

Construction and Application of a Machine Learning Potential for Analyzing the Chemical State and Behavior of Oxygen Impurity in Liquid Pb, Li, and Pb-Li Eutectic

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1. Introduction

Liquid metals have many engineering applications, including their use as coolants and functional materials in nuclear reactors. For example, sodium, lead, and the lead-bismuth eutectic are being considered as possible candidate materials for coolants of fast reactors, and lithium and the lead-lithium eutectic as tritium breeders for nuclear fusion reactors. However, many liquid metals exhibit either high corrosiveness to steels or high reactivity with air, which poses a challenge to reactor safety and requires significant engineering effort to implement. If a new liquid metal alloy that shows sufficiently low corrosiveness of steel materials and reactivity with air can be discovered, it could make a significant contribution to the development of advanced nuclear reactors.

In order to explore and newly find such an ideal liquid alloy, one has to examine various combinations and compositions of liquid metals. Without a doubt, there will be a considerable number of tests to be done, making an experimental approach an impractical choice for the search. Rather, adopting a computational method could be more efficient.

In recent years, the machine-learning-aided discovery and development of new materials, often referred to as *materials informatics*, has been attracting much attention in the field of materials engineering. Throughout many improvements, it now features high enough accuracy of its computational result with reasonably low calculation cost.

Therefore, we are developing a materials informatics approach to the search for new liquid metal alloys. As a first step to realize accurate and efficient computational simulations, preparing an automated method to construct accurate machine learning potential models is a critical task. In this research, we propose a scheme to train a machine learning potential that can model the behavior of an impurity in a liquid bi-alloy with reasonable accuracy at a manageable computational cost. To demonstrate the performance of this scheme, we make a machine learning potential that can model the behavior of oxygen impurity in any composition of the Pb-Li liquid alloy, and validate the performance of the machine learning potential on liquid material properties and the behavior of oxygen in pure liquid Pb, pure liquid Li, and the Pb-Li eutectic as test cases. The Pb-Li system was selected as it contains three liquid metals relevant to advanced reactors: Pb, Li, and the Pb-Li eutectic.

2. Methods

2.1 Training scheme of Machine-learned potential model

In this research, we use Machine Learning Interatomic Potential (MLIP) package [1] for training machine learning potential in the form of the moment tensor potential (MTP) [1].

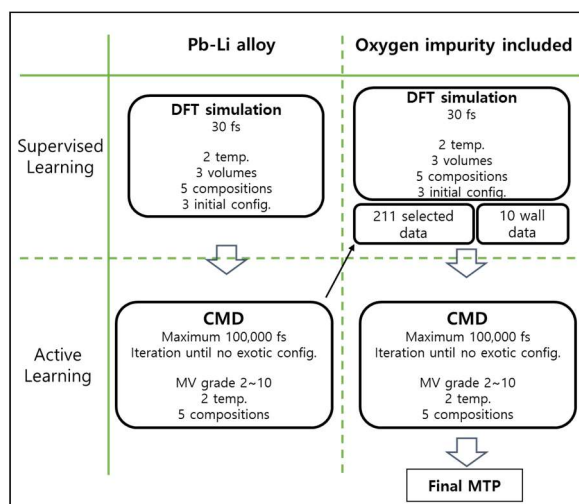


Fig. 1. Training scheme of MTP for all-range of Pb-Li liquid alloy including one O impurity in its system

We suggest a training scheme comprised of two parts: a *supervised learning* part and an *active learning* part. In supervised learning, our main goal is to make an initial MTP, which will be used for the following stages of training. This step starts with performing density functional theory (DFT) calculations on systems of Pb-Li liquid alloy to gather training dataset which is comprised of various atomic configurations, and their corresponding physical values, namely, energy, forces, and stresses. To gather a sufficiently diverse training dataset in terms of temperature and composition, data for each system are collected from 90 different simulations. These simulations vary in their settings, incorporating five different compositions (lithium fractions of 2.9%, 20.6%, 50%, 79.4%, and 97.1%), two temperatures (700K and 1200K), three different volumes (a system with a 3% expanded lattice constant, a system at zero pressure, and a system with a 3% contracted lattice constant), and three different initial configurations. Each

simulation is performed for 30 steps with a timestep of 1 fs. Then, 5 steps of configurations are uniformly sampled out of each of the simulations. As a result, a total of 450 configuration data ($5 \times 2 \times 3 \times 3 \times 5$) are obtained. Thereafter, an MTP is fitted with the obtained dataset, constructing the initial MTP which will be used in active learning.

On next active learning stage, one aims to complete the training of MTP throughout simulations of classical molecular dynamics (CMD) by actively searching for atomic configurations that are dissimilar to the configurations included in the original dataset. The similarity/dissimilarity is determined by a single value called *MV grade* defined by D-optimality criterion [2]. If a MV grade of a newly found configuration is within a certain appropriate range, the configuration is considered to be sufficiently dissimilar and added to the existing training set. Subsequently, the MTP is refitted on the updated training for improvement.

This process of active learning can be iterated by several times, until the MTP cannot find more dissimilar configurations with its current version, within long enough CMD simulation. To gather data as diverse as possible, CMD of each iteration starts with different initial configuration. When the iteration ends, we consider the training process for the MTP to be finished.

In this research, initial MTP trained at supervised learning is used in first iteration of active learning. Dissimilar configurations were searched for 100 ps of CMD at two temperatures of 700 K and 1200 K each with a timestep of 1 fs. When MV grades of a configurations are within a range of 2~10, the configurations are accepted and will be added to the training data. As a result, MTP for Pb-Li alloy was finished after one iteration of active learning.

In order to make an MTP that can cover Oxygen in Pb-Li alloy, we performed another set of supervised learning and active learning for a system of an impurity inside of Pb-Li alloy. In this case, we have constructed the training set of the initial MTP from 681 data with 450 data from supervised learning on oxygen impurity in Pb-Li alloy, 221 data from earlier dataset for Pb-Li alloy which are selected to represent the whole dataset, 10 data that contains wall structure to ensure MTP to avoid making void structure during CMD simulation. Then, we performed active learning with the same settings, and obtained trained MTP for a system of oxygen impurity inside Pb-Li alloy after two iterations of it. We confirmed that our trained MTP was fitted properly to its training set, having an error of 1.8 meV per atom from the DFT training set, which can be considered as a reasonable value compared to previous studies.

2.2 DFT calculation settings

DFT calculations including FPMD simulations were performed by using the Vienna Ab initio Simulation Package (VASP). The PBE functional was used for the exchange-correlation functional of Kohn-Sham equation.

The energy cutoff for the plane-wave basis was set to 400 eV. For reciprocal-space sampling of the band energy, a $2 \times 2 \times 2$ Monkhorst-Pack grid was used. The volume and shape of the system were fixed during an FPMD calculation. For determining the partial occupancy of each orbital, the first-order Methfessel-Paxton smearing method was used with a smearing width of 0.2 eV. Non-spin polarized calculations were performed since oxygen shows no spin polarization in Pb-Li alloy. Each electronic self-consistent calculation loop was set to repeat 100 steps but to break when the energy change of the system did not get larger than 10^{-6} eV for two continuous steps.

2.3 CMD calculation settings

CMD calculations were performed for active learning and production runs of material properties with the trained MTP. The Large Scale Atomic/Molecular Massively Parallel simulator (LAMMPS) built in the MLIP library was used.

3. Results and discussion

3.1 MTP validation

To confirm that the trained MTP accurately simulates the structure of Pb-Li liquid alloy, a neutron scattering structure factor was calculated using Dynasor package [3] from CMD simulation with the trained MTP and compared with a neutron scattering experiment data obtained by Ruppertsberg [4]. Since the referred neutron scattering experiment was conducted with Li^7 isotope and natural Pb, neutron scattering lengths for each element was set to $b_{Pb} = 9.40$ fm and $b_{Li} = -2.22$ fm in the calculation.

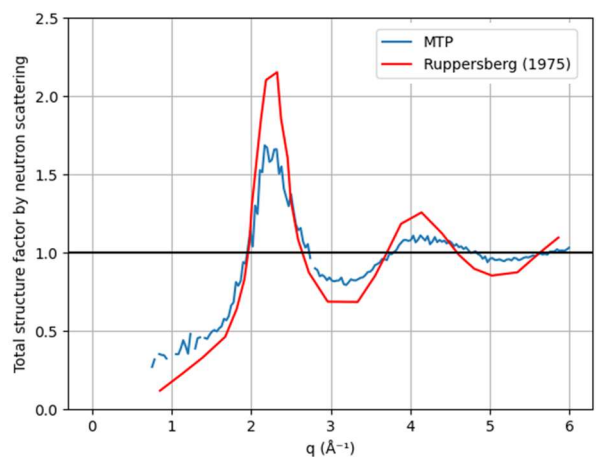


Fig. 2. Structure factor calculated by MTP at 1100 K with the experimental neutron scattering result of Ruppertsberg [4].

As shown in Fig. 2, peaks of the neutron structure factor of Pb-Li eutectic calculated by MTP match with peaks from the experimental result in terms of their

locations, placed at 2.3 \AA^{-1} and 4.2 \AA^{-1} . However, the calculation underestimates the heights of the peaks.

Densities of the system of Pure liquid Pb, pure liquid Li and Pb-Li eutectic (Li 17%) were also calculated by MTP and compared with experimentally determined values. Table 1 shows the calculation results. While densities calculated by MTP only showed 3% of deviation from an experimental data [5], MTP underestimated density of pure Pb nearly by 20% from an experimental value [6]. Among several factors that have caused this discrepancy, inaccurate DFT calculation settings for MTP training could be the main reason. For example, exchange-correlation functional that has been used on DFT calculations might not be suitable enough to determine density of Pb. In the same context, even if calculated density of Pb-Li eutectic shows only 2% deviation from an experimental data [7], this does not mean that MTP can accurately simulate the structure, because the Pb atoms in eutectic are also likely to be simulated with limited accuracy. Improving the accuracy of the DFT exchange-correlation functional is a possible future topic.

Table 1. Density of the system of pure liquid Pb, pure liquid Li and Pb-Li eutectic at 1100 K calculated by MTP in comparison with experimental results [5,6,7]

Unit: (g/cm^3)	Density by MTP	Density by experiments
Pure Pb	8.4155	10.0201
Pure Li	0.4625	0.4517
Pb-Li eutectic	9.2323	*9.3298

*Data at 1000K

3.2 Solution enthalpy of O_2

The solution enthalpy of O_2 (H_{O_2}) for each system was calculated from CMD simulations on the three systems with and without adding one oxygen impurity in each. CMD simulation settings were the same as precious simulations for density determination. The enthalpy of O_2 gas was first determined by DFT calculation at 1000 K [8], and its temperature dependence from 1000 K to 1100 K was corrected referring on NIST data [9] on thermodynamical properties of O_2 molecule.

Table 2. O_2 solution enthalpy for the system of pure liquid Pb, pure liquid Li and Pb-Li eutectic calculated by MTP and their standard error of the mean (SEM).

System	O_2 solution H (eV/atom)	SEM (eV/atom)
Pure Pb	-1.5194	0.09739
Pure Li	-5.1487	0.06616
Pb-Li eutectic	-3.6300	0.08152

In order to confirm validity of the result, we have compared the O_2 solution enthalpy with experimental results by using an enthalpy diagram illustrated in Figure 3 [8]. In Fig. 3, the blue line corresponds to the enthalpy change with available experiment data. The enthalpy change due to the dissolution of Li_2O into liquid Li can be calculated by Van 't Hoff equation on solubility experiment conducted by R.M. Yonco et al. [10], and the other data were taken from NIST database.

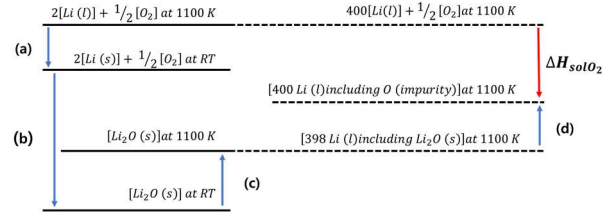


Fig. 3 Enthalpy diagram for determining solution enthalpy of O_2 with existing reference data. Directions of the arrows indicate directions for change of states.

Table 3. Enthalpy changes and their corresponding enthalpy differences determined by experiments [9,10,11] compared with O_2 solution enthalpy determined by MTP.

Enthalpy change	Li_2O (eV/atom)	PbO (eV/atom)	Reference
(a)	-0.6285	-0.3846	[9]
(b)	-6.2267	-2.2819	[9]
(c)	0.6326	0.4664	[9]
(d)	0.0083	0.0083	[10],[11]
ΔH_{solO_2} by experiments	-6.2143	-2.4226	-
ΔH_{solO_2} by MTP	-5.1487	-1.5194	-

O_2 solution enthalpy calculated by MTP predicted higher solution enthalpy values in both pure Pb and pure Li. One probable reason for this error could be, again, the inaccuracy of PBE functional for the exchange-correlation energy. The previous study indicates that a DFT using PBE functional overestimates a binding energy of O_2 by 0.9 eV [8], which partly explains the errors observed in Table 3.

Even if MTP did not perfectly work, it is evident that the solution enthalpy of oxygen in pure Pb was much higher than that in pure Li, which can be partly explained by the large electronegativity difference between O and Li, compared to that between Pb and O. However, it is notable that even when the number ratio of Pb is much higher than that of Li (83% vs 17%), the solution enthalpy of oxygen in the Pb-Li eutectic is close to that in pure Li rather than that in pure Pb. This might indicate that even in a system with Pb rich environment, oxygen

still chooses to gather up with Li atoms rather than Pb atoms due to strong interaction between Li and O atoms.

3.3 Structure of oxygen in pure Pb, pure Li and eutectic

We have calculated partial pair distribution functions for a system of pure liquid Pb, pure liquid Li and Pb-Li eutectic. CMD simulations were performed with the same settings as previous ones. The partial pair distribution functions of O-Pb and O-Li pairs in pure Pb, pure Li and eutectic systems are presented in Fig. 4. The O-Pb pair distribution function in pure Pb holds the first peak at 2.3 Å, while the O-Li pair distribution functions in Pb-Li eutectic and pure Li make their peak around 1.9 Å, clearly closer than the O-Pb pair. In eutectic system, O-Li pairs dominate over O-Pb pairs in the first neighborhoods of O.

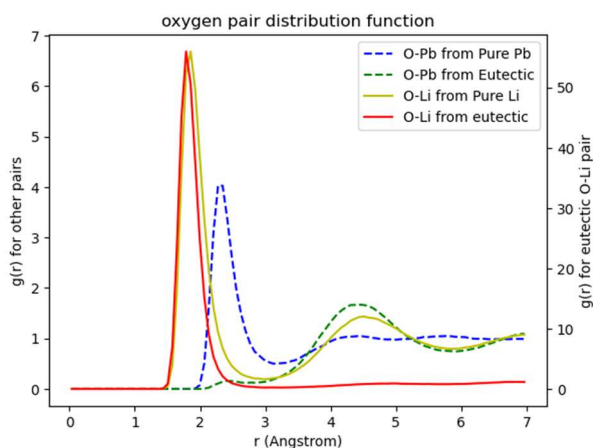


Fig. 4. Oxygen pair distribution function in a system of pure liquid Pb, pure liquid Li and Pb-Li eutectic at 1100 K

In general, Li and O are expected to make a strong interaction due to the large difference between their electronegativity. Beyond that, they might form similar structures in pure liquid Li or in Pb-Li eutectic, since the location of the first peak of O-Li does not change much even when composition of the system has dropped from 100% of Li to 13 % of Li.

To further verify this, we have calculated a coordination number (CN) for O impurity in each system by integrating the pair distribution functions from 0 to the valley after their first peak, counting first neighboring atoms around O atom. As shown in Table 4, CN for pure liquid Li and Pb-Li eutectic are similar to each other considering that they have a large difference in Li percentage. This implies a strong attractive tendency between O and Li which can even overcome Pb rich environment of eutectic.

However, the absolute difference in solution enthalpy of O_2 between pure Li and Pb-Li eutectic is not negligible. This could be explained by increased CN of Pb-Li eutectics even by comparably small amount (1.41).

Table 4. Coordination number (CN) of O impurity in a system of pure liquid Pb, pure liquid Li and Pb-Li eutectic at 1100 K.

System	CN for O impurity
Pure Pb	3.69
Pure Li	4.38 (Li atoms)
Pb-Li eutectic	5.79

It is also noticeable that CN for pure liquid Pb is somehow comparable to that for Li, yet O_2 solution enthalpy in pure Pb is much higher than that in pure Li or Pb-Li eutectic. To explain this, we have performed Bader charge analysis [12] in order to understand distribution of atomic charges in a Pb-Li eutectic system. The code developed by Henkelman research group at University of Texas at Austin was used for this analysis.

The results on Fig. 5 shows that Pb atoms tend to be negatively charged and Li atoms are positively charged in eutectic system. This trend on charge distribution is probably due to electronegativity gap between Pb and Li. Also, Li atoms exhibit sharper charge distribution in a range of 0.8 ~ 0.9 e . This can be explained by the number of valence electrons for each solvent elements, with Li atoms having no affordable number of electrons to lose more than one.

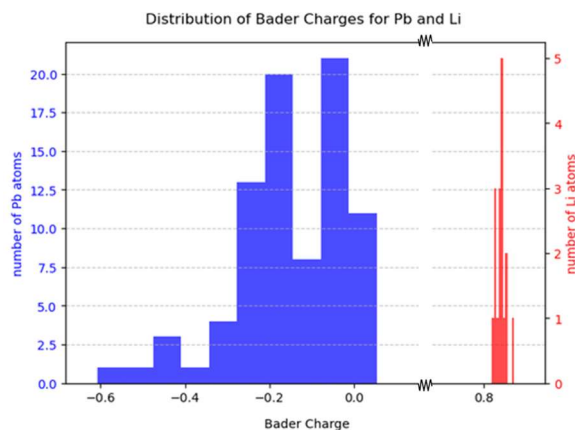


Fig. 5. Distribution of Bader charges of Pb and Li atoms in a system of Pb-Li eutectic including one O impurity. The total number of atoms is 101.

Shifting our focus on oxygen, even if there is only one O atom in the system, it shows a lowest Bader charge of -1.67 e . This should explain why Li and O atoms showed strong interaction and were able to maintain their structure even in eutectic system. In other words, the strong Coulomb interaction caused by large charge difference helped them to form such stable structures. Furthermore, this also explains why comparable CN of Pb atoms did not make comparable solution enthalpy of O_2 with pure Li or eutectic systems. As Pb atoms also have negative charge due to charge transfer between Li,

it is likely that they have failed to exhibit as strong Coulomb interaction with O as Li atoms did. In conclusion, it is likely that a strong Coulomb interaction caused by charge transfer between them forms Li-O structures, and the existence of such structures dominates solution enthalpy of O₂.

5. Conclusions

In this research, we proposed a scheme to train a machine learning MTP to simulate O impurity in Pb-Li liquid alloy by utilizing supervised learning and active learning. Our trained MTP showed non-negligible amount of deviation from experimental results on neutron scattering structure factor, densities, and O₂ solution enthalpy on systems of Pb-Li eutectic, pure liquid Li, and pure liquid Pb. We considered that these errors came from PBE functional used for the exchange-correlation energy in the present study.

Despite these errors, the MTP reproduced various liquid properties and O₂ solution enthalpy with fair accuracy. Therefore, we were able to discuss behaviors of O atom with MTP by analyzing the partial pair distribution function, coordination number and Bader charge analysis. We identified similar O-Li structures in pure Li and Pb-Li eutectic, caused by charge transfer between atoms. We concluded that due to the strong Coulomb interaction between O and Li atoms, which is caused by the large difference in their electronegativity, O-Li pairs are dominant over O-Pb pairs even in eutectic system and exert a strong influence on the solution enthalpy of O₂. Our future work will focus on expanding our analysis to the full range of Pb-Li alloy compositions with the trained MTP.

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