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Validation of potential models for Li_2O in classical molecular dynamics simulation

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Abstract

Four Buckingham-type pairwise potential models for Li_2O were assessed by molecular static and dynamics simulations. In the static simulation, all models afforded acceptable agreement with experimental values and ab initio calculation results for the crystalline properties. Moreover, the superionic phase transition was realized in the dynamics simulation. However, the Li diffusivity and the lattice expansion were not adequately reproduced at the same time by any model. When using these models in future radiation simulation, these features should be taken into account, in order to reduce the model dependency of the results.

1. Introduction

Information on the physical and thermochemical properties of blanket breeding materials is essential for establishing a secure and efficient fuel cycle in fusion reactors. In real reactor conditions, radiation defects affect the material properties of the breeder strongly, and this must be taken into account. For this requirement, a large number of experimental studies have been devoted to radiation defects [1]. However, in order to more precisely predict the behavior of the breeder material under severe radiation conditions, more detailed atomic-scale information is needed.

Molecular simulation is a promising method to use for that purpose. Among the several simulation techniques available today, molecular dynamics (MD) has the advantage of being able to handle a huge number of atoms and a reasonably long time scale, which makes radiation simulation feasible [2]. In the present work, our aim is to assess and construct acceptable potential models for Li_2O, a candidate tritium breeder, prior to radiation simulation, because a potential model is a key factor in determining the precision of MD simulation results.

From among various types of potential models, we chose the Buckingham-type pairwise potential model because of its simplicity and its reliability when applied to ionic crystals. Four sets of potential parameters were assessed: two were previously reported [3,4] and two were determined in the present work. The new models were constructed with focusing especially on melting point and

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thermal expansion behavior, which were not sufficiently predicted in the two reported models. The model assessment was performed according to the consistency of the simulated crystalline properties with the experimental values and the ab initio calculation results.

2. Calculation details

The Buckingham-type pairwise potential between two ions is expressed as follows:

$$U(r) = \frac{q_1 q_2}{r} + A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}. \quad (1)$$

Here, r is the distance between two ions, q_1 and q_2 are their effective charges, and A, ρ and C are potential parameters. The Coulombic term was evaluated by the Ewald summation technique, and the remaining terms were directly calculated with a cutoff distance of 10 Å.

The four sets of potential parameters listed in Table 1 were tested. Two of them (FIT-HF and FIT-LDA) had been reported [3,4], and the others (FIT-GGA and FIT-EMP) were created in the present work. The FIT-HF, FIT-LDA and FIT-GGA models were fitted to the ab initio calculation results by means of the Hartree–Fock (HF) calculation [3], DFT calculation with local density approximation (LDA) [4], and DFT calculation with generalized gradient approximation (GGA), respectively. On the other hand, FIT-EMP was constructed by empirical fitting to the experimental crystalline properties [5–11].

In the fitting of the two new models, the genetic algorithm was used. For FIT-GGA model, seven kinds of distortion were introduced into a Li_8O_4 conventional cell under periodic boundary conditions (PBC), and the energy variations were evaluated by plane-wave pseudopotential DFT with the GGA of the PBE functional, using the CASTEP code. The energy cutoff and Monkhorst–Pack grid for k-point sampling were set to 380 eV and $6 \times 6 \times 6$, respectively.

Four of the distortions are movement of the O sub-lattice along the (a) [100], (b) [110] and (c) [111] directions up to 0.4 Å in 0.05-Å steps, and (d) the movement of two O ions along the [100] direction and the simultaneous movement of the other two O ions in the opposite direction up to 0.4 Å in 0.05-Å steps, as in Ref. [3]. The other three distortions are (e) the expansion and contraction of the lattice constant from −1% to 3% in 0.5% steps, (f) the movement of one Li ion toward the first neighboring Li ion (along the [100] direction) up to 0.4 Å in 0.05-Å steps, and (g) the movement of one O ion toward the first neighboring O ion (along the [111] direction) up to 0.4 Å in 0.05-Å steps.

In the fitting of the FIT-EMP model, the lattice constant, the elastic constants, the bulk modulus, the Young's modulus, the Poisson's ratio and the dielectric constants were calculated under static conditions using the GULP code. Those simulated values were then assessed according to their consistency with experimental values [5–11]. Several sets of parameters that had agreed well with the experimental values were subsequently re-screened according to the melting point and the thermal expansion behavior estimated in the MD calculation using the DL-POLY code.

In the MD calculation, a $5 \times 5 \times 5$ supercell containing 500 Li_2O under PBC was used as the system. The Verlet leapfrog scheme was applied in order to update the velocity and position of each atom under the Berendsen NPT ensemble. The time step was set to 1 fs. Each calculation was conducted for 0.5–5 ns until the intended property was obtained within a negligible error margin.

3. Results and discussion

3.1. Energy variations induced by distortions

The energy variations induced by the seven distortions are given in Fig. 1. The order of strength of the inter-ionic interaction tends to be FIT-HF > FIT-LDA > FIT-GGA > (DFT) > FIT-EMP.

Although FIT-GGA was built to fit the DFT calculation results, the potential energy curves were not sufficiently consistent in some parts, especially on the (g) distortion corresponding to the O–O interaction, due to the low pliability of the Buckingham model formula. It would be interesting to investigate the influence of the applied ab initio calculation technique on the creation of the model as mentioned in Ref. [4]. However, we refrained from discussing it in the present work, on account of the incomplete depiction afforded by the Buckingham potential model.

3.2. Model assessment

The simulated crystalline properties are summarized in Table 1. As reference data, the experimental values [5–11] and the DFT calculation results in

Table 1
Summary of the crystalline properties simulated in the four potential models

			Experiment	DFT	AIM	FIT-HF	FIT-LDA	FIT-GGA	FTT-EMP
Buckingham potential parameters	Li charge (e)		–	–	–	0.944	1	0.9064	0.906
	Li–Li	A (eV)	–	–	–	0	3644.29	0	0
		ρ (A^{-1})	–	–	–	1	0.181761	1	1
		C (eV A^6)	–	–	–	0	12.141774	0	0
	Li–O	A (eV)	–	–	–	653.84	436.7792	633.8	465.54
		ρ (A^{-1})	–	–	–	0.285723	0.31412	0.291238	0.2939
		C (eV A^6)	–	–	–	0	0	7.482	0
	O–O	A (eV)	–	–	–	0	0	1331.4	0
		ρ (A^{-1})	–	–	–	1	1	0.140158	1
		C (eV A^6)	–	–	–	76.651	69.1552	67.608	0
Lattice energy (eV)			30.07[a]	–	–	28.0	31.3	25.9	25.6
Meltine point (K)			1705[b]	–	1950[i]	2250	2350	2050	1750
Supcrionic critical temperature (K)			1200[c], 1350[d]	–	1450[i]	1450	1500	1350	1350
Lattice constant (0 K) (A)			4.573[d]	4.563	4.607[i]	4.581	4.530	4.566	4.573
Elastic constants (GPa)		C_{11}	217[d]	211.6	202[i]	228.9	235.1	208.2	216.8
		C_{12}	24[d]	16.1	19[i]	67.0	69.9	59.0	52.9
		C_{44}	68[i]	60.9	59[i]	64.5	68.6	57.3	52.9
Bulk modulus (GPa)			88[d]	81.3	80[i]	120.9	124.9	108.7	107.5
Young's modulus (GPa)			185[d]	209.3	–	198.6	203.1	182.2	196.1
Poisson's ratio			0.16–0.19[d]	–	–	0.226	0.229	0.221	0.196
Dielectric constants			8[e]	–	–	5.60	6.79	5.99	7.56
E_d of Li vacancy (eV)			0.38[f], 0.42[g]	0.28–0.33[h], 0.24	–	0.24	0.23	0.21	0.14
E_f of Li Frenkel defect (eV)			2.1[c]	2.2	–	2.25	2.33	2.02	1.93

[a] Ref. [5].
[b] Ref. [6].
[c] Ref. [7].
[d] Ref. [8].
[e] Ref. [9].
[f] Ref. [10].
[g] Ref. [11].
[h] Ref. [12].
[i] Ref. [13].

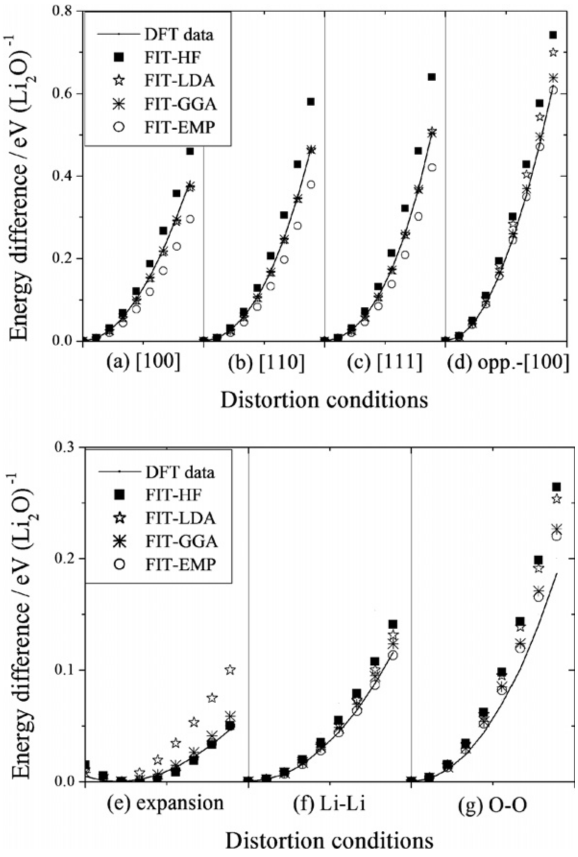

Fig. 1. Comparison between the energy variations induced by the seven distortions.

Ref. [12] and the present study are listed, together with the reported results given by the AIM model [13]. The AIM model is one of the most reliable potential models. In this model, 17 additional degrees of freedom are included for describing the state of the electron charge density of the ions [13], in a trade-off with the computational cost.

3.2.1. Properties in the statics

As seen in Table 1, the calculated mechanical properties are basically comparable to the experimental values. The discrepancy of the C_{44} value is a limitation of the pairwise potential models, due to the Cauchy relation [4]. The relatively poor agreement for the dielectric constants is ascribable to the lack of polarizability in the Buckingham potential model. The underestimation of the cohesive energy is an acceptable feature in partial charge models, such as FIT-HF, FIT-GGA and FIT-EMP.

The calculated formation energies of the Li Frenkel defect were comparable to the experimental values and the DFT calculation result, while the diffusion barrier of the Li vacancy was underestimated in the four models. In the present work, the diffusion barrier evaluated by DFT calculation was 0.24 eV in the same unit cell ($Li_{64}O_{32}$) with Ref. [12]. Although the DFT calculation results in different techniques range from 0.24 to 0.33 eV, the values obtained in the four models could be significantly small. One of the reasons of this underestimation is a unit cell size. When we utilized $2 \times 2 \times 2$ supercell ($Li_{64}O_{32}$) instead of $5 \times 5 \times 5$ ($Li_{1000}O_{500}$), the value increased to 0.28 eV (FIT-HF), 0.27 eV (FIT-LDA), 0.24 eV (FIT-GGA) and 0.17 eV (FIT-EMP), respectively. In this case, the estimated diffusion barriers are comparable to the DFT calculation results, except for the FIT-EMP model.

In summary, it can be said that the properties under the static simulation are fairly well predicted in all models, other than the underestimation (about 40%) of the diffusion barrier of the Li vacancy in FIT-EMP.

3.2.2. Properties in the dynamics

The thermal expansion behavior is shown in Fig. 2 as a function of the simulation temperatures. The degree of expansion was underestimated in FIT-HF, FIT-LDA and FIT-GGA, while the expansion in FIT-EMP was comparable to the experimental results [8].

The melting point was determined from Fig. 2 as the onset of the liquid state during a 50 K stepwise increase in the simulation temperature. The magnitude of overestimation of the melting point could be significant in FIT-HF and FIT-LDA, although

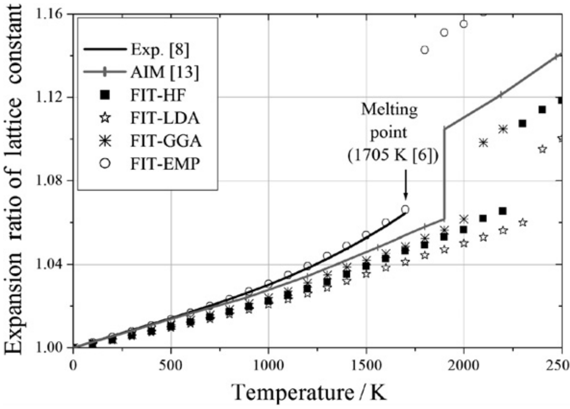

Fig. 2. Thermal expansion behavior.

the overestimation is normal due to the exclusion of the surface and defects in the simulation.

The superionics of Li ions was observed in all models, and the critical temperature of the superionic phase transition was determined from the λ peak position of the heat capacity (C_p), as in Ref. [13]. The superionic critical temperatures were overestimated in FIT-HF and FIT-LDA, as the same with the melting point. In contrast, FIT-GGA and FIT-EMP provided melting points and superionic critical temperatures comparable to the experimental results [6–8]. These results can be associated with the energy variations induced by the distortions, to which FIT-HF and FIT-LDA possess higher resistance than FIT-GGA and FIT-EMP, as shown in Fig. 1.

On the other hand, Fig. 3 indicates that the Li diffusion coefficients were overestimated in FIT-GGA and FIT-EMP, while they were comparable to the experimental results [14] in FIT-HF and FIT-LDA. The discrepancy with the experimental value for temperatures below 1000 K in FIT-HF and FIT-LDA is ascribable to the extrinsic region [14].

Since the superionic behavior is represented by the melting of the Li sub-lattice, the melting point would be represented as the melting of the O sub-lattice. By the same token, the thermal expansion behavior could be mainly determined by the O ion behavior, especially over the superionic critical temperature. These considerations suggest that FIT-HF and FIT-LDA provide a relatively good description of the Li ion behavior in the dynamics, while FIT-GGA and FIT-EMP describe the O ion behavior well. When using these four potential models in future work, these features should be taken into account, in order to reduce the model dependency of the results. We recommend to use one of the FIT-HF and FIT-LDA models and one of the FIT-GGA and FIT-EMP models for comparison.

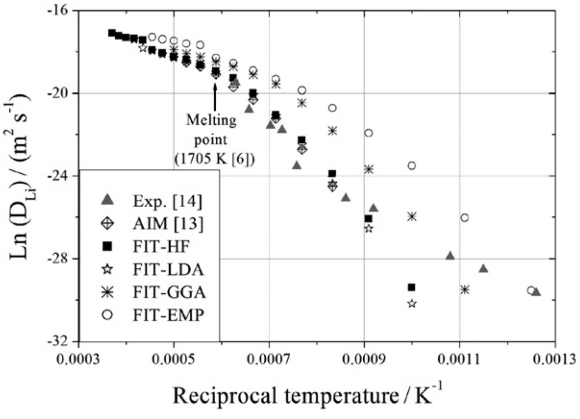

Fig. 3. Variation of the Li diffusion coefficients.

Finally, it is interesting to note that although either the Li diffusivity or the lattice expansion behavior was consistent with the experimental results, never were both consistent at the same time. Specifically, FIT-HF and FIT-LDA gave satisfactory results for the former, while FIT-GGA and FIT-EMP for the latter. This incompatibility may be the result of an inherent limitation of the Buckingham-type pairwise potential, probably due to the low pliability of the Buckingham model formula, although it cannot be concluded in the present work. Fair results were obtained only in the AIM model for all of the assessed properties at the same time.

4. Conclusions

Four Buckingham-type pairwise potential models for Li_2O were tested. In all models, the properties in the static simulation, such as the mechanical properties, showed good agreement with the experimental values, and the superionic phase transition was realized. However, the agreements with the experimental values for the Li diffusivity and lattice expansion behavior were incompatible in all models. As a tendency, in the dynamics the two reported models (FIT-HF and FIT-LDA) provided a relatively good description of the Li ion behavior, while the two newly created models (FIT-GGA and FIT-EMP) described the O ion behavior well. When using these four potential models in future work, these features should be taken into account, in order to reduce the model dependency of the results.

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References

[1] J.G. Laan, H. Kawamura, N. Roux, D. Yamaki, J. Nucl. Mater. 283–287 (2000) 99.

[2] L.R. Corrales, W.J. Weber, Curr. Opin. Solid State Mater. Sci. 7 (2003) 35.

[3] R.M. Fracchia, G.D. Barrera, N.L. Allan, T.H.K. Barron, W.C. Mackrodt, J. Phys. Chem. Solids 59 (1998) 435.

[4] J.G. Rodeja, M. Meyer, M. Hayoun, Model. Simul. Mater. Sci. Eng. 9 (2001) 81.

[5] G.V. Samsonov, The Oxide Handbook, Plenum, New York, 1982.

[6] Y.Y. Liu, M.C. Billone, A.K. Fischer, S.W. Tam, R.G. Clemmer, G.W. Hollenberg, Fusion Technol. 8 (1985) 1970.

[7] T.W.D. Farley, W. Hayes, S. Hull, M.T. Hutchings, M. Vrtis, J. Phys. Condens. Mat. 3 (1991) 4761.

[8] S. Hull, T.W.D. Farley, W. Hayes, M.T. Hutchings, J. Nucl. Mater. 160 (1988) 125.

[9] T. Osaka, I. Shindo, Solid State Commun. 51 (1984) 421.

[10] T. Matsuo, H. Ohno, K. Noda, S. Konishi, H. Yoshida, H. Watanabe, J. Chem. Soc. Farad. Trans. II 79 (1983) 1205.

[11] H. Ohno, S. Konishi, K. Noda, H. Takeshita, H. Yoshida, H. Watanabe, J. Nucl. Mater. 118 (1983) 242.

[12] M.M. Islam, T. Bredow, C. Minot, J. Phys. Chem. B 110 (2006) 9413.

[13] M. Wilson, S. Jahn, P.M. Madden, J. Phys. Condens. Mat. 16 (2004) S2795.

[14] Y. Oishi, Y. Kamei, M. Akiyama, J. Nucl. Mater. 87 (1979) 341.