

## A MOLECULAR DYNAMICS SIMULATION STUDY ON THE STRUCTURAL EVOLUTION OF LIQUID CALCIUM UNDER HIGH PRESSURE

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### Abstract

*In this study, the evolution of the atomic structure of liquid calcium under different pressures (between 0-90 GPa) was investigated by classical molecular dynamics simulations using the embedded atom method potential. First, the calcium element, which has a face-centered cubic structure, was heated up to 3500 K, which is a very high from the experimental melting point ( $T_m=1113$  K), and as a result, molten calcium was obtained. The pressure-dependent structural evolution of liquid calcium was analyzed using the pair distribution function, structure factor, and Honeycutt-Andersen method. The results showed that pressure has significant effects on the atomic structure of liquid calcium. In order to increase the reliability and acceptability of the simulations, the results obtained were discussed by comparing with the ab initio molecular dynamics simulation results and experimental results in the literature. We think that the present findings will shed light on the structural behavior of liquid calcium at high pressures.*

**Keywords:** high pressure, embedded atom method, liquid calcium, Honeycutt-Andersen method, melting point

### INTRODUCTION

At the atomic scale, it is very important to be able to quickly, accurately and reliably explain physical properties of materials such as structural, dynamic, mechanical and thermodynamic. Although experimental and quantum-based molecular dynamics (MD) simulation methods provide accurate and successful results for this aim, they have some disadvantages. Experiments are very expensive and, unfortunately, there is no possibility to control all the conditions for investigating the physical properties of the material, and quantum-based simulations are relatively slow and very costly to work with even a few hundred atoms. These disadvantages lead researchers to classical MD simulations, which are cheaper, offer a possibility to work with more atoms, are much faster, and can provide very successful results with a good modeling [1]. Today, MD simulations are successfully applied in many of the fundamental fields of physics, nanotechnology, chemistry, biology and engineering and provide valuable information about the unknown worlds of

materials [2–8]. In addition to the temperature effect, MD simulations are also suitable for examining the changes in the structural, dynamic and mechanical properties of materials, especially under high pressure [5, 9–12]. Pressure and temperature are two important parameters that affect the solidification process of materials, and the effect of temperature on the solidification process has been extensively studied. In contrast, there are few studies investigating the effect of pressure on the solidification process and liquid structures because there is no equipment that can directly observe the solidification process under high pressure conditions. Encouraged by these shortcomings, we investigated the effect of high pressure on liquid calcium (Ca) by taking advantage of MD simulations. Although there are many studies on the element Ca, there is very limited information about how it behaves at high temperatures and high pressures. One of the reasons we chose the element Ca is that it is one of the most abundant elements in nature and most needed for the survival of living things.

On the other hand, it is used in the food industry, medicine-health, chemistry and industry. In addition, the role of this element in the chemical processes applied in the production process of many different elements is quite high. In this study, MD simulations under different pressures applied on liquid Ca at 3500 K have been performed using embedded atom method (EAM) potentials and the obtained results are discussed in comparison with appropriate experimental and other MD simulation results in the literature.

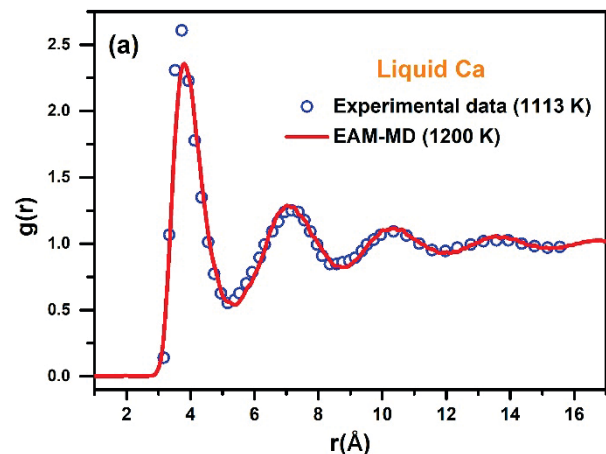
## EXPOSITION

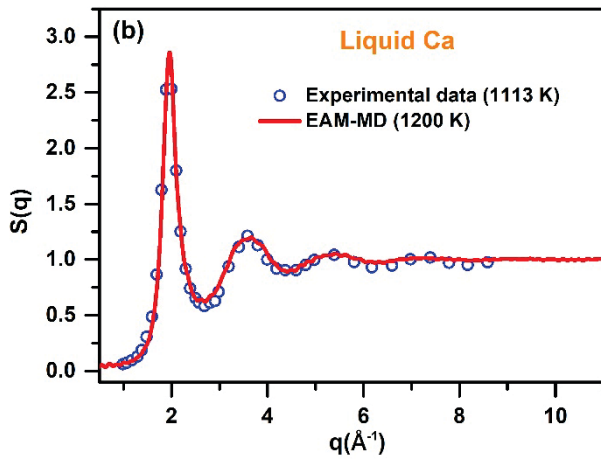
EAM is a semi-experimental technique developed to calculate the energy of an atomic arrangement. EAM potentials are among the most preferred potentials in MD simulations to investigate the atomic, dynamic, thermodynamic, and mechanical properties of pure or alloy systems at high temperatures and pressures [13]. In this technique, the energy of each atom in the system is calculated from the energy required to place the corresponding atom in the local electron density created by other atoms in the system. The total energy  $E_i$  of an  $i$  atom is given by:

$$E_i = F_\alpha \left[ \sum_{j \neq i} \rho_{\alpha\beta}(r_{ij}) \right] + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (1)$$

where  $\alpha$  and  $\beta$  are the element types of atoms  $i$  and  $j$ .  $F_\alpha$  is the embedding energy and it is expressed as a function of atomic electron density ( $\rho$ ).  $\phi_{\alpha\beta}(r_{ij})$  is the pair interaction energy between  $i$  and  $j$  atoms separated at a distance of  $r_{ij}$  from each other. More detailed information on the EAM potential data used here can be obtained from Ref [14]. The simulations have been performed using the DL\_POLY 2.0 code [15]. The simulations have been carried out with an fcc lattice consisting of 13500 atoms in a 3D periodic cubic box of size  $84\text{\AA} \times 84\text{\AA} \times 84\text{\AA}$ . Newtonian equations of motion are numerically integrated using the Verlet method with a time step of 1 fs. The isothermal isobaric (NPT) ensemble was employed to control the temperature and pressure. Firstly, the system was heated from 0 K to 3500 K (50 K intervals) and run for another 500,000 timesteps under zero pressure to obtain a well-equilibrated liquid at 3500 K. External pressure between 0-

90 GPa has been applied on the equilibrated liquid and a total of 50,000 timesteps have been given to the system at each pressure. At this stage, 40,000 steps have been devoted to equilibrating the system, and the remaining 10,000 steps have been devoted to statistical calculations. Recently, Celtek [1] conducted a detailed investigation of some physical properties of pure Ca during the heating process using the same EAM potential dataset. He observed that the EAM potential accurately predicted the physical parameters such as lattice parameter ( $a^{\text{EAM}}=5.59\text{\AA}$  and  $a^{\text{Exp.}}=5.59\text{\AA}$  [16]), cohesive energy ( $E^{\text{EAM}}=1.84\text{ eV/atom}$  and  $E^{\text{Exp.}}=1.84\text{ eV/atom}$  [17]), specific heat ( $C_p^{\text{EAM}}=26.10\text{ J.mol}^{-1}.\text{K}^{-1}$  and  $C_p^{\text{Exp.}}=25.400\text{ J.mol}^{-1}.\text{K}^{-1}$  [16]), linear thermal expansion coefficient ( $\varepsilon^{\text{EAM}}=2 \times 10^{-5}\text{ K}^{-1}$  and  $\varepsilon^{\text{Exp.}}=2.2 \times 10^{-5}\text{ K}^{-1}$  [16]), density ( $\rho^{\text{EAM}}=1.52\text{ g/cm}^3$  and  $\rho^{\text{Exp.}}=1.53\text{ g/cm}^3$  [17]) and melting point ( $T_m^{\text{EAM}}=1190\text{ K}$  and  $T_m^{\text{Exp.}}=1113\text{ K}$  [17]) calculated at the respective temperatures. In addition, the pair distribution function (PDF or  $g(r)$ ) and structure factors (SF or  $S(q)$ ) calculated for liquid Ca are shown in Figs. 1(a) and 1(b) together with the experimental data. These functions are not given here, more detailed information about them can be found in Ref [18]. We used PDF and SF curves simulated at 1200 K to compare with experimental data. The simulated both PDF and SF curves of liquid Ca are in excellent agreement with the experimental data. All these results show that EAM-MD simulations are successful and produce reliable results. Encouraged by this, we focused on what kind of effects the external pressure exerted on the liquid Ca had on its atomic structure.

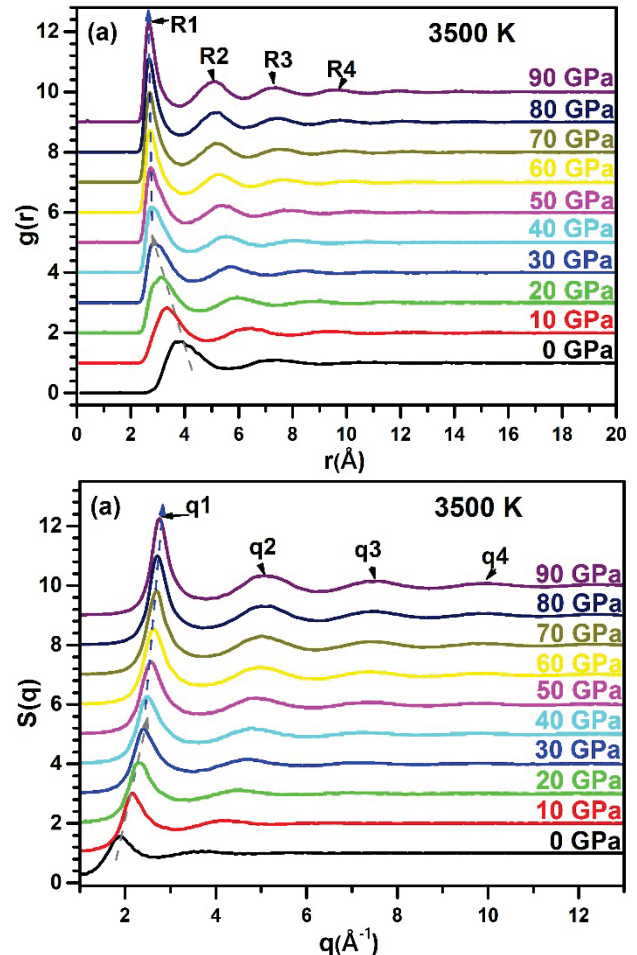




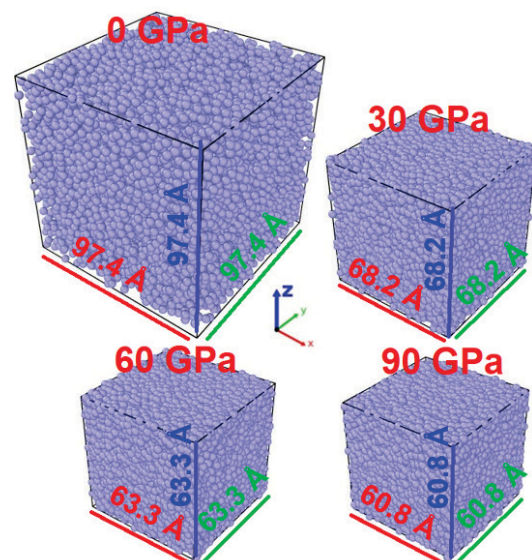
**Fig. 1.** Calculated (a)  $g(r)$  and (b)  $S(q)$  curves for liquid Ca (at 1200 K). Experimental data have been taken from Waseda (at 1113 K) [19].

PDFs and SFs calculated under different pressures are shown in Figs. 2(a) and 2(b). As seen from Fig. 2(a), the PDFs of liquid Ca mainly consist of three peaks. The first of these peaks is higher and narrower than the others. As the pressure increases, the first peak moves towards the smaller  $r$  value (especially between 0-30 GPa), the amplitude becomes narrower, and the peak height increases. Moreover, the depression between the first and second peaks gets deeper with increasing pressure. On the other hand, they become more prominent in the second and third peaks. In addition, a fourth peak occurs at high pressures, which is not visible at low pressures. The position of the first peaks of the PDFs decreases rapidly from 0 to 30 GPa, revealing that below 30 GPa the distance between the first nearest neighbor Ca-Ca atoms decreases more sharply. This behavior may be associated with the gradual occupation of interstitial sites. These changes are now much slower at pressures of 40 GPa and above. All these findings show that the applied external pressure is effective on the atomic structure of liquid Ca. As seen in Fig. 2(b), the first peaks of  $S(q)$  shift from left to right with increasing pressure and their amplitudes narrow, indicating an increase in the short range ordering of liquid Ca. The first peak positions of  $S(q)$  shift continuously towards larger values of  $q$  in the 0 to 30 GPa pressure range, much more pronounced than the pressure dependent peak position change in the 40 to 90 GPa pressure range. This is attributed to non-uniform shrinkage of liquid Ca at different pressures, and this behavior is consistent with

the pressure-dependent variation of the peak positions of  $g(r)$ . In order to evaluate this situation from a different angle, the snapshots of the simulation boxes under various pressures are given in Fig. 3 together with the box dimensions.

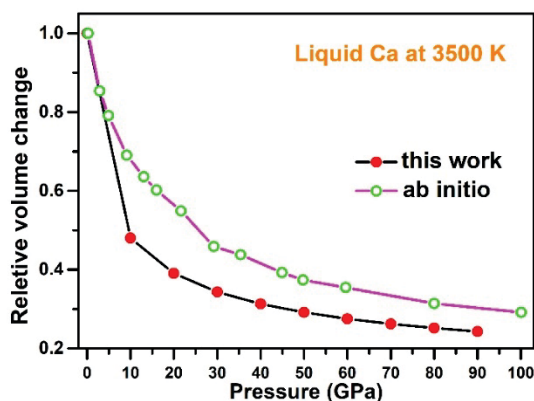


**Fig. 2.** (a)  $g(r)$  and (b)  $S(q)$  curves calculated under different pressures.



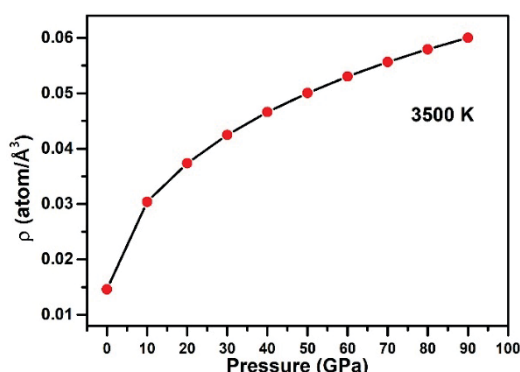
**Fig. 3.** Snapshots and dimensions of the simulation box under 0, 30, 60 and 90 GPa external pressure.

This sharp decrease in the size and therefore volume of the simulation boxes under the influence of pressure means that different atomic arrangements begin to form in the system and continue to evolve. Moreover, the relative volume-pressure ( $V_p/V_0$ , where  $V_p$  and  $V_0$  represent volumes at high pressure and ambient pressure conditions, respectively) dependence of the system is shown in Fig. 4 together with the previously reported *ab-initio* MD simulation results [20]. There is good agreement between the simulation results of EAM-MD and *ab-initio* MD under low pressures.



**Fig. 4.** Comparison of the relative volume change results for EAM-MD and previously reported *ab-initio* simulations [20].

Although there are slight differences in the results with increasing pressure, the pressure-related change in both methods is generally the same trend. This is an indication that the EAM potential accurately predicts the structural properties of liquid Ca under high temperature and pressure. Fig. 5 depicts the calculated atomic density for liquid Ca under different pressures. As expected, as a result of the decrease in volume, the atoms in the system begin to position closer to each other and as a natural consequence of this, the atomic density of the system increases.

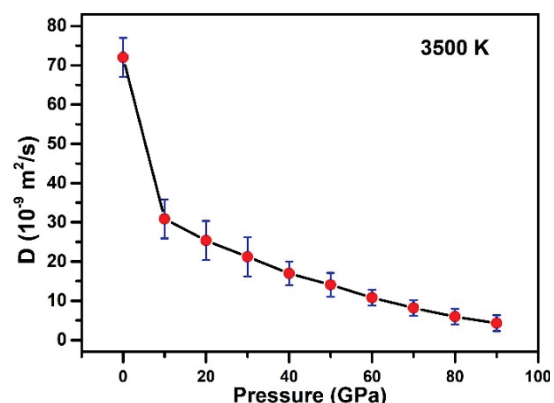


**Fig. 5.** Evolution of the atomic density of liquid Ca as a function of pressure.

To investigate the mobility of liquid Ca, we calculated the self-diffusion coefficients ( $D$ ) under different pressures from the following equation, using the long-time evolution of the mean-square displacement (MSD).

$$D = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{\partial \langle r^2(t) \rangle}{\partial t} \quad (2)$$

Fig. 6 depicts the evolution of the calculated  $D$ 's for liquid Ca at 3500 K as a function of pressure. From the figure it is observed that at 0 GPa the system has the largest  $D$  value and as the pressure is increased to 10 GPa, its value drops very sharply, which is consistent with the results discussed above. As expected, increasing pressure decreases the mobility of atoms in the system and as a result decreases in  $D$ 's. This decreasing trend continues systematically between 0 GPa and 90 GPa. All these findings and analysis results show that the pressure is effective on the system, but nevertheless it does not cause an abnormal change in the structure of liquid Ca.



**Fig. 6.** Evolution of  $D$ 's calculated for liquid Ca at 3500 K as a function of pressure.

While PDFs and SFs provide a superficial perspective, Honeycutt-Andersen (HA) [21] pair analysis method allows us to obtain more detailed information about the microstructure of the system. The HA technique is based on four integer notation ( $ijkl$ ), please refer to Ref [18, 22, 23] for more detailed information. As a result of HA analysis, 1311, 1321, 1421, 1422, 1431, 1441, 1541, 1551 and 1661 bonded pairs have been found to be the most dominant in the system. The pressure dependent changes of these pairs are shown in Fig. 7. Of these, 1551 bonded pairs represent ideal icosahedra, 1541 and 1431 bonded pairs defective icosahedra

order. The 1421 bonded pair is fcc, the 1422 bonded pair is hcp, and the 1661 and 1441 bonded pairs represent the bcc crystal structures. 1311 and 1321 bonded pairs are also other clusters mostly found in liquid structures. It is seen that 1431, 1541 and 1551 bonded pairs, which are more common in liquid and amorphous structures, are the most dominant pairs for all pressures. Within these three clusters, 1551 and 1541 bonded pairs first showed a decreasing trend with increasing pressure, then interestingly started to increase in the range of 40-50 GPa. On the other hand, 1431 couples first increase rapidly and then show a milder tendency to increase. The opposite situation has also been observed for 1311 bonded pairs. It is only the 1421 and 1422 bonded pairs that continuously increase for all applied pressures. This can be attributed to the desire of Ca, which is kept under pressure at high temperatures, to return to the fcc structure, which is its original structure at low temperatures. Except for these bonded pairs, all of the other bonded pairs decrease with increasing pressure.

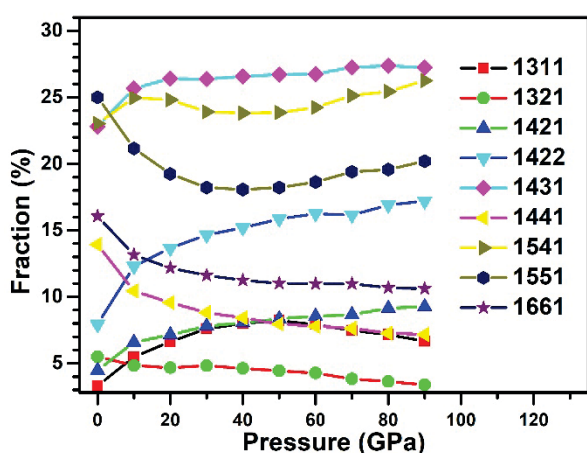


Fig. 7. Fraction of the most common HA indices simulated under different pressures.

## CONCLUSION

In summary, the atomic structure evolution of liquid Ca under various pressures ( $0 \leq P \leq 90$ ,  $\Delta P = 10$  GPa) has been studied by classical MD simulations using EAM potentials. PDFs and SFs calculated around the melting point for liquid Ca are in good agreement with the experimental data. With increasing pressure, the first peaks of the PDFs shifted towards the smaller  $r$  value, as well as their amplitudes narrowed and their peak heights increased. The relative volume changes

calculated from the EAM-MD simulations systematically decreased with increasing pressure, furthermore, our results are consistent with other *ab-initio* MD simulation results. The self-diffusion coefficients decreased regularly with increasing pressure. According to HA analyzes, 1431, 1541 and 1551 bonded pairs have been found to be the most dominant species at all pressures, and only 1421 and 1422 bonded pairs have been found to increase continuously with increasing pressure. These sluggish structural crossovers and the structural evolution of liquid Ca under pressure should motivate further investigation of its physical properties, such as dynamics and mechanics.

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