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NPT Simulation and Hypernetted-Chain Calculations of SrCl₂

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Abstract. Transition to fast-ion conducting phase and liquid phase of SrCl₂ was investigated the molecular dynamics simulation in constant pressure-temperature ensemble (NPT) and hypernetted-chain theory using the fully ionic rigid ion potential widely exist in literature. Both, the redig transition and melting temperatures were over estimated. Results suggest that a new pair potential is needed to model the interactions in SrCl₂

Keywords: Molecular dynamics, NPT ensemble, SrCl₂, hypernetted-chain.

PACS: 61.20.Ja; 61.43.-j; 66.10.-x; 66.30.-h; 65.40.De

INTRODUCTION

There are limited number of study on physical and chemical properties of strontium chloride (SrCl₂). It is an interesting material as it undergoes a second order phase transition at about 1100 K below the melting temperature. Due to the liquid like value of diffusion constant at this phase it is called as superionic conductor. Dixon and Gillan have studied SrCl₂ using molecular dynamic simulation technique with Born-Mayer type rigid ion potential [1,2,3]. They have studied the fast-ion conduction and the central peak appears as a component of the partial dynamical structure. It has been concluded that even in the highly conducting state anions are still localized in their regular lattice sites [2], the diffusion has been described in term of the motion of vacancy and interstitial defects [1] and the central peak is present above the fast ion transition temperature but absent below it [3]. The local structure of solid and molten SrCl₂ have been investigated by x-ray absorption fine structure technique together with molecular dynamics simulation [4] and the fast ion conduction state has been observed at 1073 K. In the present work, hypernetted-chain approximate theory of liquids is applied to investigate the structural properties of SrCl₂ at molten phase. Temperature dependence of ionic diffusion, thermal expansion and heat capacity were also calculated in the constant pressure-temperature (NPT) ensemble molecular dynamics simulation

POTENTIAL MODEL

The pair potential used to model the interactions in this work is Born-Mayer-Huggins potential form [7]. The functional form is given as

$$\phi_{\alpha\beta} = A_{\alpha\beta} \exp\left(-\frac{r}{\rho_{\alpha\beta}}\right) + \frac{Z_{\alpha}Z_{\beta}}{r} - \frac{C_{\alpha\beta}}{r^6}. \quad (1)$$

The repulsive force has its origin in the opposition to overlapping of closed shells of electrons, as required by the Pauli exclusion principle. Second term is the Coulomb interactions and the final term represent van der Waals the dipole-dipole interactions where $Z_{\alpha\beta}$ – the effective ionic charges, $A_{\alpha\beta}$ and $\rho_{\alpha\beta}$ – strength and hardness of the repulsion, respectively [8].

MOLECULAR DYNAMICS SIMULATION

The MD simulation of SrCl₂ have been carried out by using 1500 ions, 500 anions and 1000 cations in a cubic box sized L which is determined by the density. The calculations were carried out by the popular molecular dynamics code called MOLLY [9]. The system velocity is scaled for 10⁵ MD steps. Then we start accumulating radial distribution function information and the thermodynamic averages for 2x10⁵ MD steps. Equation of motion was integrated using Beeman's algorithm with the unit time step 1.0x10⁻¹⁵s. Born-Mayer-Huggins form pair potential [2] has been used in simulation. The simulations were performed in the NPT applying the temperature rescaling procedure. Once the system reached equilibrium –of which simulations were run for 50 ps- we calculate the properties of interests by averaging over the following 50 ps. The temperature is varied at 100 K intervals

RESULT AND DISCUSSION

The parameters of the full ionic rigid ion potential were taken from Gillan and Dixon [1,8] and are given in Table 1. Figure 1 shows the radial distribution functions (RDF) of SrCl₂ at 1073 K and 1273 K for the present study, previous MD simulation and Monte Carlo simulation and experimental data [10]. Results show that RDFs obtained from our NPT simulation agrees well with XAFS simulation results [4] at 1073 K. However, there are large discrepancies between the NPT results and the rest at 1273 K especially for $G_{\text{Sr-Sr}}(r)$. Agreement is observed when the NPT temperature was reached to 1600 K. RDFs indicate that fast-ion conduction phase is realized at about 1273 K and system is completely melted at about 1600 K

TABLE 1. Potential parameter for SrCl₂ [1].

$\Phi_{\alpha\beta}$	$A_{\alpha\beta}$ (eV)	$\rho_{\alpha\beta}$ (Å)	$C_{\alpha\beta}$ (eVÅ ⁶)
Sr-Sr	0.0	0.0	0.0
Cl-Cl	1227.2	0.3214	1.69
Sr-Cl	774.14	0.3894	0.0

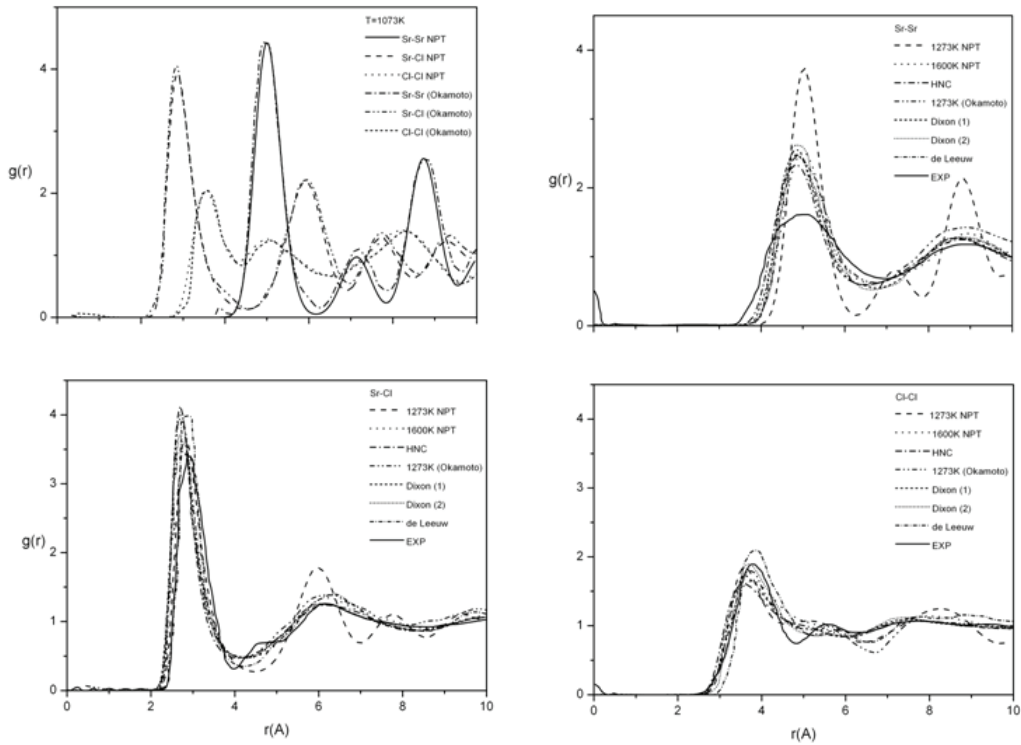


FIGURE 1. Radial distribution functions of SrCl_2

The self diffusion coefficients have been calculated from Nernst-Einstein relation and are presented in Figure 2. Although the Cl diffusion is higher than that of Sr there is no great difference. In addition, we have also calculated the constant pressure heat capacity from $C_p(T) = (\partial E/\partial T)_p$.

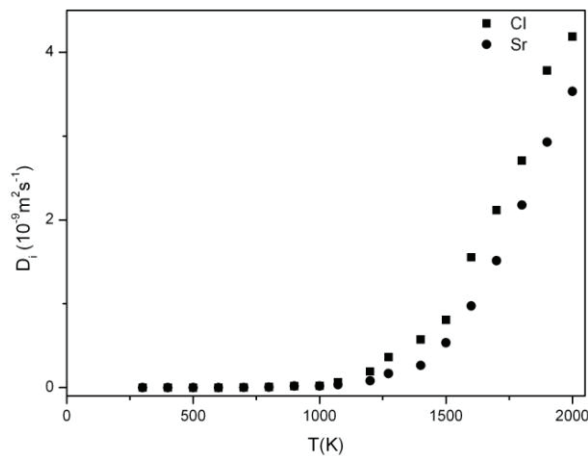


FIGURE 2. Self diffusion coefficients of Sr and Cl at different temperature

Temperature dependence of $C_p(T)$ is shown in Figure 3. The λ -shape peak is clearly emerged at about 1500 K which is indication of the transition from the ordinary solid phase to the superionic conducting phase.

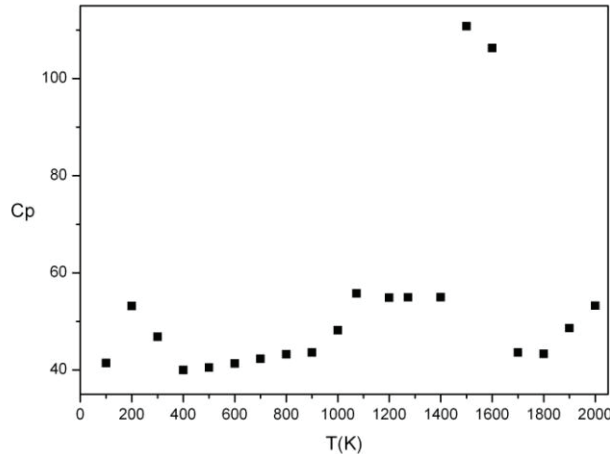


FIGURE 3. Heat capacities of SrCl_2 different temperatures

CONCLUSIONS

NPT simulation with the widely used existing rigid ion potential in literature estimates the superionic phase transition. Melting transition temperature is a few hundred degree above the recommended values. Therefore, we suggested that newly parameterized potential needed to describe the interactions for SrCl_2

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