Structural evolution in liquid calcium under pressure

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Abstract

The atomic structure evolution of liquid Ca at 3500 K as a function of pressure up to 100 GPa has been studied by ab initio molecular dynamics simulations. The pair correlation function, structure factor and respective peak positions reveal two crossovers at ~ 10 GPa and ~ 50 GPa in liquid Ca while the coordination number shows four pressure regions: about 0.1-5 GPa, about 5-20 GPa, about 20-50 GPa and above ~ 50 GPa and heat capacity shows two different pressure dependences separated at about 30 GPa, i.e., below about 30 GPa a negative one and a positive value above about 30 GPa. It is also observed below 10 GPa the first nearest neighbor Ca-Ca distance decreases more sharply as compared to above 10 GPa, this behavior is attributed to the gradual occupation of the interstitial sites. Comparisons of the pressure-dependent bond angle distribution and bond orientation order data of liquid Ca with solid crystalline phases imply that pressure-dependent atomic structural evolution in liquid calcium is, to some extent, similar to that of solid crystalline calcium reported by [Teweldeberhan and Bonev](#). [Phys. Rev. B **78** 140101(R) (2008)]. These sluggish structural crossovers that have been observed in liquid Ca under pressure will trigger more studies in other disordered systems.

1. Introduction

Due to unique phase transformations and superconductivity behavior of calcium (Ca) under pressure, a substantial amount of theoretical [1-6] and experimental [7-11] works have been carried out. The outcome of extensive work shows unexpected structural phase transitions from a maximally-packed, to a less closely-packed structure under pressure. Ca has a face-centered cubic (fcc) structure at ambient pressure, and undergoes consecutive phase transitions into a body-centered cubic (bcc) at 20 GPa, and then to the simple cubic (sc) structure Ca-III at 32 GPa [8] by increasing pressure but the stability of sc is not clear [12, 13]. New phase transitions of Ca under even higher pressures were observed [14], i.e., the sc transforms to phase IV Ca-IV at 113 GPa and then to phase V Ca-V at 139 GPa. The transition temperature for superconductivity of Ca increases linearly with pressure and reaches to 25 K at 161 GPa in the *cmca* phase [11] which is the highest record among simple elements. Aforementioned studies have been carried out mainly at or below room temperatures. Moreover, reported studies indicated that the structure and properties of materials in liquid state could be related to their solid state. Hence the studies on the structural characteristics of liquid and non-crystalline metals have received considerable attention [15-21]. Recently, a possible metal-nonmetal transition in liquid Na [22], a tetrahedral clustering of nearest neighbors in liquid Li at pressure 150 GPa [23] and their respected liquid alloys NaLi and CaLi [24] at high pressure were reported by ab initio molecular dynamics (AIMD) simulations. In alkali metal above 12.5 GPa, the breakdown of the nearly-free-electron model drives a transition of the pure liquid metal towards a less metallic, denser liquid [25]. These newly observation set a stage of unusual properties and new structural transformations in liquid metals at high pressures and temperatures, e.g., Cs [26, 27], Rb [28], and liquid Si [29].

The structure of liquid Ca under pressure has rarely been studied [30]. **Teweldeberhan and Bonev** [30] reported high-pressure phases of Ca and its finite-temperature-wise phase boundaries, as illustrated in Fig. 1. It is worth to mention that the theoretical phase diagram of Ca needs revision [31]. The following questions for liquid Ca at higher temperatures are yet unanswered: (i) What is the structure of liquid calcium under compression? (ii) Is there any liquid-to-liquid crossover? (iii) Is there any correlation in the structure appearing between solid and liquid phases? In this work, we report the pressure dependent results of liquid calcium at 3500 K through ab initio molecular dynamics (AIMD) simulations and endeavor to answer these above-mentioned questions. Our structural investigations via pair correlation function (PCF),

structure factor, bond angle distribution, bond orientation order, Voronoi tessellation, heat capacity and electronic studies (density of states, electron localized function) reveal the presence of correlation between the liquid calcium and its solid phases.

2. Computational details

The **simulations** of liquid calcium under compression are achieved, based on the density functional theory (DFT) using Vienna *ab initio* simulation package (VASP) [32, 33]. The AIMD simulations are initiated by placing 108 Ca atoms into a cubic cell with periodic boundary conditions and the canonical NVT ensemble constant (number, volume and temperature). The temperature is controlled by the Nosé-Hoover thermostat [34, 35]. The equation of motion is extracted through the velocity Verlet algorithm with a time step of 3 fs. The interaction between electrons and ions is modeled by using a Projector Augmented-Wave (PAW) method [36]. The general gradient approximation (GGA) in the form introduced by Pedrew-Burke-Ernzerhof (PBE) is used for the exchange-correlation energy functional [37]. Electron orbitals were represented by plane waves with an energy cutoff of 119.6 eV. We took eight valence electrons per atom. **Although AIMD has some limitations due to small size of the cell [38], it still can give us useful information e.g., the atomic configuration for disordered systems. Calcium was heated up to 3500 K in order to remove the crystalline symmetry and reach the thermal equilibrium. It is known that boiling temperature increases largely when the pressure is applied. Here we got condensed liquid structure factor curve for liquid Ca at 3500 K even at initial point about 0.1 GPa. Pressure is then applied step-wisely from 0.1 to 3, 5, 7.5, 10, 13, 16, 21, 25, 29, 35, 40, 45, 50, 60, 80 and 100 GPa. At each pressure, the system is equilibrated, and the internal-specific pressure was maintained by adjusting the box size, determined by the lattice vectors in the POSCAR. The pressure in the box has an uncertainty of about 0.1 GPa. Furthermore, at each pressure, 8000 MD steps were performed and the last 2000 steps were used for statistical analyses.**

3. Results and discussion

Pair-correlation functions, $g(r)$, of liquid Ca at 3500 K are calculated under various pressures ranging from 0.1 to 100 GPa in Fig. 2a. PCFs of liquid Ca at 3500 K are composed primarily of two peaks: the first one is broad and clear as compared to the second, which is even

more broad and weaker. As the pressure increases, the first peak moves toward the lower r value and becomes narrower. Moreover, the depression between the first and second peaks becomes deeper. From 0.1 to 10 GPa, the peak position decreases rapidly in Fig. 2b, revealing that below 10 GPa the first nearest neighbor Ca-Ca interatomic distance decreases more sharply. This behavior is attributed to the gradual occupation of the interstitial sites. While, in the pressure range of above 50 GPa, it decreases with pressure having a much smaller reduction rate. This implies that a sharp (resp. slow) decrease of peak position at high (resp. low) pressure, might lead to different atomic arrangements in the system. To examine this possibility the structure factor, $S(q)$, can be calculated from the Fourier transform of $g(r)$, given by

$$S(q) = 1 + n \int 4\pi r^2 \frac{\sin(qr)}{qr} [g(r) - 1] dr, \quad (1)$$

where n is the averaged number density, r is the radial distance, and q is the wave number. We have extracted the structure factor $S(q)$, by taking the average of last 2000 configurations. Fig. 3(a) demonstrates structure factor $S(q)$ of liquid Ca, acquired from XRD measurements [39] and AIMD simulations. **The consistency, in terms of peak positions, amplitudes and shapes, between the data obtained from AIMD simulations and experimental measurements is ascertained. These results validates AIMD simulations, providing reasonable configurations for further structural analyses.** The structure factors $S(q)$ of liquid Ca at 3500 K under various pressures are plotted in Fig. 3b. The first peak in structure factor $S(q)$ shifts consistently from left to right as shown in Fig. 3b, and becomes narrow with increasing amplitude, indicating an increase in the short range ordering. The first peak position again decreases rapidly in the pressure range from 0.1 to 10 GPa in Fig. 3c, which is much larger than the pressure-dependent peak position in the pressure range from 50 to 100 GPa. This shows the non-uniform contraction of liquid Ca at different pressures and develops a similar trend with the pressure-dependent peak position of $g(r)$ in Fig. 2.

The dynamic behavior of atoms can be studied by computing the coefficient of diffusivity (D) based on the calculation of the mean-square displacement. The self-diffusion coefficient calculated as a function of various pressures is given in Fig. 4(a). By increasing the pressure, D decreased, as expected; however, after 10 GPa, the diffusivity remains almost unchanged up to 50 GPa, and at above 50 GPa a slight lower diffusivity was detected. The non-uniform pressure-induced changes in D , i.e., from 0.1 to 10 GPa, from 10 to 50 GPa and above 50 GPa are a clear indicator of a structural change in the liquid, which is concordant with our previous results.

Figure 4(b) shows the MSD as a function of time for Ca at different pressures. The atomic movement of Ca atoms decreases as the pressure increases.

To recover the consecutive structural evolution in liquid Ca at upstanding pressures, bond angle distributions (BADs) were calculated, which are often used to identify topological ordering in liquid and amorphous structures. BAD is a triplet correlation, which is defined for angles between the nearest neighbors of atoms around a central atom within the specific cutoff distance. Therefore, here we use the cutoff distances of 5.4, 5.17, 5.0, 4.83, 4.78, 4.67, 4.60, 4.54, 4.45, 4.39, 4.31, 4.22, 4.16, 4.11, 4.02, 3.88 and 3.73 at the pressures of 0.1, 3, 5, 7.5, 10, 13, 16, 21, 25, 29, 35, 40, 45, 50, 60, 78 and 100 GPa, respectively. Using the cutoff distance, which is the minimum position between the first and second peaks in $g(r)$, the calculated bond angle distributions at different pressures are shown in Fig. 5. It has been found that the calculated bond-angle distribution spectacles two outstanding peaks. Both systematically move toward lower angles, i.e., from the first and second peaks at about 53° and 98.2° at 0 GPa to 43.8° and 81.1° at 100 GPa, respectively, upon applying pressure. Interestingly, the first peak initially has a higher distribution, but as the pressure increases, its relative intensity decreases while the second peak intensity becomes sharper with pressure. The bond angle distributions (i.e., color vertical solid lines) for the four different crystalline phases of calcium mentioned in Fig. 1 are also plotted in Fig. 5 for comparison. Bond angle distributions of both fcc and bcc Ca phases are higher, lying at 58.3° and 59.2° , respectively, while the liquid also shows high distribution at low pressures for the same angle region. Similarly, BAD of the other two crystalline phases are found to be located at 86.8° for pnma and 93.7° for the cmcm phases, for which the liquid phase is at higher pressures has higher BAD. In order to further investigate the local structure evolution in liquid Ca as a function of pressure, the local bond orientation order method [40, 41] is applied. The local bond orientation order q_6 , which is more accurate for identifying crystal-like atomic local structures [40], is plotted in Fig. 6(a) for liquid Ca atoms together with values for the four crystalline phases at various pressures. q_6 was well separated during compression. Initially from 0.1 to 10 GPa, it largely decreases and then gradually decreases from 10 to 50 GPa. Above 50 GPa, q_6 is very small and remains almost unchanged. This trend is also detected in the four crystalline phases, i.e., the q_6 value decreases from fcc, formed below approximately 7.5 GPa, bcc phase, formed in the range from 7.5 to 37 GPa, cmcm phase, formed in the range from 37.5 to 45 GPa, to pnma phase, formed at above 45 GPa, although the absolute q_6 values are different

in crystalline and liquid states. Hence, BAD and q_6 results of liquid Ca at different pressures indicate that local atomic packing in liquid Ca, to some extent, correlate with the crystalline phases.

By using Voronoi tessellation analysis [42, 43], the evolution of atomic packing is analyzed. In this technique, the vertical bisectors between the central atom and the neighboring atoms will form a polyhedron about the central atom, termed as a Voronoi polyhedron (VP). The distribution of various VPs has been expressed using Schlaefli's notation whereby a polyhedron is denoted by a set of indices $\langle n_3; n_4; n_5; n_6 \rangle$, where n_i is the number of faces with i vertices. The total number of faces of a VP is equivalent to the coordination number for a chosen central atom. The top seven abundant VP fractions are plotted in Fig. 6(b) for liquid Ca at various pressures. With increasing pressure, VPs having coordination number CN=11, $\langle 0,4,4,3 \rangle$, $\langle 0,3,6,2 \rangle$, $\langle 0,2,8,1 \rangle$ decrease rapidly while VPs with CN=12 $\langle 0,4,4,4 \rangle$, $\langle 0,3,6,3 \rangle$, $\langle 0,2,8,2 \rangle$ decrease slightly. Voronoi indices of $\langle 0, 3, 6, 3 \rangle$ and $\langle 0, 2, 8, 2 \rangle$ VPs are distorted icosahedral-like clusters in liquid Ca. The VPs with CN=13, $\langle 0, 2, 8, 3 \rangle$ and $\langle 0, 3, 6, 4 \rangle$ gradually increase with pressure, but at high pressure they show descending behavior. The average CN of liquid Ca using the minimum position between the first and second peaks in $g(r)$ of above 3.5 Å is plotted as a function of pressure in Fig. 6(c), which is 11.93 at 0 GPa, and then increases sharply to 12.57 at 5 GPa. Above 5 GPa, CN gradually increases with pressure up to CN= 12.95 at 21 GPa. At pressures about 21-50 GPa, CN very slightly increases and it remains almost unchanged with CN=13 at above 50 GPa. The first and second CNs for the cmcm phase are 6 and 7 having cutoffs of 2.65 and 2.95 Å while for the pnma phase are 8 and 4 having cutoffs of 2.6 and 3.4 Å, respectively. Thus, for a cutoff distance of 3.5 Å, the crystalline cmcm and pnma phases have CNs of 13 and 12, respectively, which is close to the CN of liquid Ca at pressures above 21 GPa.

For phase transitions, the heat capacity is one of the most basic quantity to be taken into account, which is usually representative for the quantities of freedom, and abruptly discontinuous in the second-order phase transition. From the theoretical perspective, the heat capacity is well defined and calculable for the solids and liquids. While examining in the canonical ensemble [44], the heat capacity can be extracted from the function method of internal energy, E , shown as below:

$$C_V(T) = \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2)$$

where $\langle E \rangle$ is the average ensemble of **internal** energy, E . Fig. 7 shows the heat capacity C_V of liquid Ca. By examining the heating capacity, it is found that initially C_V drops as the pressure increases from **0.1 GPa** to about 30 GPa, then abruptly rises from about 30 GPa up to 100 GPa, which should be correlated with the local structure change of liquid Ca under high pressure.

To know the pressure effect on atomic volume in liquid calcium, we performed the Bader analysis based on the Bader quantum theory, which is unbiased way to characterize changes in “atomic” volumes by zero electronic charge density flux surfaces [45]. Recently, the same technique was also used to monitor polymorphous transitions in Ce-Al and Ca-Al **metallic glasses** [15, 46]. Fig. 8 illustrates the volume of the system as a function of pressure, in which the total volume (V_p/V_0) extracted by the box of the size, Bader atomic volume ($V_{\text{bader-p}}/V_{\text{bader-0}}$) calculated by using the Bader method and the first nearest neighbor “volume” $(r_p/r_0)^3$ obtained from the first peak position of $g(r)$. By increasing pressure, all the volumetric parameters decrease monotonically and compressibility is higher at low pressure as compared to higher pressures. Surprisingly, the total volume (V_p/V_0) and Bader volume ($V_{\text{bader-p}}/V_{\text{bader-0}}$) ratios show strong consistency to the corresponding $(r_p/r_0)^3$ at low pressures, indicating that $(r_p/r_0)^3$ (local interatomic distance reduction) decreases somehow at a similar rate as the total volume reduction (macro-scale of the sample volume reduction). At high pressure range above 50 GPa, $(r_p/r_0)^3$ deviates from V_p/V_0 and $V_{\text{bader-p}}/V_{\text{bader-0}}$. Consequently, it is revealed that at pressures below 50 GPa the compression of liquid Ca is relatively uniformed in terms of local interatomic distance and macro-scale of the sample volume.

To evaluate the pressure-induced changes in the electronic distribution as well as the binding in liquid Ca, the electron localization function (ELF) [45] of liquid Ca at selected pressures of 0.1, 10, 29, 60, 80, and 100 GPa **is calculated and presented** in Fig. 9. Iso-surface plots with $\text{ELF} = 0.662$ at 0 GPa reveals that some valence electrons are already localized in specific zones formed by Ca atoms. By further applying the pressure, ELF iso-surface values decreases and the electrons localized in Ca-Ca bonds move to the outer regions. Thereafter, at 60 GPa the value of $\text{ELF} \sim 0.51$ corresponding to electron gas-like pair probability [46] exists in the liquid calcium.

4. Conclusions

In summary, the atomic structure evolution of liquid Ca at 3500 K as a function of pressure up to 100 GPa has been studied by *ab initio* molecular dynamic simulations. The pair correlation function, structure factor, respective peak positions and the diffusivity reveal two crossovers at ~10 GPa and ~50 GPa in liquid Ca while the coordination number shows four pressure regions: about 0.1-5 GPa, about 5-20 GPa, about 20-50 GPa and above ~50 GPa and heat capacity shows two different pressure dependences separated at about 30 GPa, i.e., below about 30 GPa a negative one and a positive value above about 30 GPa. Moreover the volume investigation as a function of pressure reveal, volume (V_p/V_0) and Bader volume ($V_{\text{bader-p}}/V_{\text{bader-0}}$) ratios show strong resemblance to the corresponding $(r_p/r_0)^3$ at low pressures while at high pressure $(r_p/r_0)^3$ show deviation. The comparison of pressure-dependent bond angle distributions and bond orientation order data of liquid Ca with solid crystalline phases imply this resemblance. The whole transition process can be divided into three relatively distinct pressure regimes, separated by pressure values of ~5-10 GPa and ~21-50 GPa. Analysis of iso-surface elucidates at low pressures the Ca attributed covalent nature, having some electrons prefer to be pair but by increasing pressure, electrons localized in the Ca-Ca bond move to the outer regions. These obtained sluggish structural crossovers and their evolution in liquid Ca under pressure should motivate more studies in other disordered systems.

Acknowledgments

Financial supports from the National Key Research and Development Program of China (No. 2016YFB0701203 and 2016YFB0700201), the National Natural Science Foundation of China (51371157, U1432105, U1432110, U1532115, 51671170 and 51671169), the Natural Science Foundation of Zhejiang Province (grants Z1110196 and Y4110192), and the Fundamental Research Funds for the Central Universities are gratefully acknowledged. The computer resources at National Supercomputer Centers in Tianjin and Guangzhou are also gratefully acknowledged.

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Figure Captions

Figure. 1. An illustration of the phase diagram of Ca reported in Ref. 30. The triangles mark the experimental melting curve from Ref. 10. Solid and dash lines are the calculated phase diagram of Ca. The diamond, star, and open circle represent the experimental room temperature phase transitions in Refs. 8, 10, and 11.

Figure. 2. (a) Pair-correlation functions, $g(r)$, of liquid Ca at 3500 K under different pressures from 0.1 to 100 GPa. (Note that, for clarity, each curve perpendicular moves from the curve below.) (b) The peak position of first peak in $g(r)$ at 3500 K as the function of pressure. Solid lines represent different zones in the liquid calcium and the intersecting lines show the cross over in the system.

Figure. 3. (a) Comparison of our theoretical with experimental reported structure factor for liquid Ca.³⁹ (b) Structure factors, $S(q)$, of liquid Ca at 3500 K under various pressures. (c) The inverse first shape diffraction peak position q_1 of liquid Ca at 3500 K with respect to pressure.

Figure. 4. (a) Diffusion coefficients of liquid Ca at 3500K as the function of various pressures. (b) Time dependence of the mean square displacement (MSD) of liquid Ca under various pressure.

Figure. 5. Bond-angle distribution functions of liquid Ca at different pressures. The curves are shifted upward for clarity. Solid line segments demonstrate the BAD for solid phases of calcium.

Figure. 6. (a) The change in bond orientational order parameter, q_6 , of each atom in liquid Ca at 3500 K versus pressure. The open symbols represent q_6 values of four crystalline phases. (b) Top eight Voronoi polyhedra fractions in liquid Ca at 3500 K as the function of pressure. (c) The average coordination number in liquid Ca at 3500 K as the function of pressure.

Figure. 7. Heat capacity (C_v) of liquid Ca originated from AIMD simulations at different pressures.

Figure. 8. Comparison of pressure dependence of total volume (V_p/V_0), Bader volume ($V_{\text{bader-}p}/V_{\text{bader-}0}$) and $(r_p/r_0)^3$ of liquid Ca.

Figure. 9. Electron localization function (ELF) for liquid Ca at 3500 K. The yellowish color represent the outside of the iso-surface.

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