

Calculation of solution energy of oxygen impurity in liquid Na by atomistic simulations

Junhyoung Gil and Takuji Oda*

Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, Republic of Korea 08826

*Corresponding author: oda@snu.ac.kr

1. Introduction

Liquid metals are promising coolants for some generation IV reactors. Representative issues in the use of liquid metals include the corrosion of structural steels and the transport and precipitation of radionuclides. To understand such phenomena, the solubility and the diffusivity of impurities in liquid metals are the key properties. However, determining these properties by experiments is not only time-consuming and costly but also technically difficult due to high temperature, reactivity, purity control, etc.

In this study, using the quantum mechanical (QM) calculation based on the density functional theory (DFT), we construct a method to calculate the solution enthalpy of gaseous impurities. We test the method for O in liquid Na for validation and compare the results with experimental data. The solution enthalpy is expected to be reasonably determined with shorter time and lower cost than experiments.

2. Methods and Results

2.1. QM calculation methods

First-principles molecular dynamics (FPMD) is performed using the VASP code [1]. Wave functions of valence electrons are represented by plane waves with a cutoff energy of 300 eV. Projected augmented wave (PAW) method is used for dealing the effects of core electrons [2]. 1st-order Methfessel-Paxton's smearing scheme is used with a 0.2-eV width [3]. A $2 \times 2 \times 2$ Monkhorst-Pack grid is used for sampling the band energy [4], which gives 4 irreducible k-points.

A model liquid Na system is prepared as a cubic unit cell containing 102 atoms with periodic boundaries. The initial configurations are brought from our previous research of liquid LBE [5]. The temperature is set to 600 K and 1000 K by applying a canonical (NVT) ensemble with a Nosé-Hoover thermostat. The cell constant is determined from finding an equilibrium volume at an atmospheric pressure.

A 20-ps simulation is performed for each temperature with the time step of 1.6 fs (600 K) or 1.2 fs (1000 K). The first 5-ps data are discarded as an equilibration run, and the remaining 15-ps data are used for the analysis.

2.2. Choosing an appropriate exchange-correlation functional: theoretical background

The DFT states that the total energy of the system E is exactly written by the functionals of electron density n as follows:

$$E[n] = T[n] + E^H[n] + E^{XC}[n] + \int V(\bar{r})n(\bar{r})d^3r \dots (1)$$

Here, T is the kinetic energy of electrons, E^H is electron-electron repulsion interaction, E^{XC} is the exchange-correlation energies of electrons, and V is the external potential such as an electrostatic potential. However, the exact functional formula of E^{XC} is unknown while there have been several approximate functionals for E^{XC} .

The accuracy of the DFT calculations is largely dependent on the quality of E^{XC} . Thus, we first select the most appropriate exchange-correlation functional of DFT calculation that well reproduces liquid Na. To select, the performances of several exchange-correlation functionals for liquid simulations – three of generalized gradient approximation (GGA), namely Perdew-Burke-Ernzerhof (PBE), Armiento-Mattsson 2005 (AM05), and PBE reparameterized for solids (PBEsol), and one of local density approximation (LDA) – are evaluated.

2.3. Choosing an appropriate exchange-correlation functional: results for liquid Na

First, a pair correlation function (PCF) is checked to validate the functionals for the atomic configuration of liquid Na. A PCF represents the variation of atomic density at radius r from a reference atom by the following expression:

$$g(r) = \frac{dn(r)}{4\pi r^2 dr \rho} \dots (2)$$

Here, $dn(r)$ is the number of atoms in a spherical volume between the radii r and $r+dr$ and ρ is the number density of atoms. Fig. 1 shows the calculated PCFs for liquid Na with the experimental data (723 K). The 600 K PCFs show a good agreement with the experimental data. The PCFs are mostly comparable to each other while the LDA-functional PCF is slightly sifted to a shorter distance by approximately 0.1 Å.

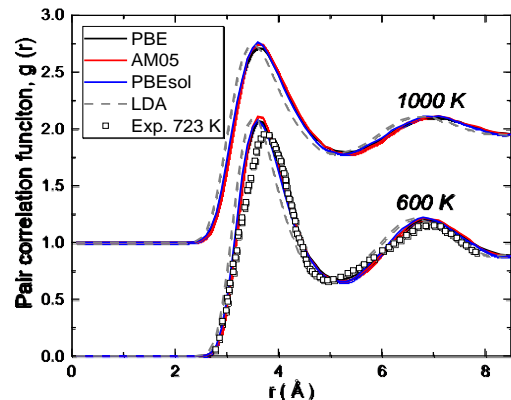


Figure 1: PCFs for liquid Na using several functionals.

Next, an equilibrium volume and a bulk modulus are evaluated. The equilibrium volume is obtained from the volume giving the zero pressure. The isothermal bulk modulus is estimated from the pressure-volume relation. For the equilibrium volume, PBE and AM05 show relatively small errors at both temperatures (less than 2%). For the bulk modulus, PBE and PBEsol show relatively small errors at both temperatures (less than 7%). In summary, it is found that the PBE functional exhibits the best performance for liquid Na [6].

2.4. Vibration analysis: theoretical background

Thermodynamic quantities such as free energy, internal energy, enthalpy, and entropy at high temperatures are needed to be obtained to calculate the solution enthalpy. They can be obtained from the partition function Z for gas:

$$Z(N, V, T) = \frac{[q(V, T)]^N}{N!} \quad \dots (3)$$

$$\text{where } q(V, T) = q_{trans} q_{rot} q_{vib} q_{elec}$$

Here, N is the number of molecules in a system, V is the volume of a system, and T is the temperature of a system. q_{trans} , q_{rot} , q_{vib} , and q_{elec} are the partition functions for a gas molecule with respect to translational, rotational, vibrational and electronic components, respectively.

While the other components of the partition function are obtained directly, the vibrational component q_{vib} can be simply obtained by applying the harmonic approximation. Under an ideal gas assumption, the vibrational contribution for the partial function q_{vib} is expressed as

$$q_{vib} = \sum_n e^{-\beta \varepsilon_n} = \sum_n e^{-\beta h \nu_n} \quad \dots (4)$$

where ε_n is the n -th vibrational energy level, h is the Planck constant, and ν_n is the n -th vibrational frequency. By applying the harmonic approximation to the molecular vibration, the eq. (4) is rewritten as:

$$q_{vib} = \sum_n e^{-\beta \left(n + \frac{1}{2} \right) h \nu_n} = \frac{e^{-\beta h \nu_n / 2}}{1 - e^{-\beta h \nu_n}} = \frac{e^{-\Theta_{vib} / 2T}}{1 - e^{-\Theta_{vib} / T}} \quad \dots (5)$$

$$\text{where } \Theta_{vib} = \frac{h \nu_n}{k_B}$$

Here, ν_n is the vibrational frequency of a harmonic oscillator and Θ_{vib} is the vibrational temperature.

Accordingly, the internal energy E and the entropy S of a system can be obtained, and finally, enthalpy H , Gibbs energy G , and Helmholtz energy A are obtained with the following relation:

$$\begin{aligned} H &= E + P\bar{V} \\ A &= -k_B T \ln Z = E - TS \quad \dots (6) \\ G &= H - TS = A + P\bar{V} \end{aligned}$$

By the QM calculation, first the binding energy of a molecule D_e and the equilibrium bond distance R_e are obtained. Then, by solving a Schrodinger equation for the obtained binding energy curve, the vibrational frequency and the energy level of vibration models are obtained. Finally, thermodynamic quantities of a gaseous molecule at a high temperature are obtained.

2.5. Vibration analysis: results for O₂

Four exchange-correlation functionals are tested to obtain the potential curve of an oxygen molecule. The results for two GGA (PBE and PBEsol) and two meta-GGA (RTPSS and SCAN) functionals are shown in Fig. 2. While r_e is similar among the functionals, the GGA functionals give a greater value of D_e .

In Table 1, the results are compared with the experimental data. The meta-GGA functionals give very good results for D_e while the GGA functionals significantly overestimate it. The r_e and the fundamental frequency ω_{01} are well reproduced with all of the four functionals. For consistency with liquid Na, the PBE functional is temporarily used for the calculation.

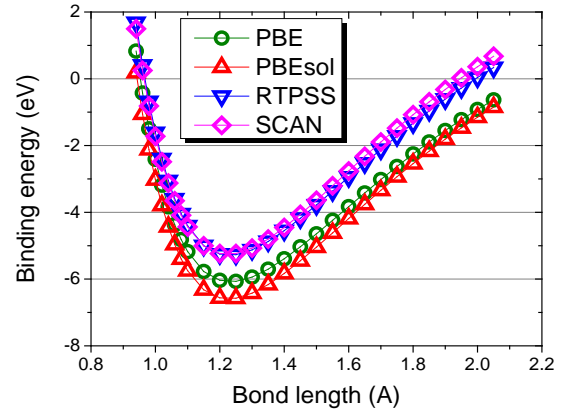


Figure 2: Potential curves of an oxygen molecule obtained by different functionals.

Table 1: Results for the potential curve of an oxygen molecule.

Functional	D_e (eV)	R_e (Å)	ω_{01} (cm ⁻¹)
PBE	6.08	1.231	1548
PBEsol	6.59	1.225	1584
RTPSS	5.29	1.227	1578
SCAN	5.26	1.222	1603
Exp.	5.23	1.208	1556

Using a developed code, the enthalpy H and entropy S are calculated and validated by the comparison with the experimental data, which is shown in Fig. 3. The entropy and enthalpy are accurately obtained with the errors less than 1%.

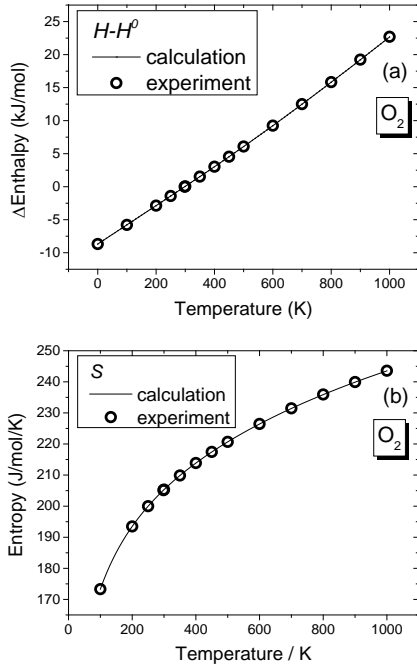


Figure 3: Enthalpy and entropy calculated and validated in various temperatures for an oxygen molecule.

2.6. Evaluation of the solution enthalpy

In order to evaluate the solution enthalpy, the enthalpy of an oxygen molecule at a temperature T needs to be obtained. The following relation is used to estimate the value at a temperature T .

$$\begin{aligned} H_{\text{O}_2}^{\text{DFT}}(T) &= H_{\text{O}_2}^{\text{DFT}}(0 \text{ K}) + \Delta H_{\text{O}_2}(0 \text{ K} \rightarrow T \text{ K}) \\ &= E_{\text{O}_2}^{\text{DFT}}(0 \text{ K}) + [\text{ZPE}]_{\text{O}_2} + \Delta H_{\text{O}_2}(0 \text{ K} \rightarrow T \text{ K}) \cdots (7) \end{aligned}$$

Here, $[\text{ZPE}]_{\text{O}_2}$ is the zero-point energy of an oxygen molecule, and $\Delta H_{\text{O}_2}(0 \text{ K} \rightarrow T \text{ K})$ is the enthalpy difference between 0 K and $T \text{ K}$.

Finally, the solution enthalpy of O in liquid Na is expressed as:

$$\begin{aligned} \Delta H_{\text{sol}}(T) &= \left[H_{\text{liq-Na+O}}^{\text{DFT}}(T) \right] - \left[H_{\text{liq-Na}}^{\text{DFT}}(T) + \frac{1}{2} H_{\text{O}_2}^{\text{DFT}}(T) \right] \\ &\simeq \left[E_{\text{liq-Na}(N-1)+\text{O}}^{\text{DFT}}(T) \right] - \cdots (8) \\ &\left[\frac{N-1}{N} E_{\text{liq-Na}(N)}^{\text{DFT}}(T) + \frac{1}{2} \{ E_{\text{O}_2}^{\text{DFT}}(0 \text{ K}) + [\text{ZPE}]_{\text{O}_2} + \Delta H_{\text{O}_2}(0 \text{ K} \rightarrow T \text{ K}) \} \right] \end{aligned}$$

Here, the term $(N-1)/N$ comes from the difference in the number of Na atoms in pure liquid Na and oxygen-containing liquid Na systems.

The procedure to calculate the solution enthalpy of O in liquid Na is shown with the results at 600 K in Fig. 4. The data for three O-including liquid Na and three pure liquid Na systems are used. For O-including liquid Na systems, the pressure-energy corrections are made in order to set the system pressure zero.

The calculated solution enthalpy is -2.8 eV. The negative value means that O is energetically more stable

in liquid Na than in vacuum. The value needs to be compared with the experimental data for validation. We find that, however, it is difficult to compare the value directly since the experimental solution enthalpy is usually obtained with reference to sodium oxide, not to an oxygen molecule in vacuum. Thus, we plan to first come up with a method to reasonably compare the calculated value with the experimental data. Then, the error is to be analyzed by applying the concept of statistical inefficiency [6] and also be decreased by investigating the cause.

O-including liquid Na	System A	System B	System C	
Average total energy [eV]	-119.51	-119.56	-119.53	
Average pressure [kB]	-0.90	-0.94	-0.96	
O-including	System A	System B	System C	Average
Total E [eV]	-119.51	-119.56	-119.53	-119.53
				Pressure-energy correction
				Average
				-119.08
Pure liquid Na	System A	System B	System C	Average
Total E [eV]	-112.55	-112.56	-112.54	-112.55
				Number correction
				Average
				-111.45
O ₂ molecule	0 K energy	ZPE	ΔH from 0 to 600 K	
Values	-9.8766 eV	0.0968 eV	0.186 eV	Sum-up
				Sum/2
				-4.8
				ΔH _{sol} (600 K) = -2.8 eV

Figure 4: Procedure to calculate the solution enthalpy and the results for an oxygen molecule in liquid Na at 600 K.

3. Conclusions

By the performance evaluation of several exchange-correlation functionals for liquid Na, PBE is considered to be the most suitable. The vibration analysis for a gas molecule is used to determine the thermodynamic quantities of an oxygen molecule at high temperatures, of which the results are accurate compared to the experimental data. The solution enthalpy of O in liquid Na at 600 K is evaluated. The results are to be validated, and the corrections are to be made. This method is expected to be useful in that it is applicable to any gaseous impurity in any liquid metals in principle.

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