The Validity of First-principles Calculation on Evaluation of Density and Bulk Modulus in Liquid Sodium

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1. Introduction

Liquid sodium fast reactor (SFR) is one of the prospective solutions for spent nuclear fuel disposal problem induced by operation of commercial water reactors. Liquid Na is expected to be a promising coolant regarding several properties, such as low thermal neutron cross section, high thermal conductivity and high boiling temperature (1156 K), which gives a large margin from the operating temperature ranging from 663 to 818 K [1]. Furthermore, liquid Na has high material compatibility with contacted structural materials, such as stainless steels and cladding materials, whereas it is a severe problem in other liquid metal candidates, for instance, liquid lead or liquid lead-bismuth eutectic alloy [1].

Despite many advantages, there are still issues that are needed to be addressed, such as the transportation of radionuclides (fission products) during an accident situation and of pollution impurities (H, O and Ar) during a normal operation in a liquid Na, which is influenced by the diffusivity and solubility of these impurities. Although the understanding of the microscopic thermodynamics is essential for radiation protection of the public and environment, there is a difficulty of experimenting the diffusivity and solubility of impurities at elevated temperature due to following three reasons [2]: (i) It needs a high technique to steadily maintain high temperature; (ii) It is difficult to detect the diffusivity and solubility of impurities under low concentration conditions in liquid Na; (iii) Liquid Na extremely reacts with water, even with vapor.

The quantum mechanical calculations based on the density functional theory (DFT) have been widely used as powerful alternative to experiment in evaluating microscopic properties in a time and cost effective manner. However, the validity of representing the basic mechanical information of liquid Na, such as equilibrium density and bulk modulus, has not been sufficiently researched.

To address this issue, the present study explores the equilibrium densities and bulk moduli of the liquid Na at 600 and 1000 K by utilizing the first-principles molecular dynamics (FPMD) calculation. In addition, the appropriateness of these properties in the solid state Na is evaluated by using the phonon-dispersion curve and the quasi-harmonic approximation (QHA). Through the experimental results as a reference, we estimate the validity of quantum mechanical calculations.

2. Computational details

Vienna *ab initio* simulation package (VASP) was used to perform FPMD calculations based on DFT. The generalized gradient approximation (GGA) exchange-correlation functional parameterized by Perdew-Burke-Emzerhof (PBE) was employed. The electronic wave functions of valence electrons were represented by 300 eV energy cutoff. The effects of core electrons were modeled by the Projected Augmented Wave (PAW) pseudopotentials. The band energy was sampled over the 2×2×2 k-points using the Methfessel-Paxton smearing method of the 1st order with a 0.2 eV smearing width. The spin polarization is not considered based on test calculations which showed that there is no energy gain by spin polarization.

In the system, 102 sodium atoms were prepared and the periodic boundary condition was imposed. Our simulations were performed at 600 and 1000 K in canonical ensemble (NVT) with a Nosé thermostat for temperature control. By taking advantage of the cell constant estimated from the experimental density [3], we prepared five systems having a lattice constant of plus/minus 0.05% and 1% at 600 K and seven systems having a lattice constant of plus/minus 0.025%, 0.5% and 1% at 1000 K in order to evaluate the equilibrium densities and bulk moduli at each temperature. Thereafter, 20 ps FPMD simulations were conducted with a time step of 1.2 and 1.6 fs at 600 and 1000 K, respectively. The equilibration time was determined to be the 5 ps based on the convergence of the total energy and the pair correlation function. In all procedures, we utilized the data after discarding the initial 5 ps results.

For confirmation, the equilibrium densities and bulk moduli in the solid state Na were evaluated by using the phonon-dispersion relation and the QHA method at below the melting temperature. The *phonopy* code developed by the Atsushi Togo research group [4] was utilized in this evaluation processes. It provides a tool for solving the eigenvalue problem of the Hermitian matrix. The Hermitian matrix is built by the derivatives of interatomic forces, which is calculated by giving a displacement distance of ca. 0.006 Å to the one atom in this research.

The pure crystalline solid Na system was firstly simulated by the geometry optimization with allowing volume relaxation. Subsequently, on the basis of the determined lattice constant, systems having a shrunk/expanded lattice constant were prepared from

98% to 104% with a 0.5% interval. In each system, the interatomic force information which is needed in the QHA was evaluated by the static first-principles calculation under 4×4×4 bcc supercell. In all cases, the grid interval was set as 0.037 Å^{-1}.

3. Results and discussion

3.1. Pair correlation function

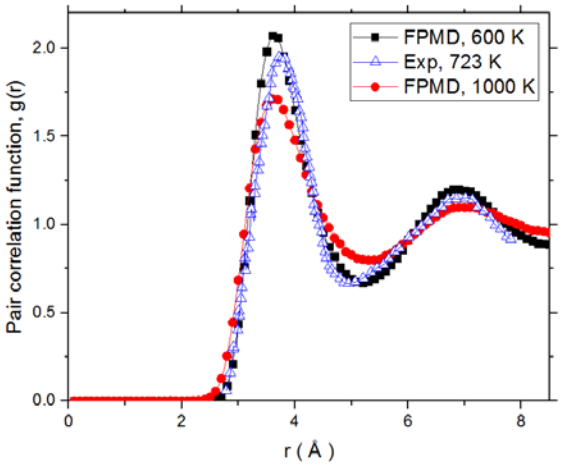

Fig.1. The pair correlation functions calculated by the FPMD calculations at 600 K (closed black squares) and 1000 K (closed red circles). The experimental result [2] (open blue triangles) determined by the neutron diffraction experiment at 723 K is simultaneously shown.

Pair correlation function (PCF) plays an essential role in analyzing the atomic configuration of a liquid system. It gives information of the probability of finding an atom at the distance *r* from a reference atom defined as,

$$g(r) = \frac{dn(r)}{4\pi r^2 d\rho}, \qquad (1)$$

where the *dn(r)* is the number of atoms in the spherical space between the radius *r* and *r+dr*, and ρ is the number density.

In Fig. 1, the calculated PCFs at 600 and 1000 K are presented with the PCF obtained by the neutron diffraction experiment at 723 K [2]. The PCF at 600 K exhibits a good agreement with the previous experimental PCF at 723 K. It indicates that our calculation configurations well represent the realistic geometry of the liquid Na.

3.2. Density and bulk modulus of liquid sodium

The equilibrium density can be estimated by the volume, which gives a zero pressure. The isothermal bulk modulus, that is a measure of how material resists compressibility stresses, is defined as,

$$B_T = -V_{eq}\left(\frac{\partial P}{\partial V}\right)_{T,V=V_{eq}} \equiv \frac{1}{K_T}, \qquad (2)$$

where the V_{eq} is the equilibrium volume giving a zero pressure and K_T is the isothermal compressibility.

In the error estimation of the time correlated data, the statistical error is no longer simply calculated. Accordingly, in this research, the concept of the statistical inefficiency, which gives a variance of the time correlated data, is utilized. To estimate the most effective cutoff period in the time correlated data, the total data points, τ_{run}, are firstly divided by n_b block which has τ_b data points. Then, the statistical inefficiency, *s*, which is a constant of proportionality, is defined as follows [5],

$$s = \lim_{\tau_b \to \infty} \frac{\tau_b \sigma^2\left(\langle P\rangle_b\right)}{\sigma^2(P)} \qquad (3)$$

where *P* is a pressure, $\sigma^2(P)$ is the total variance of a pressure and $\sigma^2\left(\langle P\rangle_b\right)$ is the variance of a mean pressure consisted with τ_b data points.

Then, the statistical inefficiency is determined by the plateau value in the plot of *s* as a function of $\sqrt{\tau}$. In Fig. 2, the statistical inefficiency of the time correlated pressure is analyzed at 1000 K, as an example. The plateau value is determined at approximately 92 value in the *y* axis despite a small fluctuation. It indicates that it is the most effective way to divide the time correlated pressure data set in blocks of 92 data points, as a view point of statistics. In present study, approximately 90 data points are determined to be the plateau value. Thus, the error in the time correlated data is defined as,

$$\sigma\left(\langle P\rangle\right) = \sqrt{\frac{s}{N}}\sigma(P), \qquad (4)$$

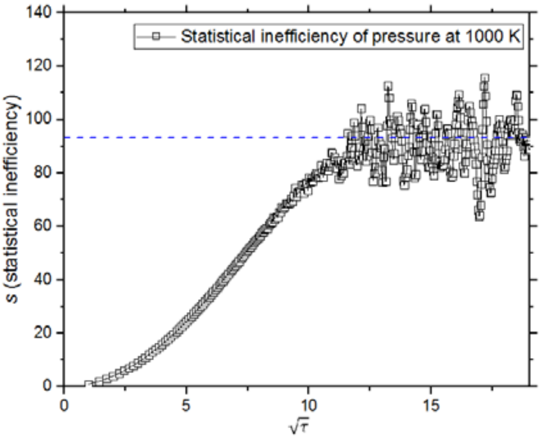

Fig. 2. The statistical inefficiency of a pressure as a function of square root of τ at 1000 K, as an example. The horizontal blue dash line indicates the plateau value.

The second polynomial fitting is drawn to approximate the relation between pressure and volume by using the error weighted regression method at 600 and 1000 K. The reciprocal value of a square of the error bar size was used as a weighting factor.

In Fig. 3, the pressure-volume relations at 600 and 1000 K are presented. The determined equilibrium volumes and bulk moduli are summarized in Table I. In the evaluation of the equilibrium volumes and bulk moduli, the maximum error from the experimental results are within 2% and 7%, respectively. Further, we observed that current results have a tendency to underestimate these quantities. The degree of underestimation becomes considerable, as temperature increases.

Table I: The determined equilibrium volumes and bulk moduli of a liquid Na at 600 and 1000 K.

Temp. (K)	Quantity	Calculation	Experiment	Error (%)
600	Volume (Å)	4458.6	4460.4	-0.04
	B.M. (kBar)	42.0	42.7	-1.78
1000	Volume (Å)	5014.3	4998.6	-1.78
	B.M. (kBar)	25.5	27.5	-7.00

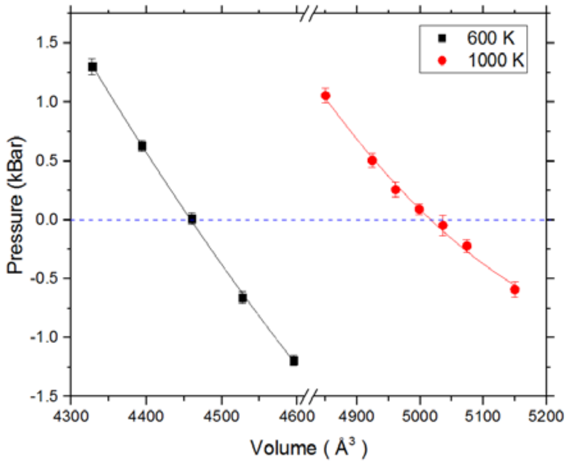

Fig. 3. The pressure-volume relations estimated by FPMD calculations at 600 K (closed black squares) and 1000 K (closed red circles). In each point, the vertical lines indicate the size of an error bar calculated by the statistical inefficiency. The solid curved lines are approximated by the 2nd polynomials. The horizontal blue dash line presents a zero pressure.

3.3. Phonon-dispersion curve

The phonon-dispersion curve gives the fundamental information on dynamic behaviors and thermal properties of materials. The estimation of the phonon-dispersion curve is directly related to the accuracy of the interatomic forces in the system.

A few paths, which are specifically selected, can be used as representatives due to its symmetric characteristics in the crystalline solid. In Fig. 4, the four paths are drawn: (i) from the Γ point to the H point along (ξ, 0, 0) direction; (ii) from the H point to the P point along (0, ξ, ξ) direction; (iii) from the P point to the Γ point along (ξ, ξ, 0) direction; (iv) from the Γ point to the N point along (ξ, ξ, ξ) direction. The experimental data summarized by S. S. Kushwaha et al. [6] are presented as several dots. Each mark stands for different experimental results conducted by the neutron diffraction method. Except for tiny disparities, our result well reproduces the experimental phonon-dispersion curve.

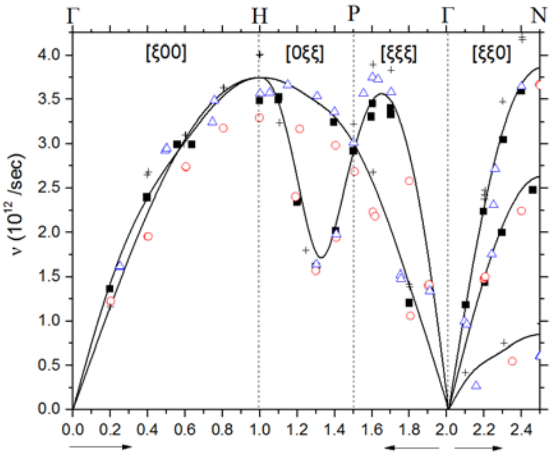

Fig. 4. The phonon-dispersion curve of the bcc Na. The calculation result is shown as solid black lines and experimental data summarized by S. S. Kushwaha et al. [6] are presented as several marks.

3.4. Quasi harmonic approximation

In the solid state, at above zero temperature, the equilibrium volumes and bulk moduli are evaluated based on the phonon information at 0 K temperature and the anharmonic energy-volume relation, so-called QHA. The anharmonic relations of energy-volume are estimated by calculating the phonon dispersion relation in the systems having a shrunk/expanded volume. In each system having a different volume, the Helmholtz free energies consisted of the zero point energy (ZPE), the vibrational Helmholtz free energy and PV term are determined. Subsequently, the equilibrium volume, that produce the minimum Gibbs free energy at constant pressure and temperature, can be calculated as follows,

$$G(T,P) = \min_{V}(ZPE + F_V(T,V) + PV) \tag{5}$$

The vibrational Helmholtz free energy is basically a function of temperature with given phonon information whereas other quantities in the right hand side in equation (5) are regardless of temperature. In Fig. 5(b), the equilibrium volumes calculated by QHA method are shown from 0 K to 350 K with a 5 K temperature interval. In the same way, the bulk moduli are presented in Fig. 5(a) by using the equation (2). At near the melting temperature, the bulk moduli tends to overestimate from the experimental data. However, the maximum errors of equilibrium volumes and bulk moduli result in 1.5% and 6.0%, respectively.

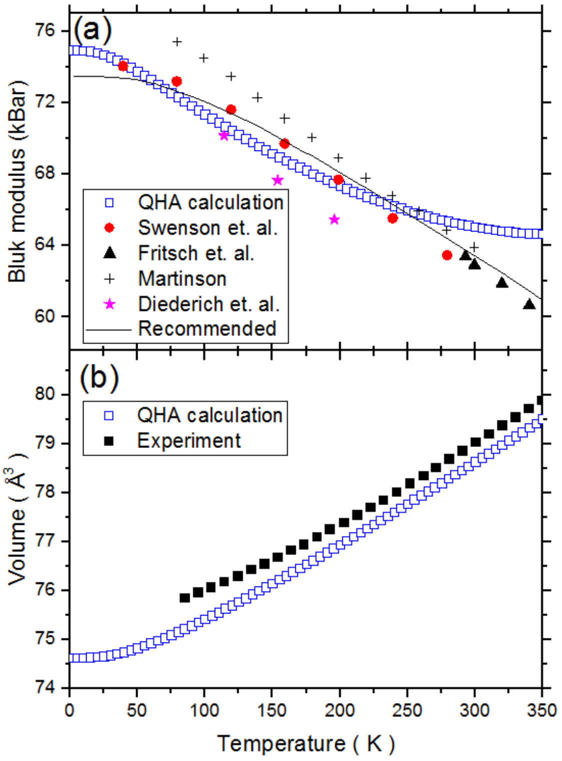

Fig. 5. The (a) bulk moduli and (b) equilibrium volumes of the solid Na calculated by the QHA from 0 to 350 K with a 5 K interval. The experimental observations summarized by R. E. Swanson et al. [7] are simultaneously presented as dots.

4. Conclusion

In the present study, we have utilized the FPMD simulations for the liquid Na and the QHA method for the solid Na to estimate the equilibrium densities and bulk moduli. We mainly dealt with the validity of representing these mechanical properties. The current calculation condition in the liquid simulation has a tendency of underestimating the equilibrium volumes and bulk moduli by approximately 2% and 7%, respectively, at the temperature region of lower than 1000 K. Further, the equilibrium volumes and bulk moduli in the solid state have been calculated based on phonon dispersion relations resulting in an accuracy within 1.5% and 6%, respectively. Accordingly, we confirmed that the quantum mechanical calculations well represent the mechanical properties of the Na within 7% even in the liquid systems. In the future work, we will evaluate the diffusivity and solubility of implanted impurities in the liquid Na system at the elevated temperature based on the delicately determined conditions in this research.

5. Acknowledgement

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