Melting line and thermodynamic properties of a superionic compound SrCl$_2$ by molecular dynamics simulation

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**ABSTRACT**

In the present paper we study the thermodynamic properties of superionic conductor SrCl$_2$ at high temperatures by means of molecular dynamics method. Firstly, we calculate the melting line. Then we compute the equations of state and the response functions (heat capacity, thermal expansion coefficient, etc.) at the temperatures up to the melting. We show that the response functions show maxima or minima. Moreover, the temperature of transition into the superionic state only moderately depends on the pressure.

Superionic conductors are crystalline ionic salts which demonstrate high electrical conductivity [1]. Their high electrical conductivity is related to very different mobilities of two types of ions in the salt: while one type of the ions remains mostly fixed at the lattice sites, another type demonstrates high diffusion. Depending on the substance the mobile type of particles can be either cation or anion. Importantly, superionic compounds are widely used in modern energetics as solid electrolytes in the batteries. Because of this, a deep understanding of their properties is of great importance for both fundamental research and technological applications [2,3].

A wide class of superionic compounds is the one of salts with the structure of fluorite [4–8]. These substances have a chemical formula CA$_2$ where C means the cation and A – the anion. In the fluorite structure the cations occupy the cites of a Face Centred Cubic (FCC) lattice, while the anions are located in the tetrahedral holes. Numerous salts with composition CA$_2$ demonstrate the fluorite structure, for instance, fluorite itself CaF$_2$, BaCl$_2$, PbO$_2$, SrCl$_2$, and so on. The mobile species of the superionic compounds with fluorite structure is the anion.

At low temperatures the superionic compounds do not demonstrate high conductivity. However, at certain temperature they experience a phase transition into the conducting state. Typically phase transitions are related to some thermodynamic peculiarities, such as the maximum of the heat capacity. The peak of heat capacity in the vicinity of the transition into superionic state was reported in a number of experimental [9,10] and theoretical [11–15] works. Several theoretical models were proposed to describe the behaviour of this peak. However, other thermodynamic response functions have been studied much less and therefore they still require a careful investigation.

In a preceding paper we discussed the properties of molten SrCl$_2$ [16]. In the present paper we study the thermodynamic properties of the superionic conductor SrCl$_2$ by means of molecular dynamics method. We calculate the melting line and thermodynamic response functions (heat...
capacity, thermal expansion, etc.). We show that close to the melting line this substance demonstrates maxima or minima of several thermodynamic properties. The temperatures of these peculiarities are rather far from the temperature of transition into conductive state. Because of this we assume that these maxima and minima are not related to this transition, but are induced by some other mechanisms, which means that the behaviour of fast ions conductors is rather complex even far from the point of transition into the conductive state.

We simulate a system of 4116 particles (i.e. 1372 atoms of Sr and 2744 atoms of Cl) in a cubic box with periodic boundary condition by means of molecular dynamics methods. We use the Born-Mayer-Huggins potential to describe the interaction between the species. It has the form

$$U_{\alpha\beta}(r) = \frac{Z_\alpha Z_\beta e^2}{r} + A_{\alpha\beta} e^{-r/r_0} - \frac{C_{\alpha\beta}}{r^6},$$

(1)

where $\alpha$ and $\beta$ mark different species (Sr or Cl), $Z$ is the charge of the nuclei and $e$ is the elementary charge. Other parameters of the potential are taken from Ref [17]. They are given in Table 1. Importantly, Refs. [15,17] themselves report a computational study of the behaviour of SrCl$_2$. In particular, the authors also discuss the anomaly of the isochoric heat capacity. However, they do not discuss the behaviour of isobaric heat capacity and thermal expansion coefficient. They also do not calculate the melting line.

All simulations of the present work are performed using lammps simulation package [18]

We start our discussion from simulation of SrCl$_2$ at ambient pressure and different temperatures. The system is simulated at fixed pressure ($P = 1$ bar) and different temperatures for 10 ns with the

![Figure 1](image)

**Figure 1.** Equation of state of SrCl$_2$ at ambient pressure and different temperatures. The jump of the density signalises that melting of the system takes place.

| $A_{Sr-Sr}$ (eV) | 0.0 |
|------------------|-----|
| $A_{Sr-Cl}$ (eV) | 774.14 |
| $A_{Cl-Cl}$ (eV) | 1227.2 |
| $p_{Sr-Sr}$ | $-$ |
| $p_{Sr-Cl}$ ($\text{Å}$) | 0.3894 |
| $p_{Cl-Cl}$ ($\text{Å}$) | 0.3214 |
| $C_{Sr-Sr}$ (eV Å$^6$) | 0.0 |
| $C_{Sr-Cl}$ (eV Å$^6$) | 0.0 |
| $C_{Cl-Cl}$ (eV Å$^6$) | 1.69 |

**Table 1.** Parameters of potential of Equation (1) used in the present study. Note that since $A_{Sr-Sr}$ is zero, the parameter $p_{Sr-Sr}$ is not required.
Figure 2. (a) Example of calculations of the melting point by Z-method. \( \rho = 2.7 \text{ g/cm}^3 \). (b) Melting line of SrCl\(_2\) obtained by Z-method calculations.

Figure 3. Equation of state of SrCl\(_2\) along several isochores. Jump at the isochore \( \rho = 2.9 \text{ g/cm}^3 \) signalises that melting of the system takes place. The points at the temperature above the jump correspond to the liquid state while below to solid. The data for liquid for other isochores are removed from the plot to make it clearer.
time step 1 fs. In these simulations we evaluate the average density of the system and monitor the structure. The dependence of the density on the temperature is shown in Figure 1. One can see that the density experiences a jump at $T = 1560$ K where it is $\rho = 2.64$ g/cm$^3$. After the jump at $T = 1600$ K the density is $\rho = 2.2$ g/cm$^3$. From investigation of the structural properties we observe that at low temperatures the system is solid, while at the high ones it is liquid. Although this method does not give accurate estimation of the melting point, it allows us to estimate the lowest density of solid SrCl$_2$ to be studied.

Having estimated the melting density at ambient pressure, we calculate the melting line on a more precise ground. For doing this we employ a so-called Z-method [19]. The density varies from $\rho_{\text{min}} = 2.6$ g/cm$^3$ up to $\rho_{\text{max}} = 3.05$ g/cm$^3$. The system is simulated for 10 ns with the time

Figure 4. (a) Equation of state of SrCl$_2$ along several isotherms. (b) Equation of state along several isobars.
Figure 5. (a) Thermal expansion coefficient of SrCl$_2$ along several isobars. (b) Isobaric heat capacity along several isobars. (c) Isochoric heat capacity along several isotherms.
step 1 fs in microcanonical ensemble (constant number of particles N, energy E and volume V). According to the Z-method, the dependence of pressure on the temperature has a Z-like shape at the melting point. Figure 2(a) shows an example of Z-method calculations for $\rho = 2.7 \text{ g/cm}^3$. One can see that the melting temperature is $T_m = 1817 \text{ K}$ and the melting pressure is $13483 \text{ bar}$. The melting line is given in Figure 2(b). Note that the melting temperature at ambient pressure obtained by Z method is $T_m = 1147 \text{ K}$, while direct simulation gave the value of $1560 \text{ K}$. This is related to the effects of superheating in direct simulations.

Another important point in the melting line of the system given in Figure 2(b) is its very high slope (about $50 \text{ K/kbar}$). We are not aware of any experimental investigations of melting line of $\text{SrCl}_2$ under elevated pressure, and therefore we are not able to make a comparison with experimental data. However, a computational model used in the present paper is fitted to the ambient pressure properties only. Because of this one can expect that the calculations under high pressure demonstrate some deviations from the experimental data.

We calculate the equation of state of $\text{SrCl}_2$ along several isochors from $T_{\text{min}} = 1000 \text{ K}$ up to $T_{\text{max}} = 2600 \text{ K}$. Examples of these equations of state are given in Figure 3(a). At some points the pressure has negative values. These points are discarded from the plot. A jump in the equation of state (shown only for $\rho = 2.9 \text{ g/cm}^3$) means crossing of the melting line. The points corresponding to liquid are also discarded since the focus of the present study is related to the crystalline state only. These equations of state do not demonstrate any unusual features: pressure monotonously increases with temperature.

In our study we simulate almost 200 data points in $(\rho,T)$ plane along several isobars. It allowed us to find the properties of the system along other thermodynamic paths like isotherms and isobars by interpolation of our data. Simple linear interpolation was enough to obtain the data along isotherms and isobars. Numerical differentiation of the pressure, internal energy or enthalpy was used to calculate the thermodynamic response functions. Figure 4 shows the equation of state of solid $\text{SrCl}_2$ along several isotherms and isobars.

Although the equation of state does not demonstrate any peculiarities neither along isobars, nor isotherms and isobars, the thermodynamic response functions do demonstrate some maxima and minima. We calculate the thermal expansion coefficient $\alpha_p = \frac{1}{T} \left( \frac{\partial V}{\partial T} \right)_p$, the isochoric heat capacity $c_V = \left( \frac{\partial U}{\partial T} \right)_V$, where $U$ is the internal energy of the system, and the isobaric heat capacity $c_p = \left( \frac{\partial H}{\partial T} \right)_V$, where $H = U + PV$ is the enthalpy of the system. The results of these calculations are given in Figure 5(a–c). One can see that all three functions demonstrate maxima and minima.

The location of the maxima and minima of the response functions is of a great interest for characterisation of the thermodynamic properties of the system. Figure 6 shows the points of

![Figure 6](image-url)
maxima and minima of $\alpha_P$, $c_P$ and $c_V$ on the phase diagram of the system. One can see that the lines of maxima of $c_V$ along isochores and minima of $\alpha_P$ along isobars are almost isotherms with $T_{c_V - \text{max}} = 1300$ K and $T_{\alpha_P - \text{min}} = 1180$ K. The line of minima of $c_P$ along isobars is located close to the melting line and goes almost parallel to it.

The most interesting is the behaviour of the line of maxima of the isobaric heat capacity $c_P$. The transition to the superionic state in $\text{SrCl}_2$ is the second-order one and it is expected that the transition temperature is close to the maximum of $c_P$. From Figure 6 one can conclude that the transition temperature demonstrates rather weak temperature dependence and therefore the transition to the superionic state should be expected to take place somewhere deeper under the melting line under elevated pressure.

Finally we evaluate the diffusion coefficients of the species at different temperatures. Figure 7(a, b) shows the mean square displacement of chlorine and strontium at the density $\rho = 2.8 \text{ g/cm}^3$ and

![Graph](image-url)

**Figure 7.** Mean square displacement of (a) chlorine and (b) strontium at $\rho = 2.8 \text{ g/cm}^3$ and different temperatures. In both cases the temperatures from $T = 1000$ K (the lowest curve) to 2000 K (the highest curve) with the step $\Delta T = 100$ K are shown.
the temperatures from 1000 K to 2000 K, i.e. up to the melting point. One can see that even at $T = 1000$ K the chlorine has finite diffusion coefficient, the diffusion coefficient of strontium at this temperature is apparently zero. Therefore, the system is in conducting state at this temperature. This is consistent with Ref [17], where the transition from insulating state to the conducting one is estimated to be about 1000 K. The mean square displacement of strontium remains shoulder-like up to the temperature $T = 1900$ K where a slight deviation at long times appears. This temperature is close to the melting point and therefore moderate diffusion of Sr due to the formation of defects can appear in the system. Figure 8 shows the diffusion coefficient of chlorine at $\rho = 2.8$ g/cm$^3$ and different temperatures. The diffusion of Sr is nearly zero at all these temperatures.

In conclusion, we performed a molecular dynamic study of thermodynamic properties of the melting line and thermodynamic properties of superionic conductor $SrCl_2$. We calculated the melting line and the location of maxima and minima of thermal expansion coefficient, isobaric and isochoric heat capacities. We find that the temperature of the transition to the superionic state demonstrates very weak dependence on pressure and therefore the transition goes deeper under the melting line at elevated pressure. The explanation of these effects should be searched into the behaviour of the defects in the system which requires further simulations.

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**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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