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## 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  $\sim 10$  GPa and  $\sim 50$  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  $\sim 50$  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 toward 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

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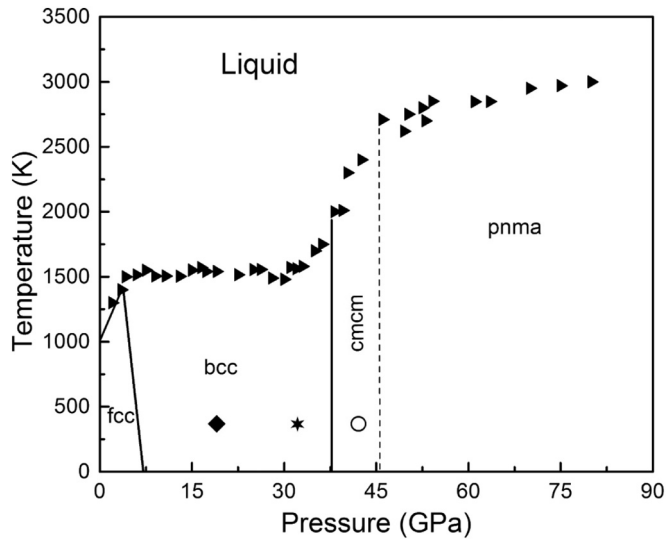


Fig. 1. An illustration of the phase diagram of Ca reported in Ref. [30]. The triangles mark the experimental melting curve from Ref. [10]. Solid and dash lines are the calculated phase diagram of Ca. The diamond, star, and open circle represent the experimental room temperature phase transitions in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

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 Perdew-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

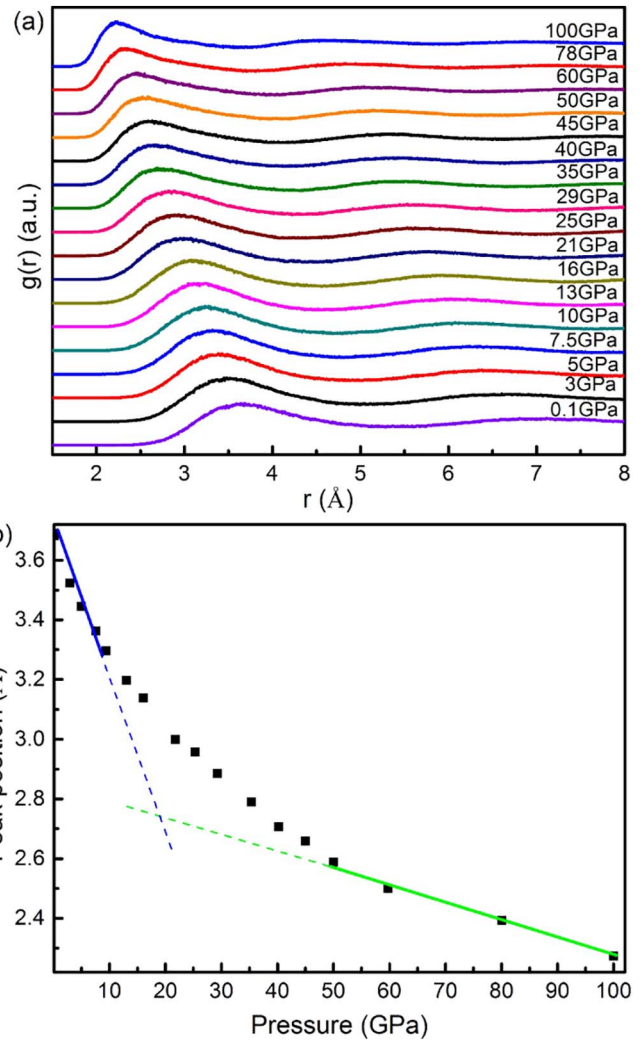


Fig. 2. (a) Pair-correlation functions,  $g(r)$ , of liquid Ca at 3500 K under different pressures from 0.1 to 100 GPa. (Note that, for clarity, each curve perpendicular moves from the curve below.) (b) The peak position of first peak in  $g(r)$  at 3500 K as the function of pressure. Solid lines represent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

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

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