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Molecular dynamics simulation of molten $CaCl_2$ and NaCl-$CaCl_2$ eutectic molten salt

Danan Chen[a], Xiaolan Wei[a*] Jing Ding [b*] Shule Liu[b] Weilong Wang[b] Jianfeng Lu[b]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

[b]School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou High Education Mega Center, Guangzhou 510006, PR China

ABSTRACT

NaCl-$CaCl_2$ binary eutectic mixture is potential high-temperature heat storage molten salt material. It has the advantages of high working temperature upper limit and good thermal stability. However, its high temperature thermophysical properties are difficult to measure. An effective solution is to calculate and predict the thermophysical properties of molten salts through classical molecular dynamics simulation. The lack of reasonable potential parameters of positive divalent chloride molten salts restricts the accurate calculation of the properties. In this study, the appropriate potential parameters of $CaCl_2$ were determined by comparing the calculated and experimental data of density and coordination number for molten $CaCl_2$ or NaCl-$CaCl_2$ eutectic mixture. The results show that the determined potential parameters of SP2 series are reasonable and can be selected to accurately calculate the thermophysical properties of calcium-containing chloride mixture molten salts.

Keywords: molecular dynamics simulation, chloride molten salt, potential parameter, thermophysical properties

1. INTRODUTION

Due to the uniform distribution of solar energy in nature and the huge energy advantage, it has become the clean and renewable energy with the most potential to replace traditional fossil energy and solve energy problems. Efficient heat storage technology is the key to overcome the intermittent and instability of solar energy. As a commonly used heat transfer and storage fluid in concentrated solar power (CSP) power plants, molten salt has the advantages of wide operating temperature range, low cost, and good thermal stability compared with other commonly used heat storage media[1] . At present, the heat storage media used in molten salt tower power stations that have been put into use are nitrate eutectic salt. For example, the 10MWe solar thermal power station in California uses 60wt%$NaNO_3$-40wt%KNO_3 binary eutectic salt (Solar salt)[2]. Although nitrate has low cost and low corrosivity, it is the first choice for commercial molten salt, but the upper working temperature of nitrate is low, and it is easy to decompose, so it is not suitable for high temperature working conditions. Among high-temperature heat storage molten salts, chloride molten salt has attracted much attention, which not only has a high working temperature, but also has high thermal conductivity. The most important thing is that the chloride molten salt is abundant in the salt lakes, which reduces its cost. Molten $CaCl_2$ is one of the most common molten chloride salts. It has high melting point and stable chemical properties, and has broad application

prospects in many fields. NaClCaCl$_2$ binary eutectic molten salt, operating temperature at 550°C-800°C, has good thermal stability, but the specific heat capacity is only about 1J·g^{-1}·K^{-1}[3]. Because its working temperature is too high, it is difficult to obtain its high-temperature physical property parameters through experiments under the existing test technical conditions.

Molecular dynamics simulation is an effective method to predict the macroscopic properties and thermal properties. Pan[4] used molecular dynamics simulation to calculate the thermophysical properties and transport properties of the positive monovalent cation chloride molten salt, using the Born-Mayer-Huggins potential as the interaction between the ions in the simulation and the RNEMD method to calculate the thermal conductivity and viscosity of the chloride molten salt; the calculation results show that this method can reasonably predict the properties of the positive monovalent cation chloride molten salt. However, for the positive divalent cation chloride molten salt, there are still difficulties in determining the parameters. Based on the existing research of $CaCl_2$ molten salt, this study determines a set of potential parameters suitable for the calculation unit $CaCl_2$ molten salt by calculating its microstructure and thermophysical properties, as well as the potential parameters for the molecular dynamics simulation of multi-chloride.

2. SIMULATION METHOD

2.1 Force field

The accuracy of molecular dynamics simulation calculation depends on the selection of the force field and the determination of the potential parameters. Generally, the Fumi-Tosi potential is used in the molten salt of chlorides[5]. The Born-Mayer-Huggins (BMH) potential energy model[6] is used for the potential function between NaCl and $CaCl_2$ molecules:

$$U_{ij}^{Fumi-Tosi} = \frac{q_i q_j e^2}{r_{ij}} + A_{ij}\, exp\left(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}$$

The first term on the right of formula (1) represents the long-range Coulomb electrostatic force, the second term represents the short-range repulsive force caused by the overlap of electron clouds, and the third and fourth terms represent the Van der Waals attraction caused by ion polarization. Where e is the unit electron charge, z is the charge carried by the ion, and r_{ij} is the distance between the i ion and the j ion. σ_{ij} is the radius sum of i ion and j ion, ρ_{ij} is the hardening parameter between i ion and j ion. The third and fourth terms on the right of equation (1) are Van der Waals attraction caused by ion polarization, C_{ij} and D_{ij} are dipole-dipole interaction coefficient and dipole-quadrupole interaction coefficient respectively. In this paper, the values of C_{ij} and D_{ij} of molten $CaCl_2$ simulation are zero, and the other parameters in formula (1) are in Table 1.

The most important part of classical dynamics simulation calculation is the selection of the potential parameters mentioned above. Therefore, in order to better simulate and analyze the heat storage properties of calcium-containing chloride molten salts, the potential parameters of $CaCl_2$ in Table 1 are sorted out from the literatures[7-10].

2.2 Molecular dynamics simulation conditions

For the $CaCl_2$ system, a supercell of 5×5×24 is selected as the initial conformation, and

Table 1 Born-Mayer-Huggins potential parameters of $CaCl_2$[7-10]

Parameters	SP1[7]	SP2[8, 9]	SP3[9, 10]	Units
q+	+2	+2	+2	e
q-	-1	-1	-1	e
A++	0.1597	4.0995	4.0995	kcal /mol
A+-	0.1749	3.0746	3.0746	kcal /mol
A--	0.1889	2.0489	2.0489	kcal/ mol
σ++	2.814	2.880	2.180	Å
σ+-	3.357	3.118	2.675	Å
σ--	3.900	3.356	3.170	Å
ρ	0.170	0.324	0.324	Å

the total number of particles is 3,600. For the NaCl-$CaCl_2$ binary system, according to the phase diagram calculated by Xie P [11], the lowest eutectic ratio of the binary chloride molten salt is 49.03mol%NaCl and 50.97mol% $CaCl_2$.

In this study, PACKMOL is used to construct the initial model, and different ions are mixed into the simulation box according to the proportion (6400 atoms in total); the size of the simulation box is determined by the density at the lowest eutectic temperature.

LAMMPS is used for molecular dynamics simulation calculation, periodic boundary conditions are selected, and the cutoff radius is set to 20 Å. The long-range Coulomb force adopts the pppm algorithm to reduce the truncation error, and the calculation accuracy is 1.0e-6;. The initial velocity obeys Gaussian distribution. Use Verlet calculation method to solve Newton's equation of motion. The system is first heated to 1200K and then cooled to different temperatures. It is balanced in the NPT ensemble with a constant pressure of 0.1 MP. Under the volume of the balance cell, the NVT ensemble was simulated using a Nosé Hoover thermostat, and the simulation time step was set to 1 fs. In order to obtain accurate calculation results, the equilibrium time of each simulation is 1 ns.

3. RESULTS AND DISCUSSION

3.1 Verification of the unit $CaCl_2$ model

3.1.1 The microstructure of $CaCl_2$ molten salt

Due to the lack of potential parameters of the classical molecular dynamics of positive divalent chloride molten salt, the three sets of existing parameters need to be compared and verified with the experimentally measured microstructure of $CaCl_2$ molten salt. Fig. 1 is the radial distribution function (RDF) of $CaCl_2$ molten salt calculated by simulation with various parameters.

From the Fig. 1, we can see that the peak positions of the RDFs of each ion pair calculated by the two sets of parameters SP1 and SP2 are basically the same. The main difference is that the peak value of the first peak of each ion pair calculated by SP1 is higher than the SP2 calculation result, while the radial distribution function calculated by SP3 is quite different from the first peak position calculated by the other two parameters. S Biggin[6] experiment measured the positions of the first peaks of Ca-Ca, Ca-Cl,

and Cl-Cl in the $CaCl_2$ molten salt to be 3.73Å, 2.78Å, and 3.73Å, respectively. The first peak position of the RDF calculated by SP3 is too small, so the ion orbit overlap rate is too large, which is different from the actual $CaCl_2$ structure.

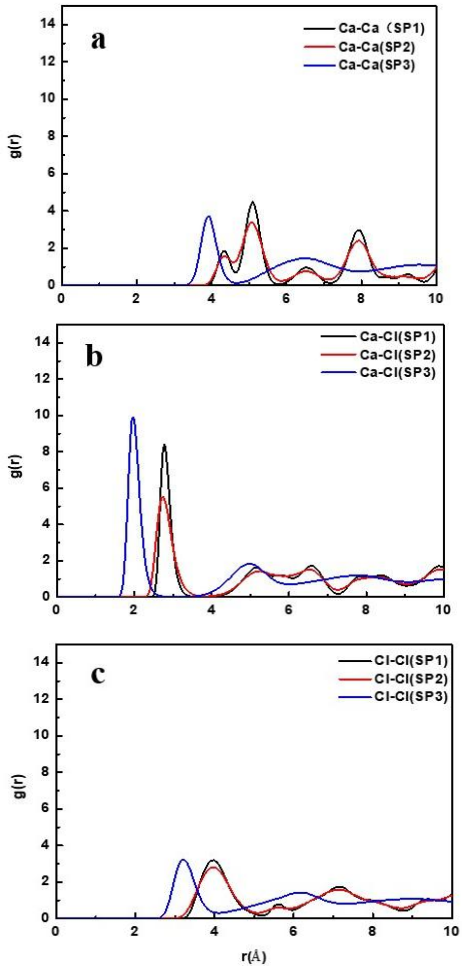

Fig. 1 RDF of molten $CaCl_2$ at T=1200K

From the coordination number curve in Fig. 2, it can be seen that the coordination number curves calculated by SP1 and SP2 basically coincide, the coordination number of $Ca^{2+}$and Cl^- is N_{Ca-Cl}=6.0, and the coordination number of S Biggin[6] experimentally obtained at 1093K is N_{Ca-Cl}=5.4. Although the result of the simulation calculation is slightly larger than the experimental result, it can be seen that $CaCl_2$ is octahedral structure in the molten state. However, the distance between ions calculated by SP3 is too small, and the amount of Cl^- that can be accommodated around Ca^{2+} ions is too little. Therefore, the microstructure calculated by SP1 and SP2 is more reasonable than that calculated by SP3.

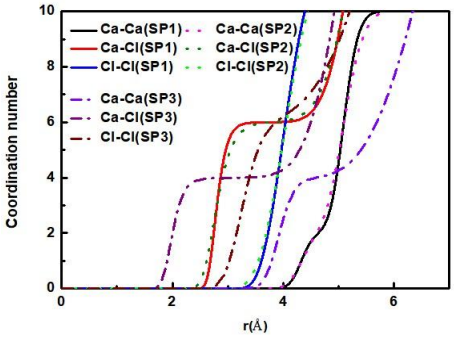

Fig. 2 Coordination number curve of molten $CaCl_2$ at T=1200K

3.1.2 Thermophysical properties of molten $CaCl_2$

The reasonableness of the density of molten salt is the basis for the analysis and calculation of the microstructure and thermophysical properties of molten salt. Fig. 3 (a) is the comparison of calculation results and experimental values of the density of molten $CaCl_2$ base on the three sets of parameters.

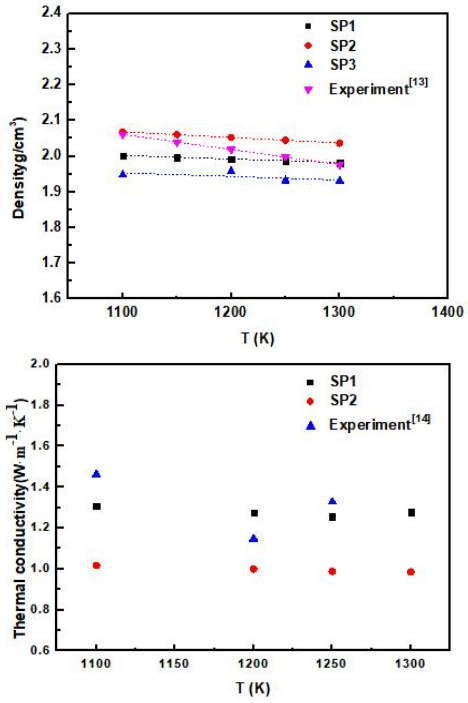

Fig. 3(a) Density of molten $CaCl_2$ at different temperatures;(b) Thermal conductivity of molten $CaCl_2$ at different temperatures

The deviations of SP1 and SP2 are within 3%, and the deviations of SP3 have an error of about 5%. The simulation calculation of kinetic properties is of great significance to the application of molten salt. From the above analysis, it is found that the two sets of parameters SP1 and SP2 are more suitable for the simulation calculation of unit $CaCl_2$ molten salt. Therefore, this paper uses SP1 and SP2 to calculate the thermal conductivity of the unit $CaCl_2$ molten salt and compares it with the experimental value. Because the error of the measured thermal conductivity of molten salt is ~ 30%, the error of the simulated value in this paper is within the acceptable range, and the variation trend of thermal conductivity with temperature is consistent with the experimental value. In the simulation calculation of dynamic properties, SP1 is more suitable for the experimental results than SP2. Therefore, SP1 can be used for the unit $CaCl_2$ molten salt.

3.2 NaCl-$CaCl_2$ eutectic salt

For the classical molecular dynamic simulation of NaCl-Type chloride molten salt, Pan[4] have a good set of BMH potential parameters and a multi-element calculation mixing rule. The SP1 potential parameters is not suitable for the calculation of binary chloride molten salt using this mixing rule. In this paper, the parameters of NaCl used by Pan and $CaCl_2$ used by SP2 and SP3 are simulated and calculated. From the density curves in Fig. 4, it can be seen that the density calculated by SP2 is basically consistent with the experimental value.

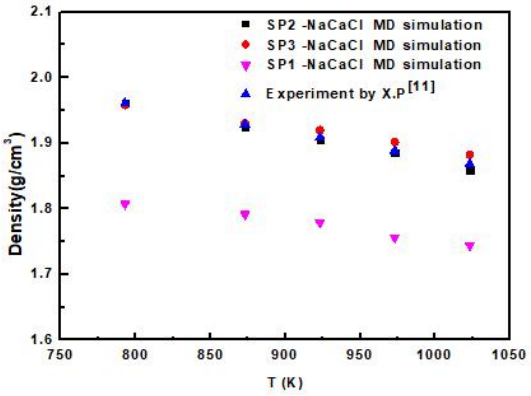

Fig. 4 Density of NaCl-$CaCl_2$ at different temperatures

Since the NaCl-$CaCl_2$ binary eutectic molten salt does not form a covalent bond and other structures after melting, the microstructure of the binary molten salt is basically similar to its unit molten salt structure.

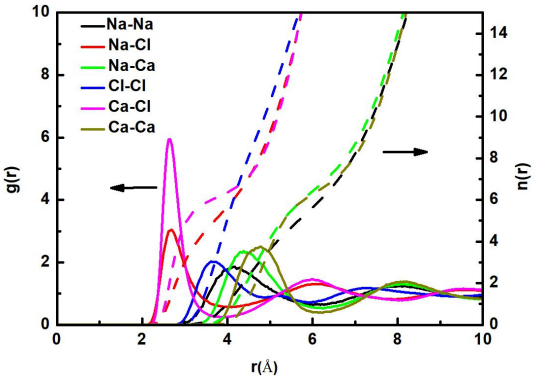

Fig. 5 RDF and coordination number of NaCl-$CaCl_2$ using SP2

It can be seen in Fig. 5 that the first peak of the RDF for Ca-Cl is relatively high, it means that the relatively stable ion clusters are formed. The coordination number curve of Ca-Cl has a large platform at 6 points, indicating that $CaCl_2$ also mainly exists in the form of octahedrons in the binary molten salt. The coordination number curve of Na-Cl also has a smaller platform at 6, indicating that NaCl also mainly exists in the form of octahedron-like in this system.

4. CONCLUSION

In this study, the MD simulation parameters of calcium-containing chloride molten salts in related literature were sorted out and verified. It is determined that

potential parameters SP1 is suitable for the simulation calculation thermophysical properties of pure molten $CaCl_2$, and potential parameters SP2 is more suitable for simulation calculation that of multi-chloride molten salt. Therefore, in the next work, potential parameters SP2 will be used for the simulation calculation of the multiple eutectic molten salt.

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