Chemical Physics Letters 653 (2016) 112–116

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Molecular dynamics prediction and experimental evidence for density of normal and metastable liquid zirconium

H.P. Wang, S.J. Yang, L. Hu, B. Wei *

MOE Key Laboratory of Space Applied Physics and Chemistry, Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China

ARTICLE INFO

Article history:
Received 27 January 2016
Revised 30 March 2016
In final form 21 April 2016
Available online 22 April 2016

ABSTRACT

The density of normal and metastable undercooled liquid zirconium was predicted by performing molecular dynamics calculation with a system consisting of 4000 atoms and measured by electrostatic levitation experiments. The results show that the density increases linearly with the descending of temperature, including a maximum undercooling of 928 K. The density is 6.00 g cm^{-3} at the melting temperature, which agrees well with the experimental result of 6.06 g cm^{-3}. Furthermore, the atomic number is increased to 32,000 on the basis of 4000 atoms and there appears only 0.02% difference. Besides, the pair distribution function was applied to display the atomic structure, which indicates the liquid structure change occurs at the first neighbor distance.

1. Introduction

As one of the most fundamental properties, the density of liquid metal is of great importance in understanding mass transfer, thermal convection, atomic distribution, performing numerical modeling, and developing novel materials [1–4]. Moreover, the thermal expansion coefficient of liquid metal can be derived from the density dependance on temperature, which is scientifically and technically important for materials design, liquid/solid phase transformation, and fluid dynamics [5–10]. Accordingly, the density of liquids is quite essential for performing quantitative investigation on the related physics and materials problems. It is well known that the density of an ordinary liquid is easy to obtain by determining the mass and volume. However, it is difficult to measure the density value of high temperature metals, especially for undercooled liquid metals due to the thermodynamic metastability. This leads to the current status that the densities of undercooled liquid metals are extremely scarcely known as compared with those of normal liquid metals [8–10].

Zirconium is widely applied in many fields such as hydrogen storage, nuclear reactors and catalytic converters due to its excellent properties, including corrosion resistance, good plasticity and low neutron absorption [11,12]. Its melting temperature is up to 2128 K. Such a high temperature ensures many important applications at extreme conditions. However, this brings great difficulties to measure the density of liquid zirconium by conventional approaches. Even so, the densities of liquid zirconium could be available from the previous Refs. [13–17]. For the early Refs. [13,14], there were only experients above the melting temperature of 2128 K. Recently, Paradis et al. [15–17] measured the densities of liquid zirconium by electrostatic levitation method. However, the discrepancies exist among these reports, which may make the readers confused. Correspondingly, for the liquid structure of zirconium [18–20], limited results are measured by using the combination of electromagnetic levitation with neutron scattering [18], and obtained by one component plasma method [19]. The structure factors are firstly obtained, and then to derive the pair distribution functions. Althouth there are results of density and structure of liquid zirconium, the information is still rather rare in highly undercooled state.

Therefore, it is desired that applying a kind of numerical simulation can produce satisfactory results of dendity and structure of liquid zirconium. It is optimal that the experimental evidence can be obtained by performing measurements. The molecular dynamics (MD) simulation, combining with a resonable potential model, has been extensively applied in the calculation of the physical properties of several metals as a powerful approach [21,22], especially in exploring metastable liquids. The embedded atom method (EAM) potential model proposed by Daw and Baskes [23,24] is always employed to study the transition-metals with fcc crystal structure such as Ni, Cu, Ag and Au. Then it was modified and developed to deal with the metals with bcc and hcp crystal structures such as Fe, Mo, Ti, Zr, V and Co. For liquid metals, it has been successfully applied in computing the surface tension, diffusion coefficient, density, specific heat, etc. As compared with the experimental measurements, a broader temperature range,

* Corresponding author.
E-mail address: bbwei@nwpu.edu.cn (B. Wei).

http://dx.doi.org/10.1016/j.cplett.2016.04.074
0009-2614/

including large undercooled regime, is easily achieved by moleculr dynamics method.

The containerless processing technique [8,10,16] is an ideal choice for achieving high undercooling of high temperature metals, such as aerodynamic levitation, acoustic levitation, electromagnetic levitation, and electrostatic levitation (ESL). In comparision with other levitation techniques, electrostatic levitation has many advantages [15–18]: It exerts negligible disturbance to the inner part of the sample, and hence is favorable for the achievement of high undercooling. Especially, its levitation stability can be maintained in a very broad temperature range because the levitation and heating are controlled independently. Therefore, the electrostatic levitation technique becomes an important approach to study the densiy of liquid metals at a larger undercooling range.

The objective of this work is to explore the density of liquid zirconium in a board temperature range, including undercooled regime. The MD method is employed to predict the density values, and then ESL experiments is performed to provide experimental evidence. Correspondingly, the atomic structure is displayed by analizing the atomic distribution.

2. Methods

2.1. Molecular dynamics calculation

Molecular dynamics method with the EAM model [25] is applied to simulate a cell containing 4000 Zr atoms, combined with the #2 potential from Ref. [25]. Nose–Hoover's NPT algorithm is performed at 100 K temperature interval. The pressure is set to 1 bar. The time step is 1 fs. The temperature is adjusted every 50 steps. In order to get the equilibrium liquid state, the system starts at 3500 K, which is far above the melting temperature of 2128 K. The ensemble of initial velocities is Gaussian distribution. The initial temperature is kept constant for 200,000 steps. At each temperature, 200,000 steps are carried out to achieve an equilibrium state. The last 100,000 steps were applied to calculate the final results. The simulations are performed using the classical MD package LAMMPS [26]. Fig. 1(a) illustrates the simulated internal energy, the sum of kinetic energy and potential energy, which indicates that the simulated cell achieves an equilibrium state at every temperature. Due to the constant mass in the simulated cell, the volume is a dominant parameter to derive the density.

2.2. Electrostatic levitation experiment

The schematic of the electrostatic levitation we have developed for density measurement is shown in Fig. 2. It consists of a vacuum chamber, a pair vertical and two pairs of side electrodes, two position sensitive detectors, two He–Ne lasers, and an infrared heating laser. In order to measure the density of the levitated sample, a long distance black/white camera is equipped with an UV light providing white background.

The key step to obtain the density in ESL is to measure the volume of the sample. When the levitated sample is melted, it keeps a spherical axisymmetric shape in vertical direction. As a result, after capturing the image of the sample by the long distance camera, its volume can be calculated through a series of image analysis process. The captured temperature curve for step cooling and the UV backlight image of the levitated sample in ESL are shown in Fig. 3.

3. Results and discussion

3.1. Predicted density of metastable liquid Zr

According to the MD calculation, the volumes are obtained from the simulated cell's boundary, and thus the density could be derived from the volume V as follows:

$$\rho = \frac{N \times M_A}{N_A V} \tag{1}$$

where N is the atomic number, M_A is the molar mass, and N_A the Avogadro constant.

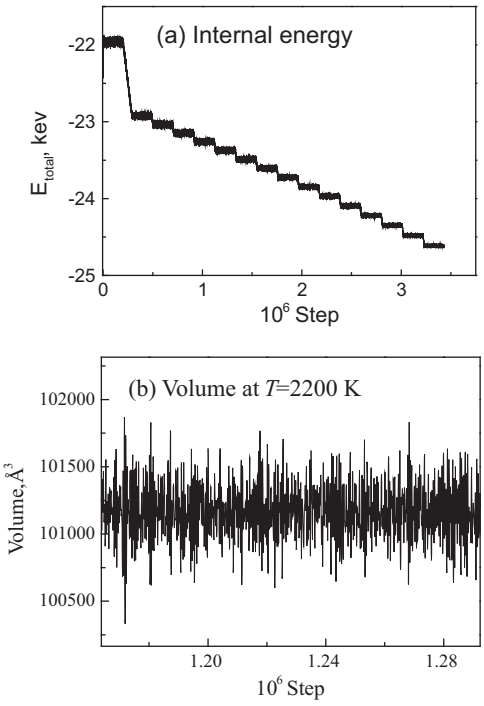

Fig. 1. The internal energy and volume of the simulated cell with 4000 atoms: (a) internal energy change with the time step; (b) volume fluctuation at T = 2200 K.

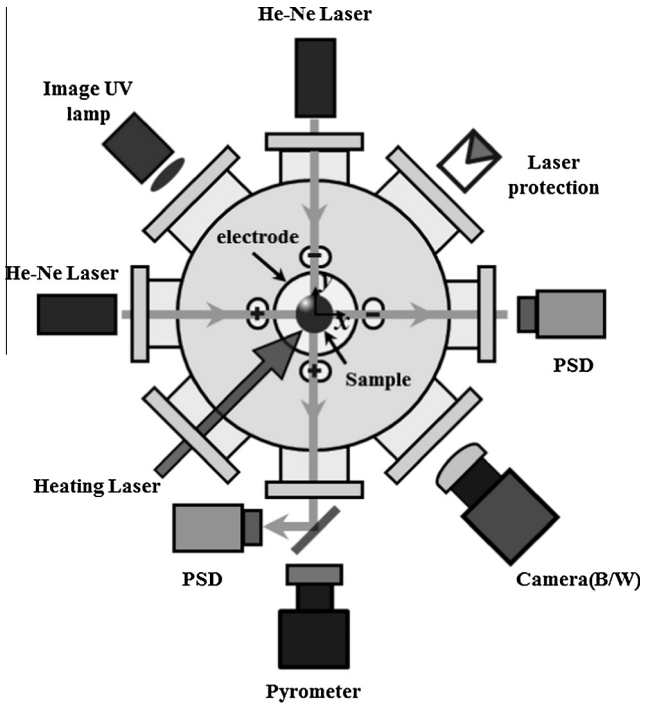

Fig. 2. Top view of the ESL chamber with components for optical detection.