

Molecular dynamics simulation of diffusion and viscosity of liquid lithium fluoride



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ABSTRACT

LiF is an important component in the mixtures of the coolant, fuel, and carrier for molten salt reactor. The studies of diffusion properties and viscous flowability of liquid LiF provide significant guidance to the development of modern molten salt reactor. In this work, the structural characteristics, diffusion properties and viscous flowability of liquid LiF are investigated by means of molecular dynamics simulations with the Born–Mayer potential. The distribution of coordination numbers of Li⁺ ions for liquid LiF is statistically calculated, and it is found that the Li⁺ ions of 3 and 4 coordination numbers are in the majority. The micro-structural analysis indicates that the Li⁺ ions and their nearest-neighbor coordination F⁻ ions mainly form planar and tetrahedral configuration. The diffusion behaviors of Li⁺ and F⁻ ions are simulated as the temperature ranged from 900 K to 1400 K. The results show that the diffusion coefficients increase with the increase of the temperature for both Li⁺ and F⁻ ions, and the diffusion coefficients of Li⁺ ions are a little higher than F⁻ ions'. In addition, the effects of pressure on the diffusion coefficients are discussed. The viscosity of liquid LiF is obtained at a temperature range of 1000–1400 K. The results confirm that the higher temperature, the lower viscosity, which is consistent with the experiential rule.

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1. Introduction

Molten salt reactor (MSR), one of the Generation IV reactor systems, is a kind of nuclear fission reactor, which uses the liquid fuel instead of solid fuel rods in the reactor and runs at high temperature and low vapor pressure to improve the economy, cleanliness, and security. Presently, the commonly used nuclear fuel of MSR is the thorium fluoride salt, the neutron moderator is graphite, and the primary coolant, fuel, and carrier are fluoride molten salt mixtures, like LiF–BeF₂–UF₄, LiF–BeF₂–ThF₄, and LiF–NaF–BeF₂–ThF₄–UF₄ [1,2]. LiF, as an important component in the mixtures, which has a rock-salt structure under ambient conditions [3], has been found to own many advantages over other alkali halides and ionic crystals, such as good chemical stability, optically transparent insulator, and high melting point. As the coolant and carrier in the MSR [4,5], LiF improves the transport properties of the eutectic which composed by the thorium fluoride salt and carrier [6,7], enhances the energy efficiency of MSR [8], and reduces the possibility of incidents and makes a safer environment [9,10]. Moreover, LiF has potential applications as a pressure transmitting

medium and a pressure calibrant in static measurements [11,12] and shock impression. So the studies of diffusion properties and flowability of LiF both are important for the practical significance.

In the past decades, LiF has attracted increasing attention for its potential applications. Andersson et al. [13] used the experiment method to measure the specific heat capacity (c_p) and thermal conductivity of LiF. Dolling et al. [3], Kushwaha [14], and Verma et al. [15] calculated the phonon dispersion curves and Debye temperature by means of the lattice dynamics. From the aspect of *ab initio* method, Gheribi et al. [7], Smirnov [16], Khambholja et al. [17], and Wang et al. [18], calculated the Debye temperature [16–18], c_p [7,17,18], thermal expansion [7,18], thermal conductivity [7] and so on. Nevertheless, the diffusion properties and viscous flowability of LiF were difficult to obtain and not well known owing to the high erosive property, high toxicity, and high melting temperature. In the previous published papers, the diffusion properties of LiF were mostly obtained from the mixtures of LiF–KF [19–21] in a limited range of temperature, while the study of pure liquid LiF [22] was relatively rare. In addition, the viscous flowability, *i.e.*, the viscosity, has been obtained by just several experiments [23–25], however, the calculated values by molecular dynamics (MD) were rather scarce.

In the present paper, the structural characteristics of liquid LiF are investigated, and the diffusion coefficients and viscosity at

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different temperatures are calculated in the liquid state of pure LiF by molecular dynamics simulations. The activation energies for diffusion and viscous flow are also calculated according to the Arrhenius relationship. The knowledge of diffusion properties and viscous flowability of liquid LiF are very significant in modern molten salt reactor, and the results in this work are helpful for the study of liquid LiF as the coolant and carrier in the molten salt reactor.

2. Calculation method

In this work, MD simulations are performed [26–28] with the parallel package DL_POLY 3.07 [29] using the Born–Mayer function [30]:

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where the three terms in sequence represent Coulomb, repulsion, and van der Waals energy, respectively. Here r_{ij} is the distance between ions i and j , q_i is the charge of ion i , A_{ij} and B_{ij} are potential parameters for the repulsion energy, and C_{ij} are van der Waals constants. All the parameters [19] used in this work are given in Table 1.

The simulation boxes of cubic shape are built with the length of a side of 6.045 nm, and include 13,500 fluorine ions and 13,500 lithium ions. All the ions are initially located on a B1 lattice. The periodic boundary condition is applied in three directions. In the molecular dynamics simulations, the temperature is controlled by using the Berendsen thermostat. The motion equations of ions are numerically integrated with the timestep of 0.001 ps. At first, the system is equilibrated in NPT ensemble for 100 ps at required temperature and pressure, and then runs in the NVT ensemble for 300 ps, in which the former 100 ps is used for equilibrium, and the rest 200 ps is used for statistically calculation. The long-range Coulomb forces are calculated through the smooth particle mesh Ewald sum (SPME) [31] with a real space cutoff of 12 Å and the precision of 10^{-6} .

3. Results and discussion

3.1. Melting temperature and liquid structure

First of all, the static properties are calculated to test and verify the reliability of the potential functions of LiF system. The results show that the lattice constant is 4.03 Å, and lattice energy is 10.785 eV for the LiF of B1 structure at zero temperature, which are in good agreement with the experiment values [32,33], *ab initio* values [16,18], and other MD results [34] as listed in Table 2.

The radial distribution function (RDF) is an important measure to reveal the structural features of a system. The RDF $g_{ij}(r)$ shows a density of probability to find atom j at the distance r from atom i [26]. In this work, the RDF of LiF is calculated over the temperature from 200 K to 1400 K. From 200 K to 800 K, the RDF curves are similar and there are a series of characteristic peaks of varying intensity on the RDF curves, which presents the structural feature of a crystalline solid. Comparing the RDFs at the temperatures from 200 K to 800 K, it is found that the intensity of peaks lowers and

Table 2

Comparison of lattice constant and lattice energy of zero temperature with the experiment values, *ab initio* values, and MD values.

	Lattice constant (Å)	Lattice energy (eV)
This work	4.03	10.785
Exp. values [32]	4.01	10.581
Exp. values [33]	4.026	–
<i>Ab initio</i> values [17]	4.022	–
<i>Ab initio</i> values [7]	3.944	–
MD values [34]	–	10.795

the width of peaks broadens with temperature increasing, which shows the degree of structural order decreases. While the temperature increases to 810 K, the radial distribution functions are distinctly different from those at 800 K, with the characteristic peaks disappearing and $g_{ij}(r) \approx 1$ within the long range. This indicates that the simulated system turns into the liquid state at 810 K. So the calculated melting point of LiF is about 810 K, which is lower than the experiment value [35] of 1122 K. When the temperatures are greater than 810 K, the RDF curves are almost the same. For clarity, Fig. 1 only shows the typical RDF curves at 600 K, 810 K and 1400 K.

In addition, to verify the simulated melting temperature of LiF from the analysis of RDF curves, the temperature dependence of lattice energy is calculated. As one can see in Fig. 2, the lattice energy increases with the increase of temperature, and there is a skip from 800 K to 810 K when the pressure is kept as zero, which means the melting point is about 810 K, and the result is consistent with the assessment from the radial distribution curves. The effects of pressure on the lattice energy and corresponding melting temperature are also presented in Fig. 2. Compared with the melting temperature of 810 K at the zero pressure, the melting temperature is up to 1020 K with the pressure kept at 1 GPa, which shows that the higher the pressure, the melting temperature is also higher. So the melting temperature in this work is lower than the experiment values not only because of the potential function, but also the effects of pressure.

For the liquid LiF, although it lacks long-range order, it possesses a certain short-range order, which is represented on the RDF curves as shown in Fig. 1. To reveal the short-range structure characteristics, we statistically calculate the coordination numbers

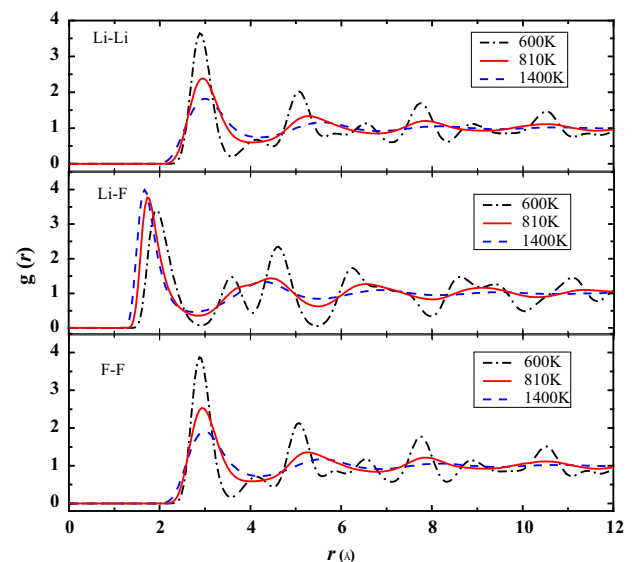


Fig. 1. Radial distribution functions of Li^+-Li^+ , Li^+-F^- , F^--F^- ion pairs at different temperatures.

Table 1
Parameters of the Born–Mayer potential used in the MD simulations [19].

	A (10 J/mol)	B (\AA^{-1})	C (10 J/mol \AA^6)
Li–Li	954487.0	3.34	439.606
Li–F	2209471.0	3.34	4817.6
F–F	4057021.4	3.34	87319.0

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