in its initial configuration and $r_i(t)$ is the position vector of ith atom at time t. The MSDs calculated from the MD simulation for each pressure are shown in Figure 5 as a function of time.

Fig. 5. Mean square displacement of liquid Mo at 4000 K under different pressures as a function of time.
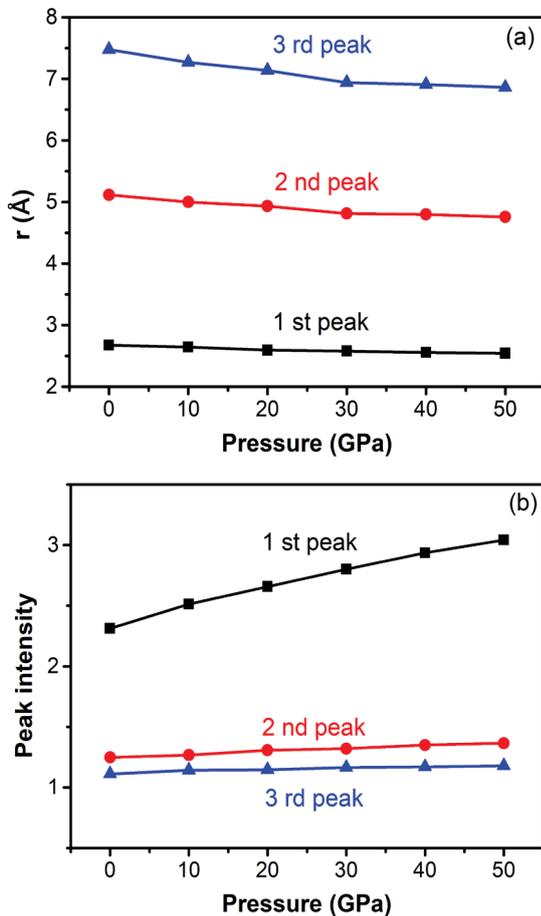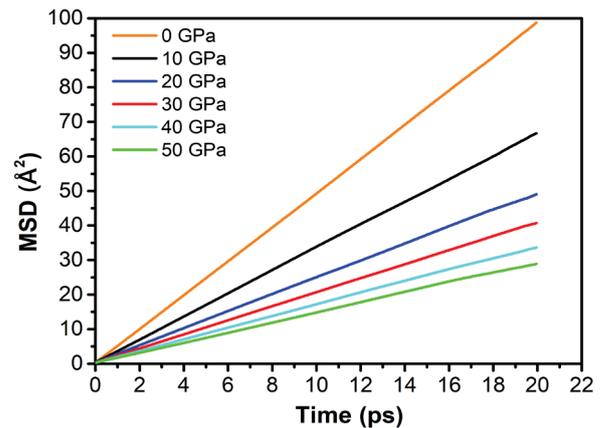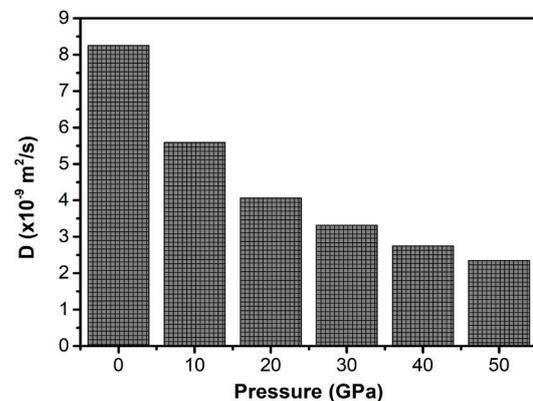

Fig. 4. Structural analysis of liquid Mo at 4000 K under 0, 10, 20, 30, 40 and 50 GPa. (a) the position of the first, second and third peaks of the PDFs and (b) the amplitude of the first, second and third peaks of the PDFs.

The mean square displacement (MSD) and diffusion coefficient (D) can be examined to

Fig. 6. The diffusion coefficients of liquid Mo at 4000 K as a function of pressure.

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The characteristic behavior of the MSD for each pressure is similar to that of an ideal liquid system. As the external pressure applied on the liquid system increases, the slope of the MSD decreases. This indicates that the mobility of Mo atoms begin to be restricted with the increase in pressure. The diffusion coefficient, which shows the measure of mobility of atoms in the liquid system, is displayed in Figure 6 as a function of pressure. When the pressure is increased from 0 to 10 GPa, there is a sudden drop in the diffusion coefficient. However, the amount of decrease observed in diffusion coefficients after 10 GPa is lower. That is, there is no linearity between the rate of pressure increase and the amount of decrease in diffusion coefficient. When the pressure is increased from 0 to 50 GPa, the decrease in the diffusion coefficient is approximately 57%. This result supports the MSD results, showing that pressure has a significant effect on the mobility of liquid Mo atoms.

CONCLUSION

The structural properties of liquid Mo under high pressure were investigated using classical MD simulation with FS potential. The liquid system was simulated at 4000 K, well above the melting temperature, and under different pressures range from 0 to 50 GPa. The volume and lattice constant of the liquid system show a non-linear decrease with increasing pressure up to 30 GPa, while after 30 GPa they decrease linearly with pressure. The first, second and third peak positions of the PDF shift towards smaller r values with increasing pressure. This indicates that Mo atoms in the liquid system become more densely packed with increasing pressure. In addition, the MSD and diffusion coefficient, which are the measure of atomic mobility in the liquid system, decrease significantly with increasing pressure. These results show that the applied external pressure significantly suppresses the mobility of liquid Mo atoms.

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