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Molecular Dynamics Simulation on Physical Properties of Liquid Lead, Bismuth and Lead-bismuth Eutectic (LBE)

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Abstract

Molecular dynamics method was applied to simulate the physical properties of liquid metals: lead, bismuth and a binary alloy--lead-bismuth eutectic (LBE). The embedded atom method (EAM), an empirical model rooted in density-functional theory, was used to represent the many-body interaction within the liquid metals. The atomic-scale interactions, structure and thermal physical properties of lead, bismuth and LBE were obtained through the simulation, and then compared to the available experimental results. The theoretical results of the physical properties calculated through the MD simulations are in good agreements with the available experimental data

Keywords: Molecular dynamics (MD); EAM; LBE; LFR; ADS; Thermal-physical properties

1. Introduction

The lead-bismuth eutectic (LBE), which is composed of 44.5% lead (Pb) and 55.5% bismuth (Bi), has been considered as one of the possible candidate coolants for lead-alloy cooled fast reactor (LFR) as well as a spallation target/coolant for the future accelerator driven system (ADS) [1]. The advantages of LBE for these applications are its high spallation neutron yield, low melting point, high thermal conductivity, low vapor pressure and no violent reaction with air and water. However, the database of thermal physical properties of LBE (e. g. density, molar

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volume, isobaric heat capacity, viscosity) is somewhat old, incomplete and partly unreliable. The available data are in general summarized in the Lead-bismuth Handbook, edited by OECD Nuclear Energy Agency. However, a "best fit" of the handbook data is often necessary because of the significant discrepancies that exist among the values given by different sources [2]. Besides, since there is high reactivity of metallic liquids at elevated temperatures, it is difficult to take the precise measurements.

In the present study, in order to complement the experimental database of physical properties of liquid LBE, classical molecular dynamics (MD) has been used to simulate the liquid LBE in the 673-1500K temperature range. The embedded atom method (EAM) [3, 4] was used to evaluate the many-body interaction between Pb and Bi. Besides, in order to validate the accuracy of the adopted EAM potentials, pure liquid Pb and Bi models were also developed and their properties were simulated. The simulations allowed calculating densities, heat capacities and viscosities of the pure liquids and the eutectic at different temperatures. The simulations were validated through comparison with experimental results when available [2].

2. Model and method

2.1. Potential model

The energy of the considered metals and metal alloys were computed using EAM potentials. The basic EAM equation of the total potential energy E of a system with N atom is [4, 5]

$$E = \sum_{i=1}^{N} \left[F(\rho_i) + \frac{1}{2} \sum_{j \neq i} \Phi(r_{ij}) \right], \tag{1}$$

$$\rho_i = \sum_j f(r_{ij}), \tag{2}$$

where ρ_i is the effective electron density at atom i due to all other atoms, $f(r_{ij})$ is the electron density at atom i due to atom j as a function of a distance r_{ij} between them, $F(\rho_i)$ is the energy required to embed atom i in an electron density ρ_i, and $\Phi(r_{ij})$ is a two-body potential between atoms i and j.

In this simulation, the potential parameters of Pb and Bi have been taken from Belashchenko [6]. These parameters were derived by fitting the properties of pure liquids. Besides, an analytic formulation of two-body alloy potentials as a function of monatomic two-body potentials was used to calculate the cross-interaction between Pb and Bi [7].

$$\Phi^{ab}(r) = \frac{1}{2} \left[\frac{f^b(r)}{f^a(r)} \Phi^{aa}(r) + \frac{f^a(r)}{f^b(r)} \Phi^{bb}(r) \right]. \tag{3}$$

According to equation (3), the pair potential of two different atoms is assumed to be equal to the weighted average of the electron densities.

2.2. Simulation detail

MD simulations were performed on the systems of 8000 atoms for pure Pb, 8000 atoms for pure Bi, and 3584 Pb-4416 Bi atoms for LBE. Verlet algorithm with a time step of 0.5 fs was used to integrate the equation of motion. Simulations in isothermal-isobaric ensemble (NPT) and canonical ensemble (NVT) were performed using Nosè-Hoover algorithm with a time constant of 0.05ps and 0.5ps for thermostat and barostat, respectively. The global cut-off was set to 9.01 A and periodic boundary conditions were imposed. Our simulations were performed using the open-source package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [8]. All systems were equilibrated for 100,000 time steps. After equilibration, the results were extracted by performing time average of 500,000 time steps. The simulation temperatures were 673K, 723K, 773K, 823K, 873K, 923K, 1173K and 1500K. All the simulations were carried out in serial mode on a desktop workstation.

2.3. Data analysis

For all simulations, data analysis was generally performed by dividing the production run into m=1000 equally sized blocks of time. Average values for a given property A were calculated for each block of time using every time steps within that block. Average values were calculated by averaging the block averages. The uncertainty ΔA for the simulation was then taken to be $\sqrt{\sigma_A^2 / m}$, where σ_A^2 is the variance of the population of block averages.

3. Results and discussion

3.1. Density and thermal expansion coefficient

The densities of liquid Pb, Bi and LBE versus temperature were computed by using NPT ensembles. The results are plotted in Fig.1, where the solid lines denote the experimental correlations [2].
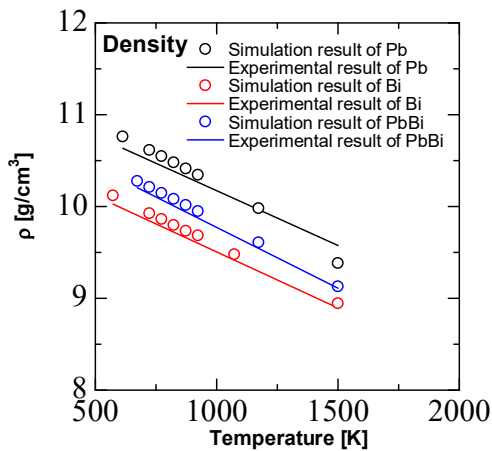

Fig.1. Simulation results of pure Pb, Bi and LBE densities versus temperature
compared to the experimental results.

The simulation results are in good agreements with the experimental results. The uncertainties of the densities are less than ±0.015 [g/cm^3]. The densities of the liquid Pb, Bi and LBE decrease with the temperature increase. The calculated linear densities of Pb, Bi and LBE versus temperature are:

$$\rho_{Pb} = 11367 - 1.1944T \quad [kg / m^3], \tag{4}$$

$$\rho_{Bi} = 10726 - 1.2208T \quad [kg / m^3], \tag{5}$$

$$\rho_{LBE} = 11096 - 1.3236T \quad [kg / m^3]. \tag{6}$$

It is known that the density of liquid metals changes with temperature due to thermal expansion related to anharmonicity of interaction forces. The density and coefficient of volumetric thermal expansion at constant pressure p are related as:

$$\beta_p(T) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p. \tag{7}$$

According to this definition, the coefficient of thermal expansion of Pb, Bi and LBE can be calculated from equations (4), (5) and (6). The resulting values are

$$\beta_{Pb}(T) = \frac{1}{8912.3 - T} \quad [K^{-1}], \tag{8}$$

$$\beta_{\mathrm{Bi}}(T) = \frac{1}{8336.2 - T} \qquad [\mathrm{K}^{-1}], \tag{9}$$

$$\beta_{LBE}(T) = \frac{1}{8583.8 - T} \qquad [\mathrm{K}^{-1}]. \tag{10}$$

The calculated Pb and Bi thermal expansion coefficients at 750K are 1.23×10^{-4} [K^{-1}] and 1.32×10^{-4} [K^{-1}], which are slightly larger than 1.14×10^{-4}[K^{-1}] and 1.24×10^{-4}[K^{-1}] experimental data. The thermal expansion of LBE at 800K is 1.28×10^{-4}[K^{-1}], which is roughly the same as the experimental result 1.32×10^{-4}[K^{-1}].

3.2. Pair distribution function

The pair distribution functions (PDF) of Pb in pure liquid Pb and Bi in pure liquid Bi at temperature of 823K were computed and compared to the experimental results [9], which were the same used by Belashchenko to derive the respective EAM parameters. The empty circles in the Fig.2 and Fig.3 represent the experimental data and the solid lines are the simulation results.
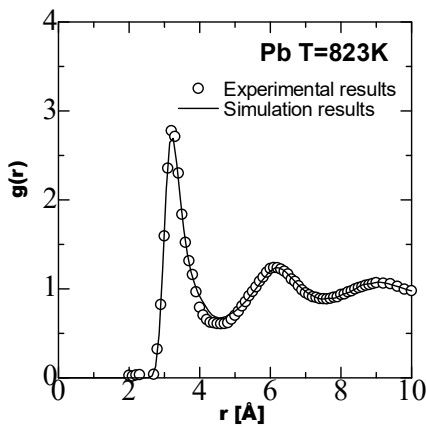

Fig.2. The simulation result of Pb PDF in pure liquid Pb at temperature of 823K compared to diffraction experiment data.
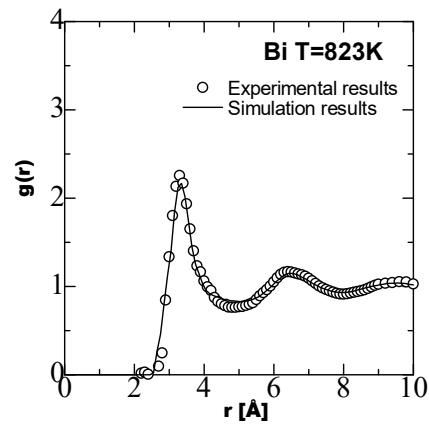
Fig.3. The simulation result of Bi PDF in pure liquid Bi at temperature of 823K compared to diffraction experiment data.

The simulation results are in quite good agreement with the experimental results. It is thus confirmed that Belashchenko's Pb and Bi models have been implemented correctly in our model.
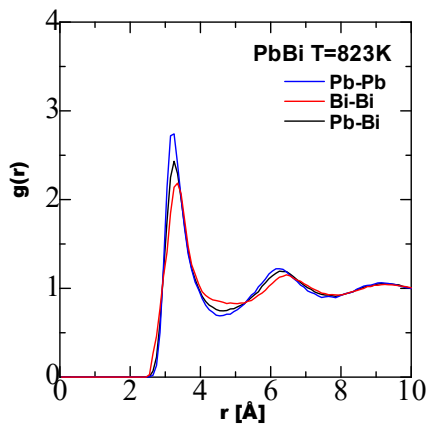

Fig.4. The PDF of Pb-Pb, Bi-Bi and Pb-Bi in liquid LBE at temperature of 823K.
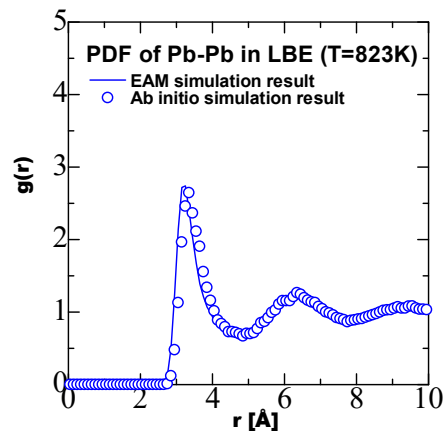
Fig.5. The simulation result of Pb PDF in liquid LBE compared to ab-initio simulation result at temperature of 823K.
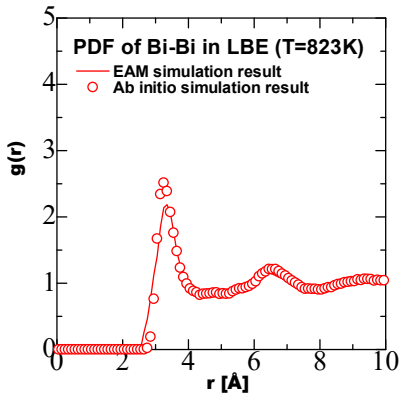
Fig.6. The simulation result of Bi PDF in liquid LBE compared to ab-initio simulation result at temperature of 823K
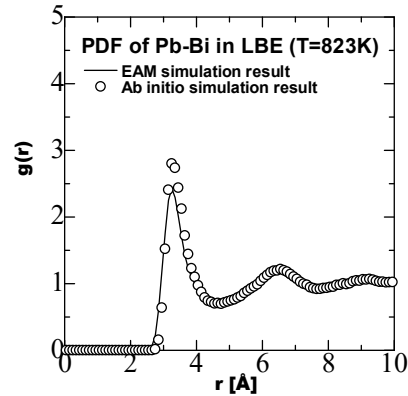

Fig.7. The simulation result of Pb-Bi PDF in liquid LBE compared to ab-initio simulation result at temperature of 823K.

The PDFs of Pb-Pb, Pb-Bi and Bi-Bi in liquid LBE are shown in Fig.4. Since there are no experimental databases on the PDF of Pb-Pb, Bi-Bi and Pb-Bi in liquid LBE, the results obtained by EAM method were compared to the PDFs computed through Ab-initio simulations. The Ab-initio MD simulations (AIMD) were performed in a PbBi 128 atoms cubic cell of eutectic composition. The PDFs were determined post processing 15 ps. AIMD simulations were performed in an NVT ensemble starting from a geometry determined with a LAMMPS NPT simulation performed at the same temperature using the cell volume determined by LAMMPS. AIMD simulations were performed using a time step of 3.0 fs and the Nosè thermostat. Simulations were performed using ultra soft pseudopotentials for Pb and Bi considering explicitly only the valence electrons. The energy was computed using the generalized gradient approximation with the PBE exchange-correlation functional [10]. A 2×2×2 K-point mesh constructed using the Monkhost-Pack scheme was used to sample the Brillouin zone. The energy cutoff was 105 eV and all simulations were performed uing VASP5.3.3 [11]. Figures 5-7 show the comparison results.

3.3. Viscosity

There are two methods to compute the shear viscosity, equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD). In this study, the NEMD was used to determine the viscosities of liquid Pb, Bi and LBE at different temperatures. However, rather than the normal NEMD method which sets the strain or shear field and measures the response of stress or momentum flux of the system, we used the reverse-NEMD (RNEMD) method [12]. RNEMD is a method that imposes the hard-to measure flux and computes the resulting easy-to measure shear field. Because energy and momentum are both conserved, RNEMD has no requirement of thermostatting.

The shear viscosity connects a shear field with a flux of transverse linear momentum. The shear rate is a gradient of one component of the fluid velocity, e.g. $\partial v_x / \partial z$. The momentum flux $j_z(p_x)$ is collinear and can also be regarded as an off-diagonal (x_z) component of the stress tensor. The proportionality coefficient is the shear viscosity η

$$j(\mathsf{p}_x) = -\eta \frac{\partial \mathsf{v}_x}{\partial \mathsf{z}} . \tag{11}$$

The uncertainties in the viscosity value for any given temperature are estimated using the rules of error propagation from the error in the velocity gradient $\frac{\partial v_x}{\partial z}$ and in momentum flux $j(p_x)$. The simulation results of liquid Pb, Bi and LBE viscosities were fitted to the Arrhenius-type equation:

$$\eta = \eta_0 \exp(\frac{E_a}{RT}) , \tag{12}$$

where η_0 is a pre-exponential constant which is associated with the nature of the liquid, R is the molar gas constant and E_a is the viscous-flow activation energy. The calculated viscosities of liquid Pb, Bi and LBE are:

$$\eta_{Pb} = 5.77 \times 10^{-4} \exp\left(\frac{5.55 \times 10^3}{RT}\right), \tag{13}$$

$$\eta_{Bi} = 4.26 \times 10^{-4} \exp\left(\frac{4.30 \times 10^3}{RT}\right), \tag{14}$$

$$\eta_{PbBi} = 4.84 \times 10^{-4} \exp\left(\frac{5.02 \times 10^3}{RT}\right), \tag{15}$$

where the temperature T is in kelvin. The viscous-flow activation energy of Pb is 5.55×10^3 J/mol, which is bigger than that of Bi and similar as that of PbBi. It is indicated that the viscosity of Pb is largely dependent on the temperature rather than that of Bi. Figures 8-10 show the simulation results of liquid Pb, Bi and LBE viscosities compared with the experimental results [2]. The plots in each figure denote the simulation results and the dashed line is the linear approximation. The solid line denotes the experimental results. The agreement between experiment and simulations is good, as the simulation results differ by less than 10% from experimental data.
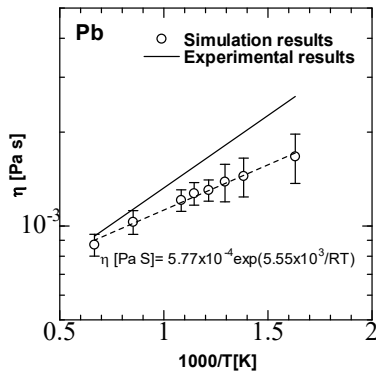

Fig.8. The simulation result of Pb viscosity compared to the experimental results.
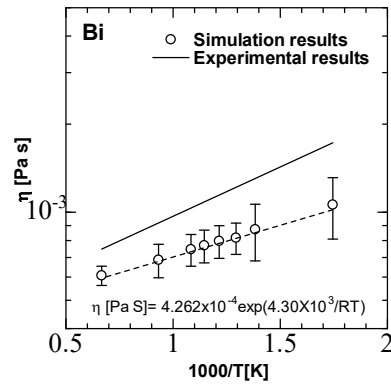

Fig.9. The simulation result of Bi viscosity compared to the experimental results.
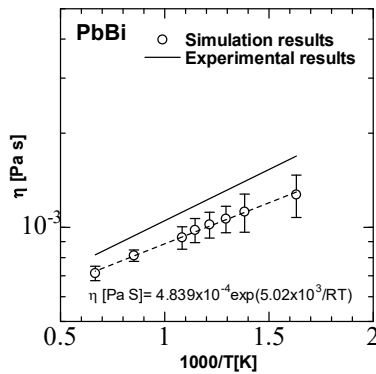

Fig.10. The simulation result of LBE viscosity compared to the experimental results.
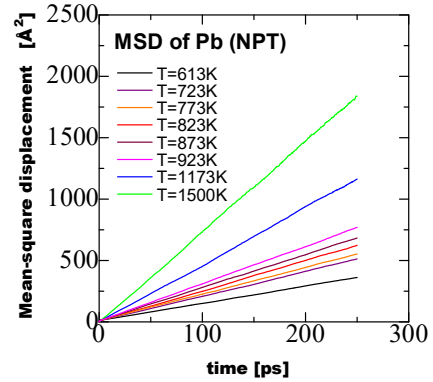

Fig.11. Mean-squared displacements of Pb in liquid lead versus different temperatures.

3.4. Self-diffusion

The diffusion coefficients of Pb atom in liquid lead $D_{Pb/lead}$, Bi atom in liquid bismuth $D_{Bi/bismuth}$ and Pb or Bi atom in liquid LBE $D_{Pb/LBE}$ / $D_{Bi/LBE}$, so-called self-diffusion coefficient, can be obtained by calculating the time-dependent mean-square displacement (MSD) defined as:

$$\langle r_\alpha^2(t)\rangle = \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}\left(r_{i,\alpha}(t) - r_{i,\alpha}(0)\right)^2, \tag{16}$$

where N_α is the number of particle α, and $r_{i,a}(t) - r_{i,a}(0)$ is the vector distance travelled by a given particle over the time interval. The MSD is linear in t if the time is sufficiently long, and the slope is proportional to the diffusion coefficient D according to the so-called Einstein relationship:

$$\langle \Delta r(t)^2 \rangle \to 6Dt + C, \tag{17}$$

where C is a constant. The mean-square displacements (MSD) of Pb atom in liquid lead, of Bi atom in liquid Bi and of Pb or Bi atom in liquid LBE at each simulation temperature were calculated during the MD simulations. Figure 11 shows an example of MSD of Pb atom in pure liquid Pb. According to Eq. (17) and the Arrhenius-type equation for diffusion

$$D = D_0 \exp(\frac{E_a}{RT}), \tag{18}$$

where D_0 is a pre-exponential constant which is associated with the nature of the liquid, R is the molar gas constant and E_a is the diffusion activation energy, the self-diffusion coefficients $D_{Pb/lead}$, $D_{Bi/bismuth}$, $D_{Pb/LBE}$, $D_{Bi/LBE}$ were calculated as:

$$\cdot\, D_{Pb/lead} = 3 \times 10^{-4} \exp\left(\frac{-1.35 \times 10^4}{RT}\right), \tag{19}$$

$$D_{Bi/bismuth} = 4 \times 10^{-4} \exp\left(\frac{-1.16 \times 10^4}{RT}\right), \tag{20}$$

$$D_{Pb/LBE} = 4.0 \times 10^{-4} \exp\left(\frac{-1.41 \times 10^4}{RT}\right), \tag{21}$$

$$D_{Bi/LBE} = 4.0 \times 10^{-4} \exp\left(\frac{-1.30 \times 10^4}{RT}\right), \tag{22}$$

where the temperature T is in kelvin. The activation energy of Pb atom diffusing in pure liquid lead is smaller than that in LBE, and Bi shows the same tendency. It can be observed that the diffusion of Pb and Bi atom in LBE exhibits a larger dependence on temperature. The Arrhenius plots of self-diffusion coefficients are shown in figures 12-14. The results are compared to the results obtained from Stokes-Einstein relation with slip boundary

$$D = \frac{k_B T}{2\pi d \eta} \text{ (slip)}, \tag{23}$$

where k_B is Boltzmann constant, T is the temperature in kelvin, d is the atom diameter, η is the viscosity.
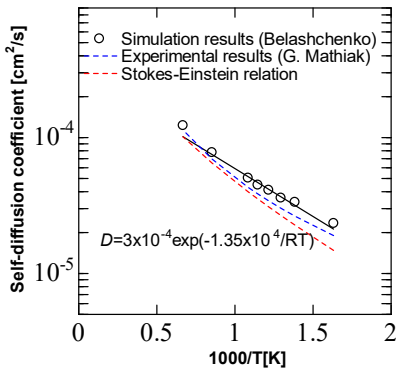

Fig.12. The simulation result of Pb viscosity compared to the experimental results.
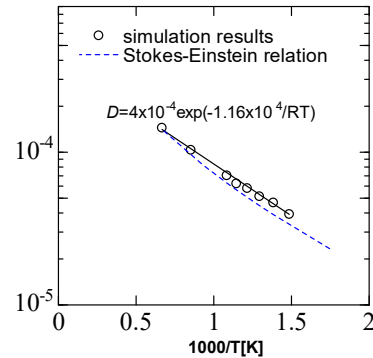

Fig.13. The simulation result of Bi viscosity compared to the experimental results.

The calculated self-diffusion coefficient of Pb in liquid lead, of Bi in liquid bismuth and of Pb and Bi in liquid LBE are in good agreement with the results determined using the Stokes-Einstein relation. This indicates the validity of using Stokes-Einstein relation in order to estimate the self-diffusion for these metals. Besides the simulation results of Pb is comparable with the experimental results derived by G. Mathiak [13]. However, there are no experimental results on self-diffusion coefficient of Bi in liquid bismuth and self-diffusion coefficient of Pb and Bi in liquid LBE, so that these predictions cannot be experimentally validated.
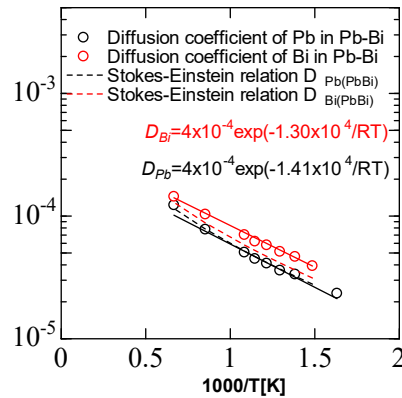

Fig.14. The simulation result of Pb viscosity compared to the experimental results.

4. Conclusion

The embedded atom method was used to simulate the liquid Pb, Bi and LBE. The computational predications of their physical properties are compared to the available experimental results. The density and thermal expansion coefficients are in good agreement with the experiments. The calculated viscosities of liquid Pb, Bi and LBE are less than 10% smaller compared to the experimental data. The self-diffusion coefficients of Pb atom in pure liquid Pb, Bi atom in pure liquid Bi and Pb or Bi atom in LBE were obtained by calculating the mean-squared displacement versus different temperatures. The self-diffusion coefficients were fitted to an Arrhenius-type expression. It was found that the activation of Pb diffusing in pure liquid lead is smaller than that in LBE, and that of Bi exhibits the same behavior. This indicates that the diffusion of Pb and Bi in LBE is more dependent on the temperature.

Overall, the good agreement between the MD simulations and the available experimental data encourages the use of this and other computational methods to explore the physical properties of other liquid metal alloys. Especially in the case of three or more components, where a systematic investigation of the effect of composition would be very time consuming, computer simulation can offer a valid aid to speed up the research effort in this field.

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