

Analysis on Chemical States of the Second-row Impurity Atoms in Liquid Lead-Bismuth Eutectic

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1. Introduction

Liquid lead-bismuth eutectic (LBE) is a promising coolant material designated for an LBE-cooled fast reactor, one of the Gen. IV advanced reactors. Its characteristics such as low melting point, high boiling point, high heat transfer coefficient, low chemical reactivity, and high neutron spallation make the material both efficient and safe to be used in a nuclear reactor [1]. However, compared to water that have been used as a coolant for most nuclear reactors, accumulated knowledge for liquid LBE is quite limited. Speaking of experiments, it is difficult to control the purity of liquid LBE. Even if experiments are done, there is a limitation in the analysis of experimental results; the material is in the liquid state, and it is not transparent. For these reasons, performing computational simulations is both practical and effective to obtain necessary information regarding liquid LBE and to analyze the information.

An important topic may be the behavior of impurity atoms inside the liquid LBE. Diffusivity and solubility of impurity atoms determine the transport of radionuclides in a coolant, and ultimately, this may affect the safety of nuclear reactors. In this research, we focused on second-row elements in the periodic table as the impurity atoms. With classical molecular dynamics (MD) and first-principles molecular dynamics (FPMD), computational simulations with both pure and impurity-including LBE systems were performed. From the results, chemical states of the impurity atoms in liquid LBE were analyzed and discussed using several analysis tools.

2. Simulation and analysis methods

2.1 Simulation methods

A cubic supercell consisting of 45 Pb atoms and 56 Bi atoms, which satisfies the eutectic composition, was prepared as a model LBE system. The system was first equilibrated at 1000 K by classical MD. The LAMMPS code [2] was used here with an embedded-atom method (EAM) potential developed by Murray S. Daw and M. I. Baskes [3]. Then, FPMD calculations using the VASP code [4] were performed at 1000 K for 15 ps to equilibrate the system. The Perdew-Burke-Ernzerhof (PBE) functionals [5] were used to evaluate the exchange-correlation interaction. The band structure was sampled by the Monkhorst-Pack scheme [6] with a $2 \times 2 \times 2$ k-space mesh.

In the resultant LBE system, an impurity atom from selective second-row elements – Be, B, N, O, and Ne – was introduced at a specific position which is expected to be sufficiently distant from neighboring atoms. Finally, for each impurity-including system, another FPMD calculation was performed at 1000 K to obtain 8-ps equilibrium data, which was analyzed by the following methods.

2.2 Pair correlation function and coordination number

The pair correlation function can represent the number density of Pb and Bi atoms surrounding an impurity atom within a certain radial cutoff distance. The function is expressed as:

$$g_{ij}(r) = \frac{1}{\rho_0 c_i c_j N} \left(\sum_i \sum_{j \neq i} \delta(\vec{r} - \vec{r}_{ij}) \right) \dots \dots (1)$$

where ρ_0 is the average number density, c_i and c_j are the concentrations of particles i and j , N is the number of particles, and r_{ij} is the distance between the particles i and j [7]. Here, if the particle i corresponds to an impurity atom, then the particle j corresponds to Pb and Bi atoms. Since all the second-row impurity atoms have smaller radii compared to those of Pb and Bi atoms, the correlation functions are expected to return different results from Pb-Pb, Pb-Bi, and Bi-Bi functions.

With a correlation function, the concept of a coordination number can be considered with the following expression:

$$N_{ij} = \int_0^{R_{\text{cutoff}}} 4\pi r^2 \rho_0 c_j g_{ij}(r) dr \dots \dots (2)$$

with R_{cutoff} being a proper cutoff distance [7]. To obtain the number of atoms up to the first neighbors, the cutoff distance is set to the first minimum point of the corresponding correlation function.

2.3 Angle distribution function

To evaluate the angle distribution of Pb and Bi atoms around the second-row impurity atoms, angle distribution function was calculated up to the first-neighboring atoms of each impurity atom. It is known that the function shows its peaks at around 60° and 120° if the atoms are located in a closed-packed manner. On the other hand, the function has its peak at around 109° if the atoms are located in a tetrahedral structure due to anisotropic interactions [7]. For each impurity-including case, the angle distribution was compared to each other as well as to the results of the pure LBE system. Then, the results were analyzed to figure out the effect of an angle distribution to the coordination number.

3. Results and Discussions

3.1 Pair correlation functions for the pure LBE system

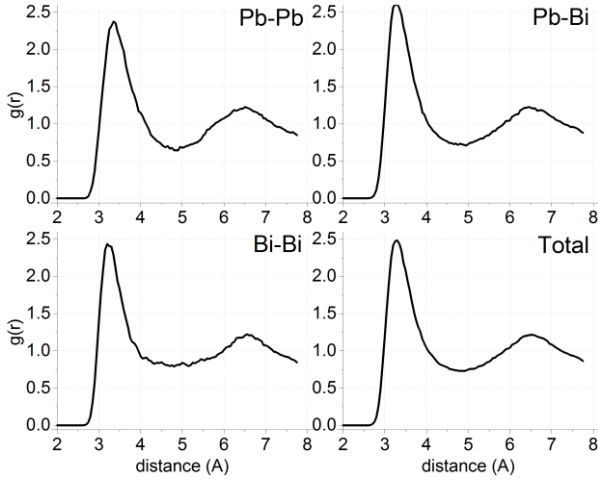


Fig. 1. Partial and total pair correlation functions obtained from the results of the FPMD calculation for the pure liquid LBE system at 1000 K.

Fig. 1 shows the partial and total pair correlation functions of the pure liquid LBE system at 1000 K. The total correlation function was evaluated by the superposition of the partial functions (Pb-Pb, Pb-Bi, and Bi-Bi) using the following expression:

$$g(r) = \sum_{i=1}^2 \sum_{j=1}^2 \frac{c_i c_j b_i b_j}{(c_1 b_1 + c_2 b_2)^2} g_{ij}(r) \dots (3)$$

with the neutron scattering lengths $b_{Pb}=9.401$ and $b_{Bi}=8.532$ [7]. The results seem well agree with the reference [7]. Speaking of the total pair correlation function as a representative, the first peak appears at around 3.3 Å, and the first minimum appears at around 4.8 Å. The first peak corresponds to the average distance between two atoms in the system, while the first minimum represents the cutoff distance to the first neighbors. From the results, the atomic radii of Pb and Bi can be estimated. In addition, the coordination numbers of Pb and Bi can be calculated using the resultant cutoff distance. The coordination numbers are 12.7 and 12.5 for Pb and Bi, respectively, which are in a good accordance with the previous studies [7].

While Fig. 1 is a general set of graphs to represent pair correlation functions, Fig. 2 may be an alternative way



Fig. 2. An alternative way to express correlation functions. In the coordination number – cutoff radius relationship, the derivative of the graph represents the correlation function.

to express the functions by coordination numbers. This can be a more intuitive way to figure out the number of neighboring atoms. The derivative of this graph represents the correlation function. The cutoff radius at which the derivative has the first maximum value corresponds to the first maximum point of the correlation function, and the same for the first minimum. Then, using this analysis method, how the derivatives, or the slopes, of the graphs vary as well as how the coordination numbers differ according to the type of impurity atoms was analyzed, which is shown in the following section.

3.2 Pair correlation functions for the impurity-including LBE systems

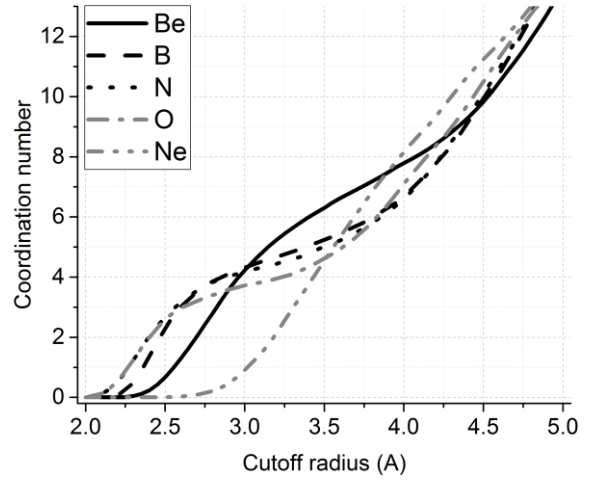


Fig. 3. Coordination number – cutoff radius relationship for the selective second-row impurity atoms in liquid LBE.

Table 1: Summarized values from Fig. 3

Impurity type	Be	B	N	O	Ne
Maximum [Å]	2.80	2.40	2.30	2.30	3.25
Minimum [Å]	3.65	3.20	3.10	3.05	4.10
Coordination number	6.76	4.67	4.31	3.78	8.75

Fig. 3 shows the relationship between coordination numbers and cutoff radii for each impurity atom in the liquid LBE system. The interval for cutoff radii in the calculation is 0.05 Å. The cutoff radii at which the derivative is maximized and minimized for the first time are summarized in Table 1. The maximum value represents the average distance between an impurity atom and its first-neighboring Pb and Bi atoms. Assuming that the size of the Pb and Bi atoms is the same for all impurity cases, the values reflect the size of the impurity atoms.

From Be to N, the average interaction distance between the impurity atom and its first-neighboring LBE atoms decreases. The cutoff distance up to the first neighbors decreases as well. As a result, the coordination number decreases as the atomic number increases. This can be explained with the decreasing atomic size of the

impurity atoms. However, for N and O, the values of the maxima and the minima stay almost the same while the coordination numbers continue to decrease. This implies there exist some factors other than the atomic size that affect the atomic distribution. Ne shows an exception due to its non-interaction nature as a noble gas.

3.3 Angle distribution function

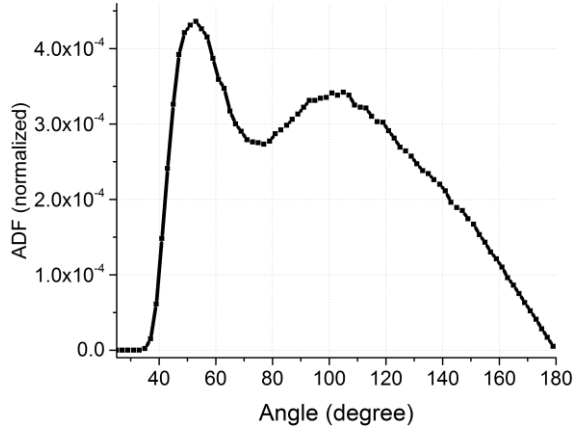


Fig. 4. Angle distribution function for the pure liquid LBE system. Note that the peaks appear at 53° and 105°

Another factor that may affect the atomic distribution is anisotropy in atomic interactions. The evaluation of the angle distribution function may give some clues about the anisotropy. Fig. 4 depicts the angle distribution function for the pure liquid LBE system at 1000 K. The interval between the angles is 2°, and the cutoff distance was set as 4.8 Å, which is up to the first neighbors. The results well agree with the previous study; there exist the two peaks: one at 53° which represents the closed-packed structure and the other at 105° which represents the incomplete tetrahedral structure [7]. With the confirmation of the calculation scheme with the pure liquid LBE, the functions were calculated for the impurity-including cases as well. The results are selectively shown in Fig. 5.

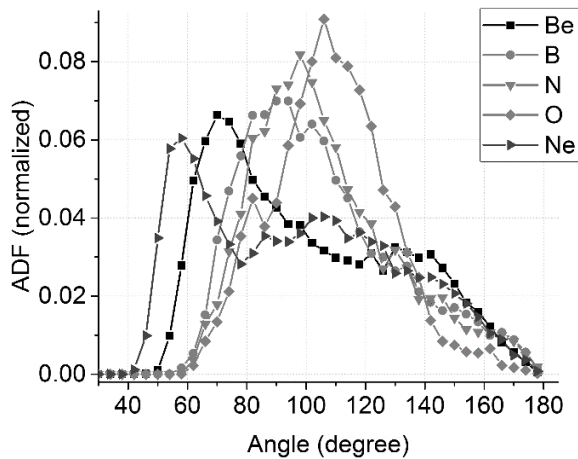


Fig. 5. Angle distribution functions for selected impurity-including liquid LBE systems.

Table 2: The peak angles at which the angle distribution function has its maximum for selective impurity cases

Impurity type	Be	B	N	O	Ne
Peak angles	70°	90°	98°	106°	58°

The interval between the angles is 4°, and the cutoff distance was set properly to include up to the first neighboring atoms of each impurity atom. Table 2 lists the peak angles from the results.

For Be, the peak angle of 70°, similar to that of a bcc structure, shows that the atomic packing around the Be atom is relatively loose compared to a closed-packed structure. For B and N, the peak angles are greater, which means the anisotropy in the atomic distribution increases, and as a result, the atomic packing becomes more loosen. Finally for O, the peak angle of 106° which implies the tetrahedral-wise structure around the O atom shows almost complete anisotropy in the atomic distribution. Meanwhile, for Ne, the distribution has a major peak at 58° and a minor peak at 106°. This is the most similar to the results for the pure liquid LBE system. This is reasonable considering the results of the pair correlation functions.

4. Conclusions

The coordination number is a quantitative index to analyze the geometrical structure at around an impurity atom. Both the size of the atom and the anisotropy in atomic interactions affect the number. As the atomic number increases within the same period of elements, generally the atomic size decreases and so does the coordination number. As the anisotropy in atomic interactions increases, the atomic packing becomes loosen even with a similar cutoff distance, and the coordination number decreases.

The anisotropy in atomic interactions may be caused by the anisotropy in atomic orbitals. For example, the electron configuration for Be is $1s^2 2s^2$, and these s-orbitals are all isotropic in space. Then, the atomic distribution would be determined primarily by the atomic size of Be. However, for B, N, and O, the atoms have both incomplete and anisotropic 2p orbitals. These may cause anisotropic atomic interactions and affect the overall atomic distribution around an impurity atom.

In addition to the pair correlation function, the electron density of states for LBE and impurity atoms was analyzed in order to deepen the understanding of atomic interactions between the impurity atom and its neighboring LBE atoms. Bader analysis was introduced as well to calculate the charge and the volume of the impurity atoms based on their charge density distribution [8]. The results are to be shown in the presentation.

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