Pressure dependence of the structure of liquid Na

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Abstract. We have carried out \textit{ab initio} molecular-dynamics simulations for Na at various pressures(densities) as a function of temperature to estimate the melting curve based on the temperature dependences of the mean square displacement, the structure factor and the radial distribution function. We have found that there exists a melting-point maximum, which is consistent with the recent experiment. The origin of the melting-point maximum can be understood from the temperature dependence of the pressure of solid and liquid states based on the Clausius-Clapeyron equation. It is also shown from the pressure dependence of the structure of liquid Na along the melting curve that the liquid Na is compressed uniformly in the pressure range from 0 to 100 GPa studied in this paper.

1. Introduction
The gradient of the melting curve in a pressure-temperature phase diagram is determined by Clausius-Clapeyron’s equation

\[ \frac{dP}{dT} = \frac{\Delta S}{\Delta V}, \]  

where \( \Delta S(>0) \) and \( \Delta V \) are the change in entropy and volume on melting, respectively. For many materials, since the volume increases on melting, i.e. \( \Delta V \) takes positive value, \( dP/dT \) is positive. In the case of low-coordination-number crystals, however, the coordination number increases on melting and the density also becomes higher, where \( \Delta V \) takes negative value and \( dP/dT \) is negative. Ice, Si, Ge are the well-known examples of negative \( dP/dT \).

It is also known that the alkali metals Rb and Cs have melting point maximum[1], the origin of which was studied by Shimojo et al.[2] using \textit{ab initio} molecular-dynamics (MD) simulations and was clarified to be the structural change due to the s-d electronic transition. The melting point maximum was predicted theoretically for liquid carbon[3]. Harada et al.[4] have shown that the coordination number of liquid carbon drastically increases from lower pressure region of the maximum melting point to higher pressure region and that the drastic change in the bonding character of liquid carbon occurs with increasing pressure.

Recently, Gregoryanz et al.[5] have performed x-ray diffraction experiments on sodium (Na) under high pressure up to 130 GPa and estimated the melting curve of Na by observing the qualitative change in diffraction pattern. They have shown that the melting temperature of Na increases with pressure, and has its maximum around 30 - 40 GPa, and then decreases. Around 100 GPa the melting temperature becomes almost room temperature.
Very recently, Hernández and Iníguez[6] have performed ab initio MD simulation for liquid and solid Na at some points along the experimentally estimated melting curve[5]. They pointed out that liquid Na is more compressible than solid Na and the difference of compressibility should be the origin of melting point maximum. They did not attempt to calculate, however, the melting curve itself of Na.

In this paper we try to obtain the melting curve of Na under high pressure by ab initio MD simulations and to reveal the pressure dependence of the structure of liquid Na. We are particularly concerned with the existence and its origin of the melting point maximum.

2. Method of calculation
We carried out ab initio MD simulations based on the density functional theory with the generalized gradient approximation (GGA)[7] and on the projector augmented-wave (PAW) method[8, 9]. Since we apply this method to Na up to extremely high pressure, ∼100 GPa, we treat (2p)⁶ states in addition to (3s)¹ state as valence states. The energy cutoff of the plane-wave basis set was taken to be 272 eV.

For MD cell we chose a cubic cell with periodic boundary condition. We chose the number of atom N = 54 and the body-centred-cubic (BCC) structure as an initial configuration, because the structure of Na crystal at the pressure less than around 70 GPa is BCC. The time step is taken to be 1.93 fs. We have performed constant-temperature MD simulation using Nosé-Hoover thermostat[10, 11] with constant-volume MD cell. Our simulation is carried out at the temperatures from 630 K to 1230 K, and densities from 1.8 g/cm³ (∼12 GPa) to 3.7 g/cm³ (∼100 GPa). We started our simulations with BCC atomic configuration and performed MD simulation for 2000 steps for equilibration and then calculated physical quantities based on the results of simulation from 2000 to 4000 steps.

We estimated the melting point at each densities from the mean square displacement (MSD), the structure factor S(k) and the radial distribution function g(r). In the crystal region, MSD takes almost constant value with time, S(k) has sharp peaks and g(r) has peaks corresponding to BCC. When MSD begins to increase with time, sharp peaks of S(k) disappear and peaks of g(r) corresponding to BCC disappear, we regard that Na melts.

3. Results and Discussions
At first, we show how we have determined the melting temperature. In figure 1 we show MSD and S(k) corresponding to the points with density 3.7 g/cm³ (∼100 GPa), in which we can see that drastic qualitative changes in S(k) and MSD occur at a certain temperature, i.e. the melting temperature. At the temperature lower than the melting point, S(k) has sharp peaks and MSD takes almost constant value with time. At the temperature higher than the melting point the sharp peaks of S(k) disappear and MSD increases with time.

In figure 2 we show pressure-temperature diagram and the estimated melting curve of Na by our ab initio MD simulations, where open and filled circles show liquid and crystal, respectively. From figure 2(a) we can see that there exists maximum in melting curve. The melting point maximum estimated from our simulations exists in the pressure range between 40 GPa and 80 GPa, the temperature range between 1030 K and 1130 K.

Figures 2(b) and 2(c) show the temperature dependences of the pressure at ρ = 1.8 and 3.7 g/cm³, respectively. In both figures pressure changes discontinuously with increasing temperature. In both crystal and liquid regions the pressure increases slightly with increasing temperature. With increasing temperature from crystal region to liquid region, the pressure jumps from lower pressure to higher pressure at ρ = 1.8 g/cm³, and higher pressure to lower pressure at ρ = 3.7 g/cm³. From these results we can say that if we increase temperature of solid Na under constant pressure, the volume of liquid Na is larger than solid Na (∆V > 0) in lower pressure region and smaller (∆V < 0) in higher pressure region. This change of sign of
Figure 1. Figures 1(a) and 1(b) show the temperature dependences of MSD and $S(k)$, respectively, at 3.7g/cm$^3$ ($\sim$100 GPa). Drastic changes of both MSD and $S(k)$ occur between 730K and 830K, which corresponds to the melting point.

Figure 2. Pressure-temperature diagram of Na obtained from our ab initio MD simulations. Filled and open circles denote solid states and liquid states, respectively. Figures 2(b) and 2(c) show the temperature dependences of pressure at densities 1.8 g/cm$^3$ and 3.7 g/cm$^3$, respectively.

$\Delta V$ means that there exists the melting-point maximum from the Clausius-Clapeyron equation. It also means that liquid Na is more compressible than solid Na, which is consistent with recent ab initio MD simulation[6].

In figure 3 we show $g(r)$ just above the melting point at some pressures. The abscissa of figure 3(b) is scaled by $(V/V_0)^{1/3}$, where $V_0$ is the volume of MD cell at ambient pressure($\sim$ 0 GPa) and $V$ is that of each simulation, while the abscissa of figure 3(a) is not scaled. The peak positions of these scaled $g(r)$ are almost same at three pressures, though the heights of first peak are different, which is partly due to the difference in temperature. We can conclude that liquid Na is compressed uniformly with increasing pressure in the range of pressure we have studied.

4. Summary
In this paper we have carried out ab initio MD simulations for Na at various pressures (densities) as a function of temperature and estimated the melting curve based on the temperature
dependences of the MSD, \( S(k) \) and \( g(r) \). We have found that there exists a melting-point maximum, which is consistent with the recent experiment by Gregoryanz et al.\(^5\) The origin of the melting-point maximum can be understood based on the Clausius-Clapeyron equation.

It is also shown that the pressure dependence of the structure of liquid Na along the melting curve can be scaled by \( (V/V_0)^{1/3} \), \( V_0 \) being the volume of the MD cell at ambient pressure, which means that the compression is uniform in the pressure range from 0 to 100 GPa studied in this paper.

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