

*Ab initio* molecular dynamics for expanded and compressed liquid alkali metals

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# ***Ab initio* molecular dynamics for expanded and compressed liquid alkali metals**

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**Abstract.** The structural and the electronic properties of liquid alkali metals along the liquid–vapour coexistence curve and along the melting curve are investigated by the *ab initio* molecular dynamics (MD) simulation, in which the Kohn–Sham energy functional is minimized for each ionic configuration of the MD step using the preconditioned conjugate-gradient method.

It is shown for the expanded liquid Rb that the calculated structural functions are in good agreement with the experiments and that the electronic states are strongly correlated with the ionic configuration and tend to localize due to the large spatial fluctuation of ionic density with decreasing density.

As for the compressed liquid Rb under high pressure, the structure obtained by the simulation agrees well with the recent experiment; that is, for the pressure less than 3 GPa the liquid contracts uniformly but above 3 GPa it starts to deviate from the simple uniform compression. This structural feature is related to the electronic s–d transition due to the high pressure, which is clearly seen in the calculated density of states.

## **1. Introduction**

Since the structural and the electronic properties of liquid metals depend strongly on the density due to the screening effect of conduction electrons, liquid metals show a variety of interesting features over a wide range of density. Recently much progress has been achieved in the experimental structural study of liquid metals under high temperatures and high pressures and many interesting results have been reported; e.g. Rb [1, 2], Cs [3, 4], Hg [5] and Se [6].

On the other hand, to understand the features of these experimental results, the *ab initio* molecular dynamics (MD) simulation method has been extensively applied to the liquid metals such as Li [7], Rb [8, 9], Cs [9], Hg [7] and Se [10].

In this paper we are concerned with the liquid heavy alkali metals such as Rb and Cs. For these metals it is known experimentally that there occurs a metal–nonmetal transition near the liquid–vapour critical point and that there exists a melting point maximum which is considered to be closely related to the electronic s–d transition.

The purpose of this paper is to investigate the density dependence of the structural and the electronic properties of liquid alkali metals along the liquid–vapour coexistence curve and along the melting curve using the *ab initio* molecular dynamics simulation.

## **2. Method of calculation**

To study the structural and the electronic properties of expanded and compressed liquid alkali metals, we carry out an *ab initio* molecular dynamics (MD) simulation [8], in which

the Kohn–Sham energy functional is minimized for each atomic configuration of the MD step using the preconditioned conjugate-gradient method. We use the plane-wave basis set to expand the wave function and employ the local density approximation, where, for the exchange–correlation functional, the parameterized form due to Perdew and Zunger is employed [11].

We perform a constant-temperature MD simulation using the Nosé–Hoover thermostat technique [12]. The equations of motion are solved using the velocity Verlet algorithm with time step  $\Delta t = 2.4 \times 10^{-15}$  s.

The supercell contains 54 Rb atoms and the periodic boundary condition is imposed. In the simulation along the liquid–vapour coexistence curve, we use the norm-conserving pseudopotential proposed by Troullier and Martins [13]. The s component is treated as a local potential, while the p component is treated as a nonlocal potential using the Kleinman and Bylander separable form [14]. In the simulation along the melting curve, we use the Vanderbilt ultrasoft pseudopotential [15], which is very useful when d states play an important role and it is the case when the liquid heavy alkali metals are compressed under high pressure.

### 3. Results and discussion

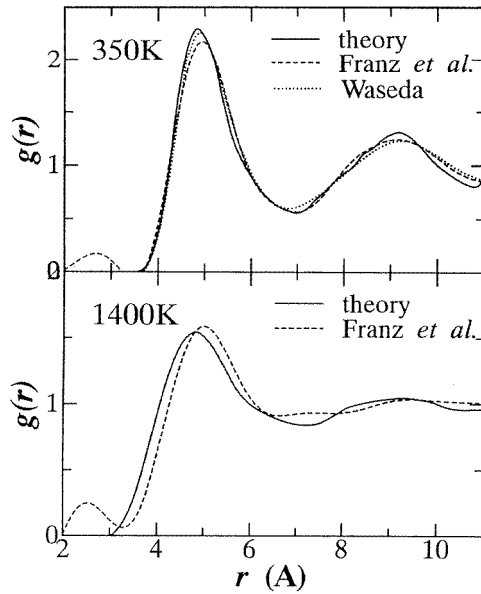
#### 3.1. Structural and electronic properties of liquid Rb along the liquid–vapour coexistence curve

In figure 1, the calculated pair distribution functions  $g(r)$  [8] of liquid Rb at 350 K and 1400 K are shown and compared with the experimental results [1, 16]. We see from this figure that the calculated results are in good agreement with the experimental results and so we have succeeded in reproducing the structure of liquid Rb for a wide range of temperature. The characteristic features of these  $g(r)$  are as follows: with decreasing density, (i) the average nearest-neighbour distance, i.e. the position of the first peak of  $g(r)$ , remains almost unchanged; (ii) on the other hand, the coordination number  $N_1$ , defined by

$$2\rho \int_0^{r_1} 4\pi r^2 g(r) dr$$

with  $r_1$  being the position of the first peak of  $g(r)$  and  $\rho$  being the number density of ions, decreases almost linearly with  $\rho$ . It is concluded from these results that, when the liquid alkali metals are expanded along the liquid–vapour coexistence curve, they do not expand uniformly but decrease their density by reducing the coordination number keeping the nearest-neighbour distance unchanged, which is a lattice-gas-like behaviour. These features are observed experimentally for Rb [1] and Cs [3] and it was also shown theoretically that these characteristic features are common to all expanded liquid alkali metals [17].

As for the density dependence of the electronic states, we have calculated the electron density distribution  $\rho(\mathbf{r})$ , the electron–ion correlation function, the density of states and the electrical conductivity [8]. We can see from these results that, while near the triple point the electron density distribution  $\rho(\mathbf{r})$  spreads over a whole space, at higher temperature and at lower density the  $\rho(\mathbf{r})$  tends to localize due to a large spatial fluctuation of atomic density, which comes from the fact that the coordination number decreases as the density is decreased. Though the density at which our calculation is carried out is not yet close to the critical density, this tendency of electron localization may play an important role in the metal–nonmetal transition near the critical point [18].

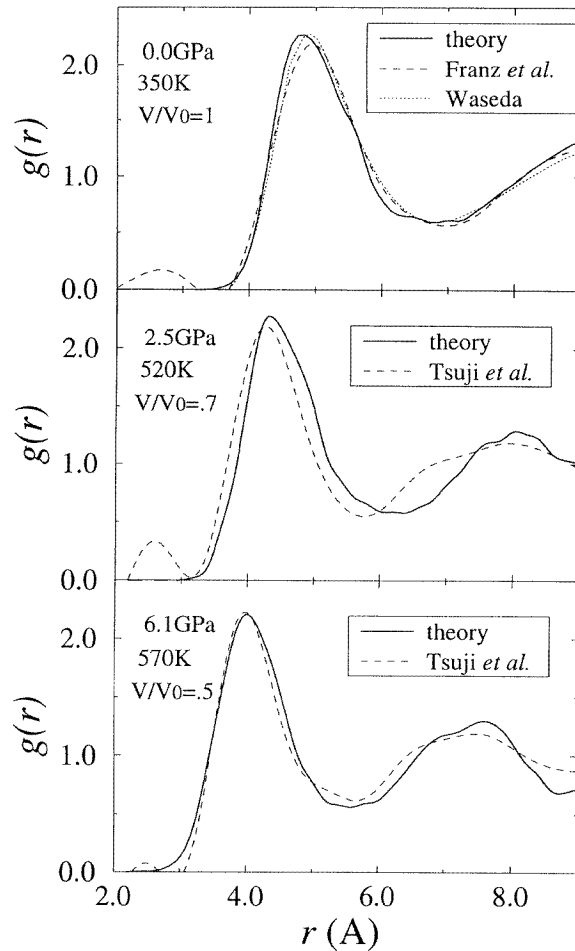


**Figure 1.** The pair distribution functions  $g(r)$  of expanded liquid Rb along the liquid–vapour coexistence curve at 350 K and 1400 K. The solid lines show the present results, and the dashed and the dotted lines show the experimental results of Franz *et al.* [1] and of Waseda [16], respectively.

### 3.2. Structural and electronic properties of liquid Rb along the melting curve

In figure 2 we show the pair distribution functions of liquid Rb at the pressures of 0, 2.5 and 6.1 GPa, obtained by our *ab initio* MD simulation and also those observed experimentally for comparison. Considering the experimental difficulty such that the  $g(r)$  is obtained by the Fourier transformation from the observed structure factor  $S(k)$ , which is available for a limited  $k$ -region, and that the determination of the density is not easy at very high pressures, the agreement between theoretical and experimental results is very good. The characteristic features of the pressure dependence or the density dependence of  $g(r)$  are as follows: with increasing pressure and density, (i) the position of the first peak of  $g(r)$  decreases in proportion to  $(V/V_0)^{1/3}$  at 2.5 GPa and its deviation from the proportionality is seen at 6.1 GPa; (ii) the coordination number calculated from the  $g(r)$  is about 8 at 0 and 2.5 GPa, and about 11 at 6.1 GPa. These results suggest that the liquid Rb is uniformly compressed at 2.5 GPa and the deviation from the uniform-compression model is appreciable at 6.1 GPa. These features are in good agreement with those observed experimentally [2]. This qualitative change in the pressure dependence of the structure corresponds to the structural change to a closer-packed structure.

To investigate the origin of the structural change of the liquid Rb due to pressure, we have calculated the pressure or the density dependence of the total and the partial (s, p and d) electronic density of states (DOS) and shown that, with increasing pressure, the contribution of the s component to the total DOS decreases and that of the d component increases particularly near the Fermi level, while that of the p component remains almost unchanged. At 6.1 GPa, where the deviation from the uniform compression is observed, the main contribution to the total DOS near the Fermi level comes from the d component, which



**Figure 2.** The pair distribution functions  $g(r)$  of compressed liquid Rb along the melting curve at the pressures of 0, 2.5 and 6.1 GPa. The solid lines show the present results. The dashed and the dotted lines at 0 GPa show the experimental results of Franz *et al* [1] and of Waseda [16], respectively. The dashed lines at 2.5 and 6.1 GPa show the experimental results of Tsuji *et al* [2].

suggests that the electronic  $s$ - $d$  transition occurs in the liquid Rb under high pressures and is related to the structural change at about 6.1 GPa. The details of the density dependence of the DOS will be published elsewhere [19].

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