THE EFFECTIVE PAIR POTENTIAL CALCULATIONS OF MOLTEN NaCl AND AgI

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In this work, we have calculated effective pair potentials for different Z values of molten NaCl and AgI. We used the Huggins-Mayer potential form parametrised by Fumi and Tosi for NaCl and the Vashishta-Rahman potential form for AgI. The interionic interactions in this last system have been modelled with the use of a semi-empirical rigid ion potential based on the functional form originally proposed by Vashishta and Rahman in 1978. The results show excellent agreement with those reported in other works.

1. Introduction

Molten salts are of considerable interest, not only from the technological point of view, but also from the standpoint of satisfying a fundamental curiosity. Structural studies of molten salts (such as alkali halides) by x-ray and neutron diffraction have been undertaken as part of a general program to determine the properties of molten salts [1, 2]. Consequently, we need the three partial structures (which characterise two-component systems) to discuss quantitatively the detailed structure. Recent studies using the neutron isotope enrichment technique have provided such information, however the neutron diffraction results are not covered in the previous studies [2, 3].

Molten salts are in many respects the simplest class of ionic liquids. We shall consider only the case in which there is a single cation and a single anion species, of which the molten alkali halides are the commonest and best understood examples. Molten salts are characterized by large binding energies and high melting temperatures and by ionic conductivities of the magnitude order 1 $\Omega^{-1}cm^{-1}$. There exist also crystalline salts that have conductivities comparable with those of the molten phase. These are the so-called "fast ion" conductors or "solid-electrolytes" in which one of the ionic species becomes liquid-like in its behaviour above a certain temperature [4].

The computer simulation studies of molten salts by Woodcock and Singer [5] and theoretical studies by Lantelme et al. [6] have been reported. The theoretical aspects have been studied by Dixon and Sangster[7] considering polarizability of the cation in molten salts.

Neutron-scattering experiments rely on the use of isotopic substitution to separate the contributions of the partial structure factors in the total measured intensity [8]. The similar experiments have been carried out for the alkali-earth halides [9] and the results are in good agreement with those obtained by computer simulations based on rigid-ion models [10].

Ideally, the alkali halides are the most interesting systems since they are known as fully ionized systems. In the computer simulation one assumes an effective pair potential of Huggins-Mayer type [11] and, then, one calculates the pair distribution function, which can be compared with the experimental data. The parameters of the pair potential are generally estimated from the information in the crystalline state. As previously shown, the agreement between calculation and experiment is good, and this implies that the used pair potential is valid. The above mentioned

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effective pair potential in liquid metals and molten salts have been reported as a semi-empirical method, i.e., the pair potential is numerically estimated from experimental structure data using an integro-differential equation such as the Percus-Yevick, Hypernetted Chain and Born-Green equations [12].

This paper is concerned with calculations of effective pair potentials for different Z values of molten NaCl [11] and AgI [13]. In this work we consider the changes produced by different ionic charges. In the case of NaCl and AgI, we consider the fully ionized case (|Z| = 1), a partially or incompletely- ionized case (|Z| < 1) and the neutral case (|Z| = 0). The same potential form was used to study the molten silver and copper halides [14-18]. The potential was originally proposed by Vashishta and Rahman [19] for studying the K to ϑ transition in AgI. Parrinello et al. [20] have constructed a single set of effective inter atomic pair potentials which are given in section 2 to describe both ϑ-AgI and the ϑ-K phase transition in AgI. The iodine ions are treated as polarizable but the silver ions are not. The calculations have been carried out using the hypernetted chain approximation, which gives accurate results in the molten salt regime [21].

The layout of the paper is as follows; in section 2 are presented the basic elements of theory in which particular attention is given to the details of the potentials. In section 3 we discuss the results of our calculations for $\phi_{ij}(r)$ for different Z values of these systems. The conclusions are draw in section 4.

2. Theory

The use of effective pair potentials in the study of condensed matter have shown that in order to determine or approximate the effective pair potential it is essential to have good and, preferably, simple initial guess. The simplest of all potential models is the hard sphere (HS) [22] potential, which represents a pure repulsive interaction and plays an important role in the theory of liquid structure. The HS potential is defined as

$$\phi_{ij}(r) = \begin{cases} \infty & r < d_{ij} \\ 0 & r > d_{ij} \end{cases} \tag{1}$$

where $d_{ij} = \frac{1}{2}(d_{ii} + d_{jj})$ is the closest approach distance. Despite the fact that attractive interactions must be included in all real fluids, there are several related reasons why HS potential can be used. Firstly, all real fluids have potentials that are strongly repulsive at short distance and an adequate theory must be able to deal with this feature. Secondly, at high density, for weakly interacting fluids, the structure of the liquid at a given volume and temperature is largely determined by the repulsive part of the potential. The third reason is that the repulsive force model serves as a starting point or the reference system for the perturbation theory of liquids.

The essential features of ionic liquids (molten salts or electrolytes) can be simply modelled by the charged hard spheres model (CHS). The effective pair potential between two ionic species i and j is assumed to be,

$$\frac{\phi_{ij}(r)}{k_B T} = \begin{cases} \infty & r < d_{ij} \\ \dfrac{Z_i Z_j \Gamma a}{Z^2 r} & r > d_{ij} \end{cases} \tag{2}$$

where

$$Z^2 = \sum_i X_i Z_i , \tag{3}$$

a is the mean ion sphere radius,

$$a = \left(\frac{3}{4\pi\rho_0} \right)^{1/3} \tag{4}$$

and the plasma parameter Γ is given by

$$\Gamma = \frac{Z^2 e^2}{k_B T a} \cdot \tag{5}$$

For the rare gas liquids an approximate description of the pair potential is known as the Lennard-Jones potential $\phi(r)$,

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{6}$$

which contains an attractive term and a repulsive term in accordance with the Van der Waals form. The exponent of the repulsive term, 12, is arbitrarily chosen for convenience. It is free to choose the parameter ε and σ in order to fit selected properties of the real system. In the case of liquids metals, detailed form of the effective ion-ion interaction is strongly influenced by effects arising from the presence of a gas of conducting electrons. Without going into the detailed assumptions, the qualitative form of the potential is a short range repulsion, a deep attractive well and a long range oscillatory tail [23,24].

The Huggins-Mayer form of the potential, as parameterised by Fumi and Tosi [11], provides a good starting point for describing the interactions in the alkali halides like NaCl. The general form of the Fumi-Tosi (FT) potentials is:

$$\phi_{ij} = B_{ij}\, exp\left(-\frac{r}{\eta_{ij}} \right) + \frac{Z_i Z_j}{r} - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} \cdot \tag{7}$$

It incorporates an exponential form for the overlap repulsive forces, with the coulomb forces between the charged ions and Van der Waals attractions. FT considered those alkali halide salts which crystallise in the rock salt structure. Briefly, it was assumed that each ion carries the full charge Z_i, Z_j and the values determined by Mayer [25] for the coefficients C_{ij} and D_{ij} were used. The parameters appearing in the overlap repulsive part of the potential were then fitted to experimental data on the crystalline solid. The number of independent parameters were reduced by assuming a consistent set of ionic radii for the ions. It was then assumed that $\eta_{ij} = \eta$ is independent of i and j but could be different for different crystals. The constant B_{ij} has following form

$$B_{ij} = b_{ij}b\, exp\left[\frac{\sigma_i + \sigma_j}{\eta} \right] \tag{8}$$

where b is a constant for all crystals, σ_i and σ_j are ionic radii and b_{ij} are the Pauling factors,

$$b_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j} \tag{9}$$

and n_i, n_j are the number of electrons in the outer shells. Thus, the repulsive part of the potential $\phi_{ij}^{rep}(r)$ is written as

$$\phi_{ij}^{rep}(r) = b_{ij}b\, exp\left[\frac{\sigma_i + \sigma_j}{\eta} \right] exp\left[\frac{-r}{\eta} \right] \tag{10}$$

We refer to the above potentials as rigid-ion potentials since they do not explicitly take into account the polarisability of the individual ions. A detailed review has been given by Tosi [26]. The way in which FT potentials are constructed gives a good description of the thermodynamic properties of the rock salt alkali halides crystals. However FT's potentials are not very successful in reproducing the structure of the melt and there are also discrepancies between theory and experiment for the phonon dispersion curves. Various similar approaches have produced other rigid-ion potentials with different functional form or parameters chosen for the repulsive overlap interaction or differing in the choice of values for the Van der Waals coefficients.

In 1978 Vashishta and Rahman (VR) [19] studied the nature of the ionic motion in ϑ-AgI using the Molecular Dynamics simulation method. AgI has a different nature in the solid, in liquid phase and in the melting process, compared with alkali halides. VR were able to construct a set of effective pair potentials which achieved considerable success. The functional form of the potentials is given by,

$$\phi_{ij} = \frac{H_{ij}}{r^{\eta_{ij}}} + \frac{Z_i Z_j}{r} - \frac{P_{ij}}{r^4} - \frac{C_{ij}}{r^6} \tag{11}$$

with

$$H_{ij} = A_{ij}(\sigma_i + \sigma_j)^{\eta_{ij}} \tag{12}$$

and

$$P_{ij} = \frac{1}{2}(\alpha_i Z_j^2 + \alpha_j Z_i^2). \tag{13}$$

The first term in equation (11) has the Pauling form of the repulsive potential which arises from the overlap of the outer closed shell of electrons. A_{ij} and η_{ij} govern the strength and hardness of the repulsion respectively and σ_{ij} gives a measure of the size of the ions. In materials such as AgI the crystal structure is determined principally by anion-anion and anion-cation close contacts. Therefore, the knowledge of the crystal structure is sufficient to determine the size of the ions. The ionic radii of the anion and cation, σ_+ and σ_-, are fixed and given by the following relations:

$\sigma_- + \sigma_-$ = anion-anion nearest neighbour distance

$\sigma_+ + \sigma_-$ = anion-cation nearest neighbour distance

The second term describes the Coulomb attraction or repulsion between the charged ions with the effective charges Z_i and Z_j. The third term which arises when an ion is polarised in the Coulomb field of another ion, is an approximate attractive interaction, which describes the monopole-induced dipole attractive interactions. The final term represent the Van der Waals attractions.

3. Results and discussion

In Table 1 we give the input data which has been used to determine the parameters for the effective pair potential of NaCl and AgI.

Table 1. The input data for temperatures and densities.

Data	NaCl	AgI
$T(^{0}K)$	1165	933
$\rho(ion/(\text{Å})^3)$	0.0314	0.0281

Tables 2 and 3 show the values of the potential parameters used in eqs. (7) and (11) for NaCl and AgI, respectively. The potential parameters are taken from Ref.[11] for NaCl and from Ref.[13] for AgI. We use angstrom (Å) as the unit of length and $e^2/$ Å = 14.39 eV as the unit of energy. For the system studied $|z+| = |z-| = |z|$ and we consider below the three cases $|Z| = 1$, 0.5, 0 for NaCl system and $|Z| = 1$, 0.6, 0 for AgI system.

Table 2. Effective pair potential parameters for NaCl.

ϕ_{ij}	B	$\sigma_i + \sigma_j$	D_{ij}	b_{ij}	C_{ij}
Na – Na	3.15	2.340	0.030	0.014663	0.0730
Cl – Cl	3.15	3.170	10.106	0.014663	5.0313
Na – Cl	3.15	2.755	1.666	0.014663	0.4860

Table 3. Effective pair potential parameters for AgI.

ϕ_{ij}	η_{ij}	H_{ij}	P_{ij}	C_{ij}
Ag – Ag	11	0.014804	0	0
I – I	7	446.64	2.3472	6.9331
Ag – I	9	114.48	1.1736	0

In Fig. 1 we show the potentials for NaCl for different Z values. Fig. 1a shows the effective pair potentials $\phi_{ij}(r)$ for the fully ionized case, whereas Fig. 1b show the potentials for the partially ionized case. There are several important differences to note between two cases. Firstly $\phi_{NaNa}(r)$ is crossed by $\phi_{NaCl}(r)$ in Fig. 1b but not crossed in Fig 1a. Secondly the minimum of ϕ_{NaCl} (r) for $|Z| = 1$ is deeper and at a smaller value of r, as compared to the corresponding minimum for $|Z| = 0.5$. Finally, the $\phi_{jj}(r)$ for the incompletely ionized case, in Fig. 1b, decays more rapidly than the fully ionized case for NaCl, in Fig. 1a. In Fig. 1c we show the potentials for the neutral case NaCl. Deprived of charge ordering the results obtained for the potentials will allow to study the effects due to size differences.

In the fully ionized case, the Coulomb repulsion always dominates; but in the partially ionized case, the difference between Coulomb and core repulsion is slightly larger for the Na ions as compared to the Cl ions. This difference shows up in the way single particle properties change with the charge.

The results for the effective pair potentials of AgI are presented in Fig. 2 for different Z values. Fig. 1a shows the fully ionized case, Fig. 1b shows the partially ionized case and in Fig. 1c shows the neutral case. The difference in size between the positive and negative ions plays an important role for determining the potentials at short range, as we see from $\phi_{ii}(r)$ and $\phi_{jj}(r)$. The difference between the depth of $\phi_{AgI}(r)$ for $|Z| = 1$ and for $|Z| = 0.6$ is mainly due to the different values of effective charge.

It is seen that in Fig. 2a and 2b, the curves of $\phi_{AgAg}(r)$ cross $\phi_{AgI}(r)$. The $\phi_{AgAg}(r)$ potentials starts from smaller r and is vertical for $|Z| = 0.6$ as opposite to the case $|Z| = 1$. In both cases the $\phi_{AgI}(r)$ and $\phi_{II}(r)$ shows similar behaviour. Considering the curves of effective pair potential for the neutral case, they are more separated in AgI system, but closer in NaCl system.

A comparison of the effective pair potentials for the fully ionized case and the neutral case for both systems are given in Fig. 3a and 3b, respectively. It is seen from the figures that potentials for AgI are deeper and decay more rapidly than those for NaCl but the curves of NaCl start at smaller r.
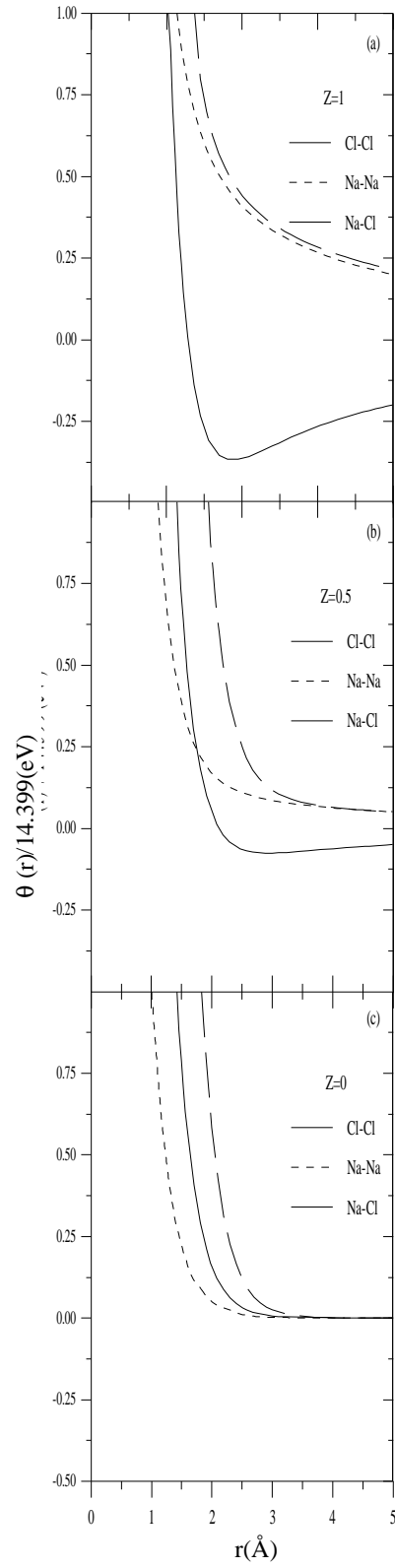
Fig. 1. Effective pair potentials of NaCl for different Z values.
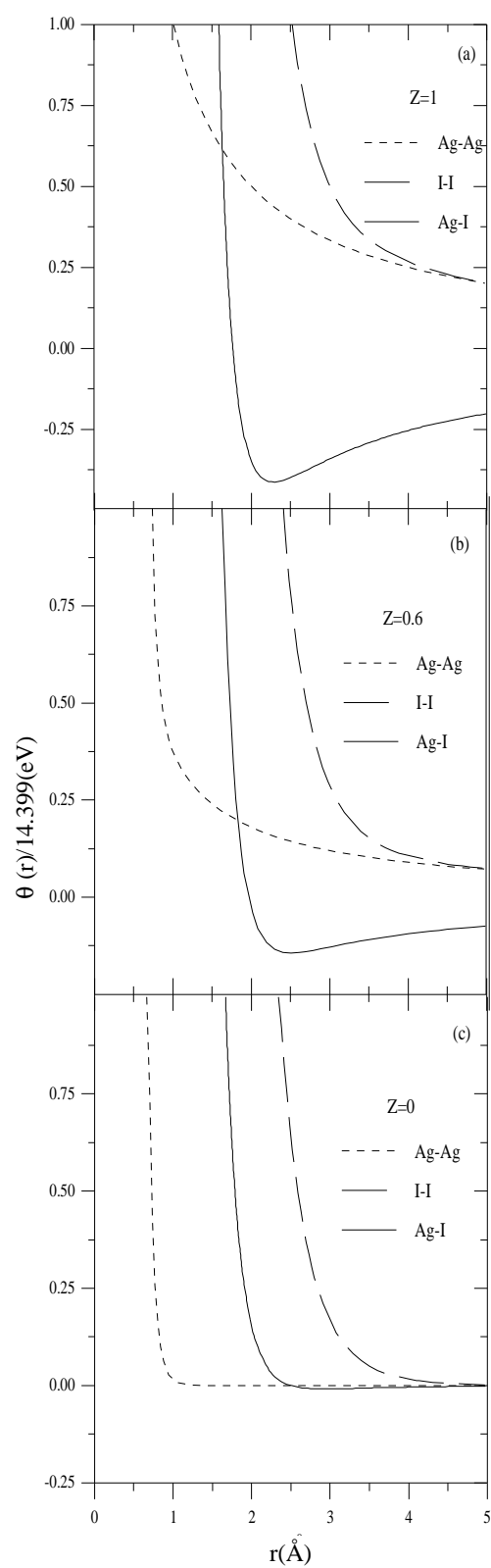a. z = 1; b. z = 0.5; c. z = 0.

Fig. 2. Effective pair potentials of AgI for different Z values.
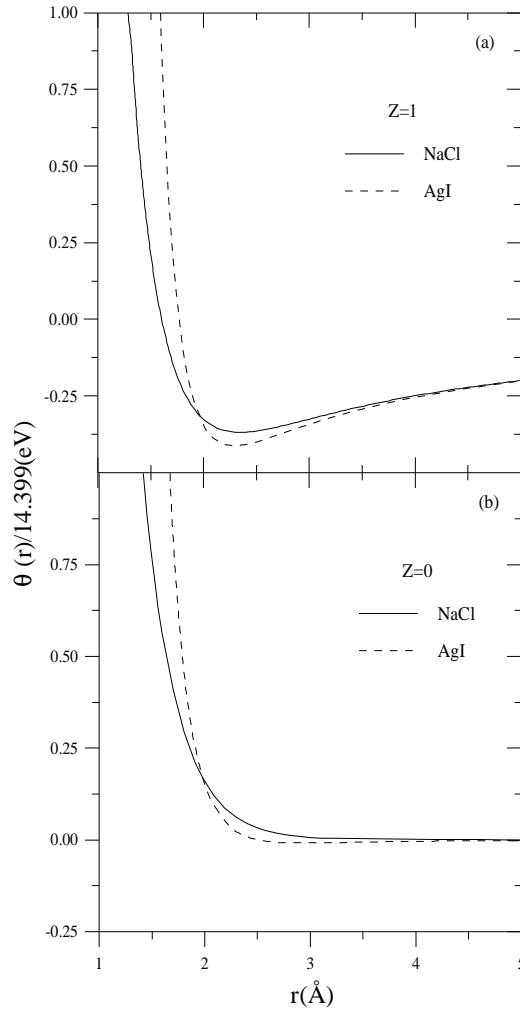a. z = 1; b. z = 0.6; c. z = 0.

Fig. 3. Effective pair potentials of NaCl and AgI.
a. z = 1; b. z = 0.

4. Conclusions

We have presented a theoretical study of the effective pair potential of simple salts (NaCl) and ionic salts AgI. We have tried to convey a unifying descriptions of these system. All the calculations that we have carried out involve the use of integral equations of liquids.

A semi-empirical rigid ion potential which was first proposed by Vashista and Rahman has been used to model the interactions for AgI and the Huggins-Mayer potential parameterised by Fumi and Tosi for NaCl, have been used. Our calculations which have been carried out using the hypernetted chain approximation of liquid state theories provide a good quantitative agreement with available experimental and computer simulation results in the literature. At more detailed level, however, there are some important differences between computer simulation and hypernetted chain approximation due to limited potential.

The previous arguments are clearly very tentative. However, as with every semi-empirical rule, they allow for simple calculations which do not fall easily into any given benchmarking classification of liquids.

It is obvious that the modified potential given in Eq (11), which has different exponent to describe ϕ_{AgAg}, ϕ_{AgI} and ϕ_{II} repulsive terms, in conjunction with molecular dynamic technique

which allows for variations in the shape and size of the cell, successfully describes the ϑ-K transition in AgI.

The semi-empirical potentials we have used are the effective pair potentials derived from ab-initio potentials, which also included many body forces, so that they could be used in both solid and liquid states calculations. There are potentials, available in the literature, that are valid for the melting temperature of the system of interest and hence, are not of much use in the study of liquid state properties. The fact is that potentials developed for the solid state are not always transferable for liquid state properties. While the solid state properties are normally calculated with reference to the bottom of the potential well, the liquid state properties depend on a delicate balance between kinetic and potential energy contributions and detailed knowledge of the potentials is, therefore, required.

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