

Thermal neutron scattering data for liquid molten salt LiF-BeF₂

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Abstract. Ab initio molecular dynamics (AIMD) methods were used to calculate the density of states (DOS) for liquid molten salt Li₂BeF₄ (LiF-BeF₂) in different temperatures. The Egelstaff and Schofield effective width model was used to obtain the diffusion-type spectrum of the DOS and the corresponding partial s (α , β). Finally, the thermal neutron scattering data for liquid molten salt LiF-BeF₂ were given.

1 Introduction

As one of the candidates of the Generation IV reactor concepts, the molten salt reactors (MSR) was originally developed and tested in the 1950s, 1960s and 1970s [1-4]. The liquid molten salt LiF-BeF₂ are proposed as a coolant and carrier of fuel in MSR, because of the material properties, such as high passive safety, high temperature stability, high heat capacity atmospheric operating pressure and also the small neutron absorption cross section. Many experimental researches into the properties of molten salt LiF-BeF₂ have been carried out. The existing experimental data include density, diffusion coefficients, electrical conductivity, viscosity, thermal conductivity, and heat capacity.

Meanwhile, the molten salt LiF-BeF₂, liquid mixture of fluorine, lithium and beryllium has high moderating ratio, so it can be considered as a moderator and may has effects on the neutronics. Several works have been done to generate the thermal neutron scattering data for liquid molten salt LiF-BeF₂. Mei and Cai [5] generated the thermal neutron scattering data based on the dynamics of for molten salt Flibe. They used the solid crystalline models and density functional theory (DFT) simulations to calculate the solid-type spectrum and performed the effective width model [6] to treat the diffusive mode in calculations. In Zhu and Hawari's calculation [7], they developed a liquid state classical molecular dynamics method of Flibe, calculated the diffusive motion in liquid by the effective width model. Then the bound vibrational DOS were separated from the diffusive DOS in the whole spectrum and the thermal neutron scattering data of fluorine, lithium, beryllium in liquid FLiBe were generated. In fact, because the calculation methods of DOS in these two simulations are different, the results of total scattering cross sections are obviously different.

In this work, AIMD methods are used to obtain the velocity autocorrelation function (VACF) for liquid molten salt LiF-BeF₂ (2:1). The effective width model is considered to calculate the diffusion-type spectrum of the

DOS and the corresponding partial scattering law. Finally, the thermal neutron scattering data for liquid molten salt LiF-BeF₂ are given.

2 AIMD simulation

AIMD based on the DFT [8-10] has proven to be a reliable method for studying the many-body quantum systems. The electrons are described by quantum mechanical wave functions, and the ions are treated as classical particles governed by the Newtonian mechanics.

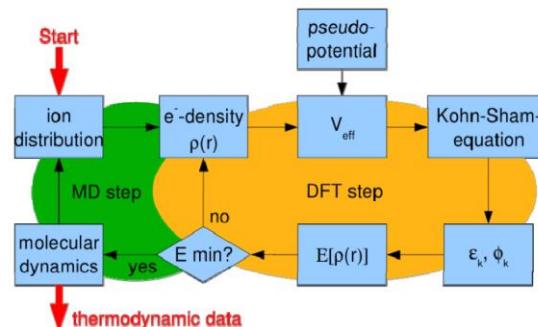


Fig. 1. Framework of AIMD

The prediction of reliable DOS of LiF-BeF₂ system from AIMD simulations requires an equilibrated system. To reduce computational requirements in the AIMD simulation, the system of 288 LiF molecules and 144 BeF₂ molecules are used. The supercell, shown in Fig. 2, is the LiF-BeF₂ system with blue as Li⁺ ions, green as F⁻ ions and brown as Be²⁺ ions. The projected-augmented-wave (PAW) [11] pseudo-potentials and plane waves are used. The exchange and correlation effects are described within PBE [12]. The cut-off energy for the plane-wave expansion is set to 500 eV. 4000-time steps with 1.0 femtoseconds per time step are considered.

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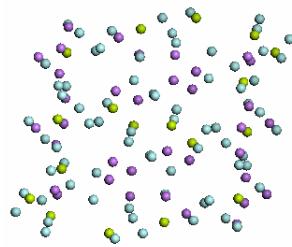


Fig. 2. Supercell of LiF-BeF₂ system (288 LiF molecules and 144 BeF₂ molecules)

The calculated density of liquid molten salt LiF-BeF₂ (shown in Fig. 3) is within the experimental range [13-15]. It can be seen that the results of our simulations are smaller than the experimental results.

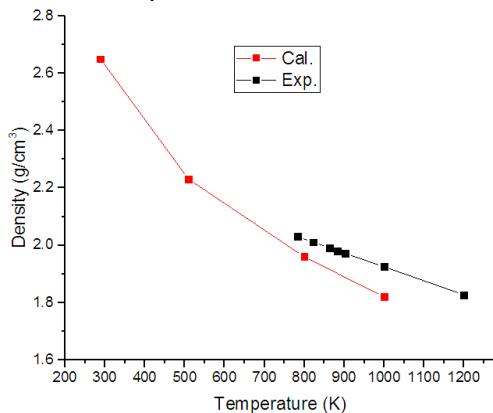


Fig. 3. Calculated density of liquid molten salt LiF-BeF₂ in comparison to the experimental data

The self-diffusion coefficient D can be obtained using the Einstein equation by estimating the slope of mean square displacement.

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \left(\frac{d \langle (r(t) - r(0))^2 \rangle}{dt} \right) \quad (1)$$

The calculated self-diffusion coefficients of the three ionic species in the LiF-BeF₂ system are shown in Fig. 4. As can be seen that the most mobile species is Li²⁺, while the F⁻ and Be²⁺ ions have a very similar diffusion.

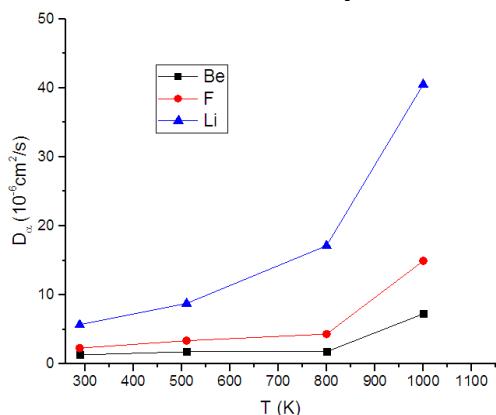


Fig. 4. Diffusion coefficients of Li²⁺, F⁻ and Be²⁺ in liquid molten salt LiF-BeF₂

The DOS can be generated as the Fourier transform of the VACF. The calculated DOS for liquid molten salt LiF-BeF₂ at 800K and 1200K are shown in Fig. 5.

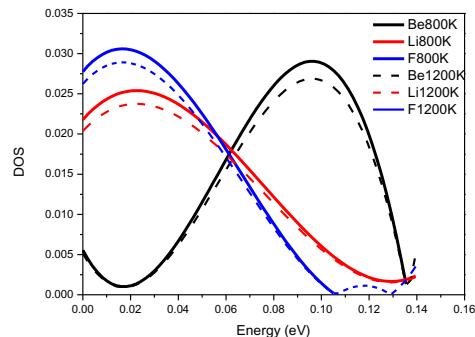


Fig. 5. Calculated DOS for Be, F, Li in liquid molten salt LiF-BeF₂ at 800 K and 1200 K

3 Thermal neutron Scattering data

For liquid, there are no elastic scattering [16, 17]. The expression of the double differential inelastic scattering cross section is

$$\left(\frac{d^2\sigma}{d\omega dE'} \right)_{inl} = \frac{\sigma_b}{4\pi k_B T} \sqrt{\frac{E'}{E}} \exp\left(-\frac{\beta}{2}\right) S(\alpha, \beta) \quad (2)$$

Where subscript *inl* means inelastic scattering, T is the temperature of the scattering medium, σ_b is the characteristic bound scattering cross section for the material, k_B is the Boltzmann constant, E and E' are the incident neutron energies and the scattering neutron energies in the laboratory system, respectively. $\alpha = \frac{E' + E - 2\mu\sqrt{EE'}}{Ak_B T}$ means the momentum transfer and $\beta = \frac{E' - E}{Ak_B T}$ means the energy transfer, $S(\alpha, \beta)$ is the thermal neutron scattering law.

The frequency spectrum is decomposed into a sum of simple excitation spectra, including a solid-type spectrum, a translational spectrum and discrete oscillators. The sum of all the weights of the partial spectra must equal 1.

The neutron scattering from many important liquids are represented using a solid-type spectrum of rotational and vibrational modes combined with a diffusion term. The scattering law for the solid-type modes is calculated using a phonon expansion of the Gaussian approximation in the same way as for solid [18]. The effective width model proposed by Egelstaff-Schofield is applied for diffusion component. The expression of diffusion scattering law (S_{diff}) and diffusion component of the spectrum (ρ_{diff}) are

$$S_{diff}(\alpha, \beta) = \frac{2d\alpha\sqrt{c^2 + 0.25}}{\pi\sqrt{\beta^2 + (2d\alpha)^2}} e^{2d\alpha c} \quad (3)$$

$$K_1 \left[\sqrt{(c^2 + 0.25)(\beta^2 + (2d\alpha)^2)} \right]$$

$$\rho_{diff}(\beta) = \frac{4d}{\pi} \sqrt{c^2 + 0.25} \sinh\left(\frac{\beta}{2}\right) K_1\left(\sqrt{c^2 + 0.25}\beta\right) \quad (4)$$

Where $K_1(x)$ is a modified Bessel function of the second kind, $w_t = \frac{M_a}{M_{diff}}$ is the translational weight, $c = \frac{M_{diff}D}{h}$ is the diffusion constant, $d = cw_t$.

In order to compute these parameters, the diffusion coefficients and the effective mass are needed. In this work, the diffusion coefficients are obtained from molecular dynamics simulations as mentioned above. The effective mass of liquid molten salt LiF-BeF₂ is considered to be 100, for the reason that no molecular cluster structure information is achieved from the simulation and no measurement data are available to estimate the effective mass. Table 1 shows the parameters used in effective width model calculations.

Table 1. Parameters for the effective width model (Effective mass of LiF-BeF₂=100)

	w _t	c	d	D (-10) m ² /s
Be	0.09	0.277	0.025	1.76098
F	0.19	0.6806	0.1293	4.32195
Li	0.07	2.6969	0.1888	17.12683

The calculation of thermal neutron scattering data for liquid states is performed using the LEAPR module of the NJOY code [19, 20]. The total scattering law is obtained by convolution of the diffusion scattering law and the solid-type scattering law. Also, the final effective temperature are the combination of solid-type and translation modes. Fig. 6 to Fig. 8 show the thermal neutron scattering law $S(\alpha, \beta)$ for fluorine, lithium and beryllium in liquid molten salt LiF-BeF₂ at 800K, respectively. The comparison of the thermal neutron scattering cross sections for fluorine, lithium, beryllium in liquid molten salt LiF-BeF₂ between this work and free gas model at 800K is shown in Fig. 9. Fig. 10 shows the comparison of the thermal neutron scattering cross sections for fluorine, lithium, beryllium in liquid molten salt LiF-BeF₂ at 800K and 1200K.

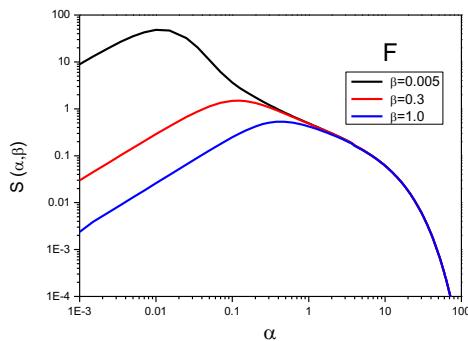


Fig. 6. $S(\alpha, \beta)$ at different β for F at 800K

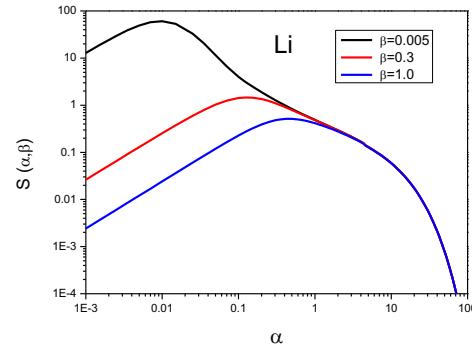


Fig. 7. $S(\alpha, \beta)$ at different β for Li at 800K

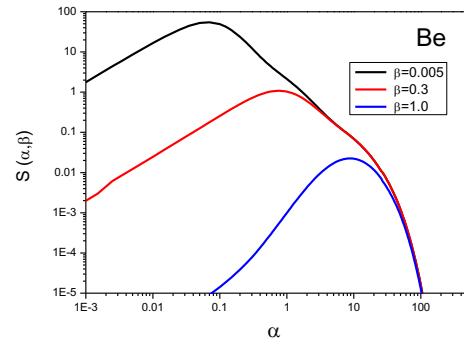


Fig. 8. $S(\alpha, \beta)$ at different β for Be at 800K

As can be seen, for beryllium and fluorine, higher temperature liquid molten salt LiF-BeF₂ systems exhibit a lower thermal neutron scattering cross section. On the contrary, for lithium, when the temperature of liquid molten salt is higher, the thermal neutron scattering cross section is higher.

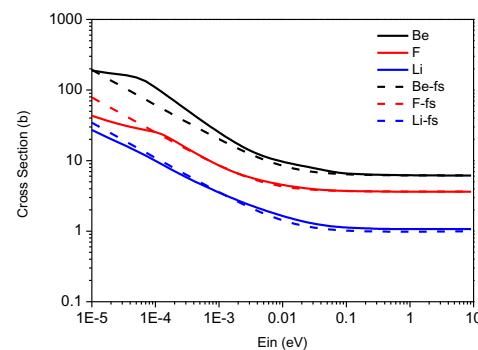


Fig. 9. Thermal neutron scattering cross sections for F, Li, Be at 800K

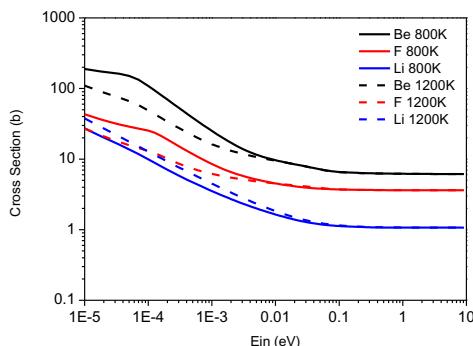


Fig. 10. Thermal neutron scattering cross sections for F, Li, Be at 800K and 1200K

Though the comparison of the thermal neutron scattering cross section between our work and the other two literatures is not shown in figure. It must be emphasized that the calculated scattering cross sections have significant difference with each other. In Mei and Cai's calculation, the solid crystalline models and DFT simulations were used to calculate the solid-type spectrum. Actually, it is not a consistent way to treat the DOS for liquid. In Zhu and Hawari's calculation, classical molecular dynamics method was performed to calculate the DOS for liquid, and subtract the diffusion-type spectrum from the DOS to get the continuum spectrum. But, the equation of diffusive component of spectrum shown in their paper is different from Egelstaff and Schofield literature. In this work, the simulation system for liquid LiF-BeF₂ is a small one.

4 Conclusions and future work

In this paper, we simulated the liquid molten salt LiF-BeF₂ using AIMD method. Properties such as density and diffusion coefficient were investigated and compared to the experimental data. The DOS were calculated from the Fourier transform of the VACF. The effective width model was used to obtain diffusion-type spectrum of the DOS and partial $S(\alpha, \beta)$. The thermal neutron scattering data for liquid molten salt LiF-BeF₂ are generated in ENDF format data. However, to validate these calculated thermal neutron scattering data and to clarify the discrepancies in the different simulations, experimental data are eagerly needed.

An exhaustive comparison of the effect of size of supercell is left for future work. Also, we plan to improve the simulation by using classical molecular dynamics with the potential developed by ab initio simulations.

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