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Thermal and Transport Properties of Molten Chloride Salts with Polarization Effect on Microstructure

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Abstract: Molten chloride salt is recognized as a promising heat transfer and storage medium in concentrating solar power in recent years, but there is a serious lack for thermal property data of molten chloride salts. In this work, local structures and thermal properties for molten chloride salt—including NaCl, MgCl₂, and ZnCl₂—were precisely simulated by Born–Mayer–Huggins (BMH) potential in a rigid ion model (RIM) and a polarizable ion model (PIM). Compared with experimental data, distances between cations, densities, and heat capacities of molten chloride salts calculated from PIM agree remarkably better than those from RIM. The polarization effect brings an extra contribution to screen large repulsive Coulombic interaction of cation–cation, and then it makes shorter distance between cations, larger density and lower heat capacity. For NaCl, MgCl₂, and ZnCl₂, PIM simulation deviations of distances between cations are respectively 3.8%, 3.7%, and 0.3%. The deviations of density and heat capacity for NaCl between PIM simulation and experiments are only 0.6% and 2.2%, and those for MgCl₂ and ZnCl₂ are 0.7–10.7%. As the temperature rises, the distance between cations increases and the structure turns into loose state, so the density and thermal conductivity decrease, while the ionic self-diffusion coefficient increases, which also agree well with the experimental results.

Keywords: molecular dynamics simulation; high-temperature heat transfer and storage; molten chloride salt; polarizable ion model; thermal and transport properties

Citation: Lu, J.; Yang, S.; Pan, G.; Ding, J.; Liu, S.; Wang, W. Thermal and Transport Properties of Molten Chloride Salts with Polarization Effect on Microstructure. *Energies* **2021**, *14*, 746. <https://doi.org/10.3390/en14030746>

Academic Editor: Adrián Mota Babiloni

Received: 30 December 2020

Accepted: 27 January 2021

Published: 31 January 2021

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1. Introduction

Concentrating solar thermal power (CSP) is a promising technique for high temperature solar energy utilization [1]. Molten salts have the advantages of wide working temperature range, high heat capacity, low viscosity, low vapor pressure, and low material prices [2]; consequently, they are widely used as heat transfer and storage materials in CSP. Molten salts include alkali or alkali earth halides (chloride salts, fluoride salts, and so on), and oxyacid salts (carbonates, nitrates, and so on). In recent years, molten chloride salts including LiCl, NaCl, KCl, MgCl₂, and ZnCl₂ have been researched as promising heat transfer materials with high operating temperature [3]. Another unique advantage is the tremendous nature resources worldwide, and it is reported that there are 38.81 billion tons magnesium chlorides in Qinghai salt lake of China [4].

Many researchers experimentally reported the microstructure and properties of molten chloride salts. McGreevy [5] investigated the experimental structure of molten alkali halides by the technique of neutron scattering and energy-dispersive X-ray diffraction (EDXRD). Biggin and Enderby [6] researched the structural characteristic of ZnCl₂ at melting point by neutron diffraction technique. Besides, high-energy X-ray diffraction method was taken to obtain the structure of ZnCl₂ by Zeidler et al. [7], showing the result of corner-sharing and edge-sharing tetrahedral unit. Pavlatou et al. [8] studied the vibrational spectra of network-forming ionic melts (LaCl₃ and ZnCl₂) by the Raman and infrared spectra.

The structure of molten KCl-ZnCl₂ system was examined by Takagi and Nakamura [9] with XRD measurement, and the polymer of ZnCl₂ is dissociated with the increasing mole fraction of KCl. Yoko et al. [10] researched the density of molten ZnCl₂-M (M = Li, Na, K) system with the Archimedean method. Differential scanning calorimetry (DSC) tests were conducted by Mohan et al. [11] to measure the heat capacity of ternary NaCl-KCl-MgCl₂. Janz et al. [12–14] experimentally investigated density, viscosity and other thermal properties of molten chloride salts in a narrow temperature range, and the thermal conductivity of NaCl at 1100 K measured by coaxial cylinder technique is 0.999 W/(m·K). Nagasaka et al. [15] used the forced Rayleigh scattering method to obtain the thermal conductivity of NaCl, which is 0.519 W/(m·K) at 1100 K. According to available experimental results, there is a large discrepancy between the different measurement methods. Moreover, it is difficult to obtain the complete database of experimental microstructures and thermodynamics properties over the whole working temperature due to the high temperature and strong corrosion.

Molecular dynamics simulation (MD) is an effective method to obtain the properties of molten salts. Solar salt has been industrially applied in CSP plants and its thermodynamics properties were calculated by Ding et al. [16] with the MD method. Wang et al. [17] evaluated the local structure and transport properties of LiCl, NaCl, KCl, and other molten chlorides in rigid ion models (RIM) with Born–Mayer–Huggins potential [18]. Pan et al. [19] acquired the thermal and transport properties and the local structure characters of binary molten NaCl-KCl by MD simulations with BMH potential. The first principle molecular dynamics simulation (FPMD) was carried out by Tang et al. [20] to study the properties and phase transition of binary molten NaCl-MgCl₂. Liang et al. [21] studied the microstructure evolution of molten KCl-MgCl₂ in composition dependence with FPMD method. The reverse non-equilibrium molecular dynamics (RNEMD) method was applied to forecast thermal conductivities of molten salts in recent researches [22–24]. Additionally, Huang et al. [25] computed the local structure of MgCl₂ at 998 K by MD simulations, which agrees well with the experimental results by neutron diffraction technique except the distance of Mg-Mg. Gardner et al. [26] calculated pair radial distribution functions, coordination numbers and internal pressure of ZnCl₂ at 1200 K with different parameters in RIM, but the distances of Zn-Zn in all simulations are in excess of more than 23% of experimental value. Rollet and Salanne [27] studied the polarization effect in the structure of molten metal halides by polarizable ion model (PIM) introduced by Wilson and Madden [28], which can improve the simulated results. The force-matching procedure based on the first-principles density functional theory calculation was performed by Salanne et al. [29] to acquire the potential parameters of molten alkali chlorides and fluorides in PIM. Sharma and Wilson [30] improved the simulation results of structure factors for MgCl₂ and ZnCl₂ by PIM. However, there is still a lack of precise thermal and transport properties of MgCl₂ and ZnCl₂ over the whole working temperature.

In order to estimate the properties of molten chloride salts more precisely, MD simulations with PIM are first carried out to obtain thermal and transport properties of molten NaCl, MgCl₂, and ZnCl₂ with polarizable effect on microstructures. The evolution of microstructure including partial radial distribution function and coordination number is analyzed by considering polarization effect. In addition, the thermal and transport properties of molten chloride salts calculated by PIM and RIM are both compared with experimental data.

2. Numerical Model and Conditions

2.1. Force Field

Among all of the force fields presented in molten salts, it has been recommended that a pair potential can represent the interactions. Tosi and Fumi [18] have come up with Born–Mayer–Huggins potential of rigid ion model (RIM) as follows

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + A_{ij} \exp[B_{ij}(\sigma_{ij} - r_{ij})] - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (1)$$

where the first term is electrostatic potential, the second term is repulsion potential and the last two terms represent dipole dispersion energies. The potential parameters in RIM of NaCl and ZnCl₂ are reported in the research [31,32]. A new series of parameters in RIM of MgCl₂ used in this paper are put forward. The interactions between Cl–Cl pairs are adopted from Seo et al. [32] and the rest pair parameters are adopted from Yuen et al. [33], which are listed in Table 1.

Table 1. Potential parameters of RIM for molten chloride salts.

Model	Pair	A_{ij} (kJ·mol ^{−1})	B_{ij} (Å ^{−1})	σ_{ij} (Å)	C_{ij} (Å ⁶ ·kJ·mol ^{−1})	D_{ij} (Å ⁸ ·kJ·mol ^{−1})
RIM	Na ⁺ –Na ⁺	25.4435	3.1546	2.340	101.172	48.1771
	Na ⁺ –Cl [−]	20.3548	3.1546	2.755	674.479	837.088
	Cl [−] –Cl [−]	15.2661	3.1546	3.170	6985.68	14,031.6
	Mg ²⁺ –Mg ²⁺	0.54392	7.6920	1.320	2.2230	0
	Mg ²⁺ –Cl [−]	0.60668	6.8960	2.620	200.403	0
	Cl [−] –Cl [−]	0.66944	6.2500	3.920	18,066.1	0
	Zn ²⁺ –Zn ²⁺	0.50208	8.3333	1.200	0	0
	Zn ²⁺ –Cl [−]	0.58576	7.1429	2.560	0	0
	Cl [−] –Cl [−]	0.66944	6.2500	3.920	18,066.1	0

In order to improve the force field, the polarization ion model (PIM) is researched by Madden and Salanne [34,35]. The PIM is shown by Wilson and Madden [28] with the shell model. In this model, the polarizability of ion is combined by representing an ion as the two-particle system with a charged core and a charged shell connected by an atomic spring. The induction effect is included in the polarization term. The pair potentials are described as

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - f_6(r) \frac{C_{ij}}{r_{ij}^6} - f_8(r) \frac{D_{ij}}{r_{ij}^8} + U_{pol} \quad (2)$$

$$U_{pol} = \sum_i \frac{|\mu_i|}{2\alpha_i} + \sum_{i,j} \left[\frac{z_i r_{ij} \mu_j}{r_{ij}^3} f_{ij}^4(r_{ij}) - \frac{z_j r_{ij} \mu_i}{r_{ij}^3} f_{ji}^4(r_{ij}) \right] + \sum_{i,j} \left[\frac{\mu_i \mu_j}{r_{ij}^3} - \frac{3(r_{ij} \mu_i)(r_{ij} \mu_j)}{r_{ij}^5} \right] \quad (3)$$

$$f_{ij}^n(r_{ij}) = 1 - c_{ij}^n \exp(-b_{ij}^n r_{ij}) \left[\sum_{k=0}^n \frac{(b_{ij}^n r_{ij})^k}{k!} \right] \quad (4)$$

where the α_i is the polarizability of the i ion and the $f_{ij}^n(r_{ij})$ is the Tang–Toennies dispersion damping functions [36]. In Equation (3), the first term is the energy cost for the deformation of electron cloud and the last two terms represent the charge–dipole and dipole–dipole energies.

The polarization effect is the deformation of the outer electron cloud caused by the influence of an external electric field [37]. The deformation of the electron cloud and the induced dipole of anions result in the structural changes of ions. Thus, the potential parameters in PIM of molten chloride salts should be restudy. Salanne et al. [35] used the

first-principles calculation method to obtain the PIM parameters of NaCl; also, Sharma and Wilson [30] provided the PIM parameters of MgCl₂ and ZnCl₂, which are listed in Table 2.

Table 2. Potential parameters of PIM for molten chloride salts.

Model	Pair	A_{ij} (kJ·mol ⁻¹)	B_{ij} (Å ⁻¹)	$b_{ij}^6 \& b_{ij}^8$ (Å ⁻¹)	C_{ij} (Å ⁶ ·kJ·mol ⁻¹)	D_{ij} (Å ⁸ ·kJ·mol ⁻¹)	$b_{ij}^4 \& b_{ji}^4$ (Å ⁻¹)	$c_j^4 \& c_{ji}^4$
PIM	Na ⁺ -Na ⁺	2625.5	9.4486	3.2125	674.536	836.279	0	0
	Cl ⁻ -Na ⁺	177,221	3.2616	3.2125	2732.73	3023.84	3.326	3.0, 0.7
	Cl ⁻ -Cl ⁻	722,275	3.3958	3.2125	8071.37	4520.43	0	0
	Mg ²⁺ -Mg ²⁺	70,888.5	2.9412	2.9412	126.836	0	0	0
	Mg ²⁺ -Cl ⁻	135,791	2.9412	2.9412	1091.94	0	3.118	1.4, 1.4
	Cl ⁻ -Cl ⁻	165,407	2.9412	2.9412	10,550.4	0	0	0
	Zn ²⁺ -Zn ²⁺	51,485.8	2.9412	2.9412	2306.11	0	0	0
	Cl ⁻ -Zn ²⁺	132,669	2.9412	2.9412	5154.14	0	2.929	1.0, 1.0
	Cl ⁻ -Cl ⁻	192,914	2.9412	2.9412	11,530.5	0	0	0
	$\alpha_{Na^+} = 0.90\alpha.u., \alpha_{Mg^{2+}} = 0.49\alpha.u., \alpha_{Zn^{2+}} = 2.85\alpha.u., \alpha_{Cl^-} = 20.0\alpha.u.$							

2.2. Simulation Details and Conditions

The RIM simulations were carried out by LAMMPS code [38] and the PIM simulations were performed by CP2K package [39]. All the simulations were carried out under the Periodic Boundary Condition (PBC), removing the side effects. The PPPM solver was used to conduct long-range corrections and the precise was set equal to 1.0×10^{-6} . The initial velocity was set up to obey Gaussian distribution. Newtonian equation of motion was solved by Verlet computing method [40]. The PIM simulations include the iterations for induced dipoles in CP2K, so that the computational complexity of PIM is higher than that of RIM. The number of ions, space group and the details of unit cell are listed in Table 3. The sizes of initial simulation boxes in RIM are $45.12 \times 45.12 \times 90.23$ Å, $40.60 \times 40.60 \times 83.76$ Å and $43.19 \times 43.19 \times 82.65$ Å for NaCl, MgCl₂, and ZnCl₂ respectively, while those in PIM are $22.56 \times 22.56 \times 45.12$ Å, $24.36 \times 24.36 \times 41.88$ Å, and $21.59 \times 21.59 \times 41.32$ Å. The cutoff distance was set to 20 Å and 10 Å for RIM and PIM, which is slightly shorter than the half of edge length. Although the ions in the PIM simulations are less than the RIM simulations, the PIM simulated results have higher accuracy, which will be illustrated in Section 3.

Table 3. Details of simulations for chloride salts at solid state.

Salts	Unit Cell Parameters						Space Group	Number of Ions	Code and Model
	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)			
NaCl	5.642	5.642	5.642	90	90	90	Fm-3m	8192	LAMMPS (RIM)
								1024	CP2K (PIM)
MgCl ₂	4.060	4.060	4.188	90	90	90	P-4m2	8640	LAMMPS (RIM)
								1080	CP2K (PIM)
ZnCl ₂	5.400	5.400	10.350	90	90	90	I-42d	6144	LAMMPS (RIM)
								768	CP2K (PIM)

The experimental melting points of NaCl, MgCl₂, and ZnCl₂ are 1073 K, 987 K, and 591 K [14]. For all the MD simulations, the system was firstly heated to 1700 K and then the system was cooled down to different temperature for simulations in NPT ensemble with the Nosé–Hoover thermostat and barostat at a constant pressure of 0.1 MP. The damping parameters were 100 fs and 500 fs for thermostat and barostat, respectively. After that, the system was simulated on the equilibrated cell volume in NVT ensemble. The simulated time step was set to 1 fs. In order to get precise calculation results, the equilibrium time lasted 1 ns for each simulation.

2.3. Properties Evaluation

2.3.1. Partial Radial Distribution Functions

Partial radial distribution function (RDF) is the typical local structure characteristic of liquid molten salts, which defines the distribution probability of j -type ions centered on i -type ion within a radius r

$$g_{ij} = \frac{1}{4\pi\rho_j r^2} \left[\frac{dn_{ij}(r)}{dr} \right] \quad (5)$$

where ρ_j denotes the number density of species j and n_{ij} denotes the number of j -type ions locating in a globular of radius r around the center of an i -type ion.

2.3.2. Coordination Number

The quantity of j -type ions locating in a globular of radius r_{min} around the center of an i -type ion is the definition of coordination number (CN), and r_{min} is the first peak valley position of RDF. N_{ij} can be calculated as

$$N_{ij}(r) = 4\pi\rho_j \int_0^{r_{min}} g_{ij}(r) r^2 dr \quad (6)$$

2.3.3. Density

The densities of molten salts could be computed from the formula

$$\rho = \frac{NM}{N_a V} \quad (7)$$

where M is the molar mass, N is the number of particles, N_a is the Avogadro's constant, and V denotes the equilibrated volume of the simulation system at the given temperature in NPT ensemble.

2.3.4. Specific Heat Capacity

Specific heat capacities were calculated from enthalpies with the formula

$$C_p = \left(\frac{\partial H}{\partial T} \right)_P \approx \frac{\Delta H}{\Delta T} = \frac{\Delta(U + PV)}{\Delta T} \quad (8)$$

where U is the total internal energy of the system consisting of kinetic energy and potential energy. Thus, the value of heat capacity can be calculated from the slope of enthalpy variation with temperature.

2.3.5. Thermal Conductivity

The reverse non-equilibrium molecular dynamics (RNEMD) method [22–24] can be applied to forecast thermal conductivities of molten salts. RNEMD method executes kinetic energy changes between the center and the bottom slabs and measures the inducing temperature gradient with linear response theory. At first, the system is equilibrated at object temperature for 1 ns. After that, the system is simulated in NVE ensemble to swap kinetic energy between different slabs for 5 ns. Thermal conductivity is calculated from the total transformation of kinetic energy and the ultimate temperature gradient [22] as

$$j_z = -\lambda \frac{\partial T}{\partial z} \quad (9)$$

$$\lambda = -\frac{\sum_{\text{transfer}} \frac{m}{2} (v_{\text{hot}}^2 - v_{\text{cold}}^2)}{2tL_x L_y (\partial T / \partial z)} \quad (10)$$

where t is the swap time of kinetic energy, L_x and L_y denote the lengths of simulation box in x and y directions, respectively.

2.3.6. Self-Diffusion Coefficient

Ion self-diffusion coefficient could reveal the ion transport characters of molten salts. In the cubic cell, the time-dependent mean square displacement (MSD) method [41] was carried out to compute the ion self-diffusion coefficient. In the recent researches [42,43], this method has been carried out to obtain the self-diffusion coefficients of molten salts, which agree well with the experiment results. MSD and ion self-diffusion coefficient are calculated as

$$M(t) = \left\langle \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2 \right\rangle \quad (11)$$

$$D = \frac{1}{6} \frac{d[M(t)]}{dt} \quad (12)$$

where the brackets $\langle \dots \rangle$ denote the time averages and r_i is the position of ion i .

3. Results and Analyses

3.1. Local Structures in PIM

To study the relation between microstructure and thermodynamics, the simulated partial radial distribution function (RDF) and coordination number (CN) are illustrated as Figures 1 and 2 and Table 4. It can be seen that all the RDFs have comparatively high first peaks and the height of other peaks decrease gradually, which demonstrates the disorder microstructures of molten chloride salts in long distance. For the ion pair of cation–anion, the first peak is sharper and the first valley is lower than that of cation–cation, indicating that cation–anion pair has a stronger interaction.

Figure 1 and Table 4 show the curves and characteristic values of RDFs by PIM simulation. Compared with the experiments by neutron diffraction technique [5], the first peak position of $\text{Na}^+ - \text{Na}^+$ from PIM is slightly overestimated by 3.8% at 1100 K. Near the melting point, RDFs of MgCl_2 in PIM also have a good agreement with the experimental values [25]. For ZnCl_2 , the first peak position of $\text{Zn}^{2+} - \text{Zn}^{2+}$ at 600 K is 3.80 Å [6], and the PIM simulation result is 3.79 Å. Thus, the PIM can provide the reasonable force field between particles and obtain the accurate structures of molten chloride salts. When the temperature increases, the first peak positions of RDFs for cation–anion decrease while those for cation–cation increase, showing that the distances between cations and anions become closer while the distances of cations become larger.

Figure 1. Cont.

Figure 1. PIM simulated results of RDF: (i) The RDF of cation–anion in PIM (a) NaCl; (b) MgCl_2 ; (c) ZnCl_2 . (ii) The RDF of cation–cation in PIM (d) NaCl; (e) MgCl_2 ; (f) ZnCl_2 .

Figure 2. Cont.

Figure 2. Coordination number in different temperature of molten chloride salts: (a) NaCl; (b) MgCl₂; (c) ZnCl₂.

Table 4. First peak positions of RDF for molten chloride salts.

Salt	Pair	T/K	PIM/Å	EXP/Å	Calculation Error
NaCl	Na ⁺ -Na ⁺	1100	4.05	3.90 [5]	3.8%
		1500	4.14	—	—
	Na ⁺ -Cl ⁻	1100	2.67	2.76 [5]	3.3%
		1500	2.64	—	—
MgCl ₂	Mg ²⁺ -Mg ²⁺	1000	3.95	3.81 [25]	3.7%
		1500	4.03	—	—
	Mg ²⁺ -Cl ⁻	1000	2.52	2.42 [25]	4.1%
		1500	2.50	—	—
ZnCl ₂	Zn ²⁺ -Zn ²⁺	600	3.79	3.80 [6]	0.3%
		1000	3.86	—	—
	Zn ²⁺ -Cl ⁻	600	2.49	2.29 [6]	8.8%
		1000	2.45	—	—

The coordination number curves of NaCl, MgCl₂ and ZnCl₂ in diverse working temperature condition are displayed in Figure 2. It can be observed that the coordination number diminishes from low temperature to high temperature in all simulations. For NaCl, the coordination number of Na⁺-Cl⁻ from PIM is 5.06 at 1100 K, which agrees well with the experimental value of 4.83 [5]. As the temperature rises, the coordination number of Mg²⁺-Cl⁻ changes from 5.21 to 4.72, while that of Zn²⁺-Cl⁻ changes from 5.36 to 5.02. According to the analysis of RDF and CN, the structure of molten chloride salts becomes looser under high temperature condition.

3.2. Polarization Effect on Structures

To research polarization effect on structures of molten chloride salts, RIM and PIM simulations are performed with the same conditions in Section 3.2. The simulation results of RDF and CN in RIM and PIM are displayed in Figure 3 and Table 5. The first peak position of Na⁺-Na⁺ is 4.05 Å from PIM and 4.10 Å from RIM, which are slightly different from experiment value of 3.90 Å. However, there is a large difference between PIM simulated distances of MgCl₂/ZnCl₂ and those in RIM. When polarization effect is included, the first peak position of Mg²⁺-Mg²⁺ changed from 4.38 Å in RIM to 3.95 Å in PIM, comparing with the experiment value of 3.81 Å. In Figure 3b, the first peak position of Zn²⁺-Zn²⁺ in PIM is 3.79 Å and fits very well with the experiment value of 3.80 Å, while that in RIM is 4.30 Å.

Figure 3. Simulated RDF and CN of molten chloride salts in PIM and RIM: (a) MgCl_2 at 1000 K; (b) ZnCl_2 at 600 K.

Table 5. First peak positions of cation–cation for molten chloride salts.

Pair	T/K	EXP/Å	RIM/Å	RIM Error	PIM/Å	PIM Error
Na^+-Na^+	1100	3.90 [5]	4.10	5.10%	4.05	3.80%
$\text{Mg}^{2+}-\text{Mg}^{2+}$	1000	3.81 [25]	4.38	14.9%	3.95	3.70%
$\text{Zn}^{2+}-\text{Zn}^{2+}$	600	3.80 [6]	4.30	13.2%	3.79	0.30%

In addition, the coordination number of $\text{Zn}^{2+}-\text{Zn}^{2+}$ in PIM is larger than that in RIM, indicating that the cation clusters in PIM are more compact than the cation clusters in RIM. That is to say, the large repulsive coulombic interactions between divalent cations lead to the larger distance between ions in RIM. As soon as the induced dipoles of anions are considered, the large Coulombic force of cation–cation can be screened by the polarization effect, which brings an extra contribution to take the shorter distance of cation–cation. The higher polarizability of Zn^{2+} leads to the stronger polarizable force between ions, so that the PIM performs better to derive the first peak position of $\text{Zn}^{2+}-\text{Zn}^{2+}$. In Figure 3, the second peaks of $\text{Mg}^{2+}-\text{Mg}^{2+}$ and $\text{Zn}^{2+}-\text{Zn}^{2+}$ in PIM show characteristic of the intermediate-ranged order, which reveals the network structure of MgCl_2 and ZnCl_2 . Besides, the snapshots of network structures for molten salts are plotted in Figure 4. Thus, the PIM simulations are more reasonable and correspond better to the physical laws.

Figure 4. Snapshots of ion local structures in molten chloride salts: (a) MgCl_2 at 1000 K, Mg^{2+} in orange, Cl^- in green; (b) ZnCl_2 at 600 K, Zn^{2+} in blue, Cl^- in green.

3.3. Density

Density is the critical thermodynamics property of molten chloride salts, which reflects the change of the system volume. The experimental melting points of NaCl, MgCl₂, and ZnCl₂ are 1073 K, 987 K, and 591 K [14]. The systems were heated to molten state at 1700 K in NPT ensemble. After that, the systems in both models were cooled down to the target temperature and equilibrated in the NPT ensemble for 1 ns. Specific heat capacity was also computed with the similar method.

In Figure 5, the simulated densities of molten chloride salts are compared with the experimental results by Yaffe et al. [44], Janz et al. [14] and Angell et al. [45]. It is obvious that the density is in linear negative correlation with temperature. For molten ZnCl₂, the PIM simulated densities decrease from 2.50 g/cm³ at 600 K to 2.28 g/cm³ at 1000 K, which is slightly smaller than the experiment values by 1.1%. When the temperature is over 773 K, the RIM simulated densities of ZnCl₂ become into a gross difference from experiments. Besides, the slope of density in RIM is different from that in PIM for MgCl₂ and ZnCl₂. Combined with the analysis of polarization effect on local structure in Section 3.2, the large Coulombic interactions of ions induce the longer distance between cations in RIM for lack of the polarization effect. In addition, the looser coordination structures and longer distance between cations in RIM cause the greatly larger volume of system at high temperature, so the densities from RIM are much smaller than real values. As listed in Table 6, the fit formulas of PIM simulation results agree well from the experimental data, with the mean percentage errors of 0.3%, 9.5%, and 1.1% for NaCl, MgCl₂, and ZnCl₂ respectively. The error of MgCl₂ is larger than others, which may be caused by the error of the fitting potential parameters searched for MgCl₂. The polarization effect included in the potential of MgCl₂ can bring extra contribution to screen repulsive Coulombic force, but the repulsive force is still slightly larger and induced larger volume for MgCl₂.

Figure 5. Simulated and experimental density results of molten chloride salts. (a) NaCl; (b) MgCl₂; (c) ZnCl₂.

Table 6. Densities of molten chloride salts in experiment and simulation.

Salts	Range (K)	EXP	RIM Error	PIM Density Function (g/cm ³)	PIM Error
NaCl	1080–1500	Ref [44]	6.1~6.3%	$\rho = 2.145 - 5.439 \times 10^{-4}T$	0.1~0.6%
MgCl ₂	1000–1500	Ref [14]	12.5~19.4%	$\rho = 1.976 - 4.614 \times 10^{-4}T$	9.2~9.8%
ZnCl ₂	600–1000	Ref [45]	0.5~8.8%	$\rho = 2.836 - 5.538 \times 10^{-4}T$	0.7~1.6%

3.4. Specific Heat Capacity

As shown in Figure 6, the enthalpy variations of molten chloride salts are in linear relation with temperature, which indicates the specific heat capacity is constant from Equation (8). Listed in Table 7, the specific heat capacities of NaCl, MgCl₂ and ZnCl₂ in PIM are respectively 65.5 J/(mol·K), 99.7 J/(mol·K) and 111.7 J/(mol·K) and their errors are 2.2%, 7.8% and 10.7%. Simulated heat capacities of NaCl in RIM and PIM are both in good agreement with experiment [24], while the results of MgCl₂ and ZnCl₂ in RIM are 38.8% and 32.9% larger than the experimental data [14,46]. In conclusion, the polarization effect can reflect the accurate ability of thermal storage for molten divalent chloride (MgCl₂ and ZnCl₂).

Figure 6. Enthalpies of MgCl₂ and ZnCl₂ with temperature in PIM.**Table 7.** Heat capacities of molten chloride salts in experiment and simulation.

Salts	EXP (J·mol ⁻¹ ·K ⁻¹)	RIM (J·mol ⁻¹ ·K ⁻¹)	Error of RIM	PIM (J·mol ⁻¹ ·K ⁻¹)	Error of PIM
NaCl	67.0 [24]	68.2	1.9%	65.5	2.2%
MgCl ₂	92.5 [14]	128.4	38.8%	99.7	7.8%
ZnCl ₂	100.9 [46]	134.1	32.9%	111.7	10.7%

3.5. Thermal Conductivity

The RNEMD method was used to compute the thermal conductivities. To input a heat flux and obtain a temperature distribution, the simulation box was evenly split into 20 bins along the 'z' axis. The 1st bin was defined as the 'cool' bin, and the 11th bin was defined as the 'hot' bin. The heat flux was generated by swapping the kinetic energy of an atom in the cool bin and one in the hot bin, which results in the increasing temperature in the hot bin and decreasing temperature in the cool bin [22]. After equilibrating for 1 ns, the simulations transferred the kinetic energy over 5 ns in NVE ensemble. Different swap rates were tried for the simulations, and it was found that kinetic energy swap rates between 100 and 400 time steps brought about the linear temperature gradients. The total average kinetic energy exchange as well as the slopes of linear temperature gradient in Figure 7 were

substituted into Equation (10) to calculate the thermal conductivities. The swapping rates are same for all molten chloride salts at 400 fs.

Figure 7. Mean temperature gradient in different temperature with kinetic energy swap rate: (a) Different swap rates; (b) MgCl_2 at 400 time steps; (c) ZnCl_2 at 400 time steps.

In order to approximate the finite-size effect on thermal conductivity of molten chloride salt by RNEMD method, a series of different size simulations are carried out, and the lengths in x and y dimension are the same while the length of z dimension is changed. The size-dependent thermal conductivities of molten chloride salt are displayed in Figure 8. It is obvious that the simulated thermal conductivity increases non-linearly with increasing length of z dimension and approaches a stable value when the length of z dimension is over 100 Å.

As shown in Figure 9, the thermal conductivities of molten chloride salts are in negative linear correlation with temperature. For molten NaCl , the simulated results of RNEMD decrease from 0.571 W/(m·K) to 0.424 W/(m·K). There is a mean percentage error of 8.1% between simulated results and experiments from Nagasaka et al. [15], so it proves that RNEMD method is suitable for calculating the thermal conductivities. Compared with the experimental values from Singh et al. [47] and Cornwell [48], the RNEMD simulated results of MgCl_2 and ZnCl_2 agree well and are completely predicted over the whole operating temperature. In general, the simulated thermal conductivities of molten chloride salts in different temperature are in the range of 0.213–0.571 W/(m·K).

Figure 8. Length dependence of thermal conductivities on L_z .

Figure 9. Thermal conductivities of molten chloride salts in different temperatures.

3.6. Ionic Self-Diffusion Coefficient

In order to research the transport property of molten chloride salt ions, the ionic self-diffusion coefficients were calculated for 1 ns in NVT ensemble with the mean square displacement (MSD) method. It is evident that the MSD presents positive linear temperature dependence in Figure 10. Compared with experiments from Janz et al. [14], there are mean percentage errors of 5.9% and 5.7% between simulated results and experiments of Na^+ and Cl^- from 1100 K to 1500 K in Figure 11a, respectively. In Figure 11b, both Zn^{2+} and Cl^- are difficult to move near melting point with quite small self-diffusion coefficients, because of the glassy state with the network structure [49], while Na^+ and Cl^- can move more easily at melting point without the network structure. When the temperature increases, the ions become easier to move for the break of network structure. It can be seen that self-diffusion coefficients of all cations are larger than Cl^- in Figure 11, resulting from the limited mobility of Cl^- by the larger mass and ionic radius.

Figure 10. PIM simulated results of MSDs in different temperature: (a) Na ion and Cl ion; (b) Mg ion and Cl ion; (c) Zn ion and Cl ion.

Figure 11. PIM simulated results of self-diffusion coefficients in different temperature: (a) Na ion and Cl; (b) MgCl₂ and ZnCl₂.

4. Conclusions

Microstructure and thermophysical properties of molten chloride salts (NaCl, MgCl₂, and ZnCl₂) were researched by molecular dynamics simulations with RIM and PIM. Compared with results from RIM, PIM simulations reveal that the polarization effect

brings an extra contribution to screen the large Coulombic interactions, which makes the shorter distance between cations. For divalent chloride, the high charge density of divalent cation leads to more deformation of the electron cloud, so that the polarizable force between anion and cation is stronger. The RIM simulations are unable to precisely predict the densities and heat capacities of divalent chloride (MgCl_2 and ZnCl_2) for lack of considering polarization effect, while PIM simulations improve the accuracy of simulated densities and heat capacities. Thus, the PIM performs better for molten divalent chloride. There are 0.3%, 1.1%, and 9.5% mean errors between PIM simulated densities and experiments for NaCl , ZnCl_2 , and MgCl_2 respectively, and those of heat capacities are 2.2–10.7%. As the temperature rises, the distance between cations increases and the structure turns into loose state, so the density and thermal conductivity decrease, while the ionic self-diffusion coefficient increases, which agree well with the experimental results. This work provides an alternative way to build the property database of molten chloride salts for the precise design and regulation of high-temperature thermal storage system.

Author Contributions: Conceptualization, J.L.; Methodology, G.P.; Software, S.Y.; Validation, S.Y., G.P., and S.L.; Formal analysis, S.Y.; Investigation, J.L.; Writing—review and editing, J.L.; Project administration, J.D.; Funding acquisition, J.L. and W.W. All authors have read and agreed to the published version of the manuscript.

Funding: This paper is supported by National Natural Science Foundation of China (52036011, U1601215), and Natural Science Foundation of Guangdong Province (2017B030308004).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

A	BMH repulsive parameter
B	BMH repulsive parameter
C	Van der Waals parameter
D	Van der Waals parameter
L	length dimension
n	number of particles
q	charge of ion
r	distance between ions
T	temperature of the system
t	simulation time
U	Born–Mayer–Huggins–Tosi–Fumi potential
V	volume of the system
v	velocity

Greek symbols

α	polarizability of the ion
ρ	number density
σ	BMH repulsive parameters

Subscripts

i	ion i
j	ion j
k	slab k
x	direction x
y	direction y

Abbreviations

BMH	Born–Mayer–Huggins
CN	coordination number
PIM	polarizable ion model
RDF	partial radial distribution function
RIM	rigid ion model

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