

## IMPROVED RIGID ION MODEL OF MOLTEN ZINC CHLORIDE

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We have developed a new rigid ion model for the simulation of molten  $\text{ZnCl}_2$ . A molecular dynamics simulation of this model under a constant pressure of 1 atm and a constant temperature of 1200 K resulted in a successful description of the short-range order in the liquid state. The resulting short range structure is presented with respect to the coordination of the  $\text{Zn}^{2+}$  ions and the Zn–Cl–Zn bond angle. Improvements offered by this model over the currently existing ionic potentials are discussed with particular regard to the Zn–Zn correlation.

### 1. Introduction

$\text{ZnCl}_2$  glass is a technologically important material with respect to its potential use as a low-loss optical transmission medium in the near infrared region [1]. The structure of molten  $\text{ZnCl}_2$  has long been considered by molten-salt chemists to be different from other halide salts due to the very high viscosity of the melt, the very high tendency of molten  $\text{ZnCl}_2$  to supercool to a glassy state, and the existence, according to Raman studies, of complexes of the form  $\text{ZnCl}_3^-$  or  $\text{ZnCl}_4^{2-}$  [2]. The molten state, in as much as it is different from other halide salts, has also certain structural peculiarities described variously as a “polymeric network” [12]. The presence of ionic complexes such as  $\text{ZnCl}_3^-$  or  $\text{ZnCl}_4^{2-}$  and species such as  $\text{Zn}^{2+}$ ,  $\text{ZnCl}^+$  in the melt make the study of the liquid state quite difficult. However, the structure of molten and vitreous  $\text{ZnCl}_2$  has been studied and neutron diffraction data are available [3, 4]. Biggin and Enderby [3] investigated the structure of molten  $\text{ZnCl}_2$  by applying the technique of neutron diffraction to isotopically enriched samples. They have extracted the three partial structure factors and pair distribution functions related to Zn–Zn, Cl–Cl and Zn–Cl correlations from the experimental data (see fig. 1c).

These radial distribution functions show an approximate equality between the Zn–Zn and

Cl–Cl distances indicating close similarity of the Zn–Cl–Zn and Cl–Zn–Cl angles in triplets of neighbouring ions. Further, these functions also reflect an arrangement of the  $\text{Cl}^-$  ions which provide tetrahedral sites for zinc with a ratio of  $r_{\text{Cl-Cl}}/r_{\text{Zn-Cl}} = 1.62 \pm 0.04 \sim \sqrt{8/3}$  for interionic distances.

Molecular dynamics (MD) simulations represent a currently popular and powerful tool for deriving the macroscopic and microscopic properties of assemblies of classical particles using realistic interatomic potentials. However, to date, attempts to utilize purely ionic potentials have failed to predict the topology of the network in  $\text{ZnCl}_2$  liquids and glasses.

MD consists of essentially solving the classical equations of motion of an assembly of particles interacting through realistic interatomic potentials. The solution of these equations of motion provides important quantitative information about the structure and thermodynamic properties. While experiment continues to be the major source for obtaining information regarding the structure and properties of amorphous materials, recent advances in computational procedures such as MD may prove valuable in making a significant contribution to materials research especially in circumstances in which either the appropriate experiments are difficult to perform accurately or the experimental results are open to ambiguous interpretation. Hence, one can

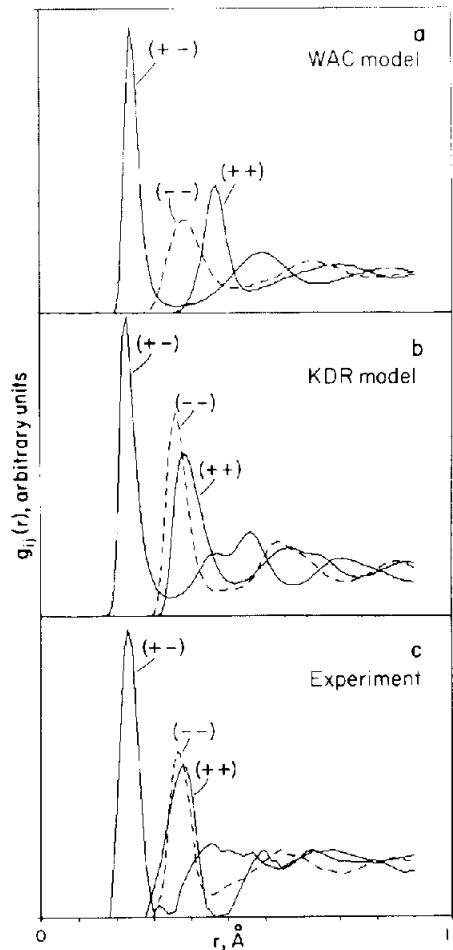


Fig. 1. Partial radial distribution functions of molten  $\text{ZnCl}_2$  generated with the WAC (ref. [6]) and KDR (this paper) interionic potential compared with the experimental functions (ref. [3]) labelled as (a), (b) and (c), respectively. The unlike ion distribution function  $g_{+-}$  and like ion distributions  $g_{++}$  are represented by solid lines while the anion-anion distribution  $g_{--}$  is represented by dashed lines. The distributions are given in arbitrary units and distances in Å.

foresee the dominant role MD can play in the study of amorphous  $\text{ZnCl}_2$ .

## 2. Current models of $\text{ZnCl}_2$

Molecular dynamics (MD) simulations of molten  $\text{ZnCl}_2$  based on rigid ionic models have been reported in the literature [5, 6]. Woodcock et al.

[5] have reported applications of MD calculations to the vitreous state for simple ionic  $\text{MX}_2$  type glasses such as  $\text{ZnCl}_2$ . They performed simulations at constant volume using a Born–Mayer–Huggins type pair potential. Their simulations resulted in total cohesive energy values over 17% in excess of the experimental value. They report a range of values for the unlike ion coordination, ( $n_{\text{Zn-Cl}}$  extending from 4–5). No description of short-range ordering was provided in this model.

Gardner and Heyes [6] extended the work of Woodcock et al. by modifying their original potential, but did not obtain a more precise description of the structure of molten  $\text{ZnCl}_2$ . Inoue et al. have moderately refined the potential by using new values for the zinc ionic radius and reported MD calculations of infrared absorption spectra of  $\text{ZnCl}_2$  and  $\text{ZnCl}_2$ –KBr glasses [10]. While the simulations are able to predict the Cl–Cl and Zn–Cl component correlation functions, they fail to account for the relative arrangement of the cations. Moreover, the simulations give significantly different values for the total cohesive energy in comparison to the experimentally obtained values. Hirao et al. [14] have recently modelled  $\text{ZnCl}_2$  glass using constant volume MD simulation and a modified version of Inoue’s potential that uses a higher Zn ionic radius. Although their constant volume simulations predict very good Zn–Cl, Cl–Cl and Zn–Zn correlations, simulations we performed with Hirao et al.’s potential at constant pressure fail to give good Zn–Zn correlation, as shown later in this paper.

The reason for the gross disagreement in the Zn–Zn correlation in the original potential developed by Woodcock et al. [5] was speculated by Gardner and Heyes [6] to be due to the relatively large degree of covalency in the system ( $\sim 57\%$  calculated from electronegativity of species Zn, Cl), which implies a sufficient degree of directional bonding in the system. Ballone et al. [7] have qualitatively examined the relationships between the interionic forces and the structure of  $\text{ZnCl}_2$ . In their study, they stress the need to incorporate angle-dependent interatomic forces for more realistic computer modelling of molten  $\text{ZnCl}_2$ .

Since computer simulation in standard ionic models was unable to globally describe the several distinctive features of liquid  $\text{ZnCl}_2$ , Ballone et al. [7] qualitatively examined different models for a 2:1 ionic melt corresponding to the thermodynamic state of  $\text{ZnCl}_2$ . Models based on the hypernetted chain approximation (HNC) were solved using charged hard sphere type assumptions. They pointed out that the large cation-cation distance (4.7 Å) observed by Woodcock et al. is a consequence of the strong Coulomb repulsion between the doubly charged cations, and the absence of angle-dependent bonds. Ballone et al. also presented qualitative features of effective pair potentials consistent with the gross topology of  $\text{ZnCl}_2$  in liquid and vitreous states, and suggested that the angular dependence of the interionic forces could be, to some extent, simulated by incorporating a combination of distance dependent dielectric screening. This results in reducing the range of the Zn–Zn Coulomb repulsions except near the measured value of  $r_{\text{Zn–Zn}}$ .

Further, they also suggested use of non-additivity of ionic radii, which they predicted would crudely mimic the angular dependence.

In this paper we present a successful attempt to simulate molten  $\text{ZnCl}_2$  by development of an improved rigid ion model. We have followed the guidelines of Ballone et al. [7] to generate a set of effective pair potentials (referred to as KDR hereafter) which results in accurate Zn–Zn correlations. We have performed constant pressure, constant temperature molecular dynamics calculations of the model at high temperature (1200 K). The partial radial distribution functions of the model are in good agreement with the experimental data. The difference between the equilibrium volume of the liquid at the studied temperature and experimentally determined molar volume at the same temperature is inferred to be due to the discrepancy in the long-range arrangement and coordination of the ions in the  $\text{ZnCl}_2$  model.

### 3. Model and method

For computational convenience, it is usually assumed in MD that the interaction between the

ions in the system is central pair-wise additive. Born–Mayer–Huggin type potentials are typically used,

$$\phi_{ij}(r) = \frac{q_i q_j e^2}{r} + b_{ij} \exp\left(\frac{\sigma_{ij} - r}{\rho}\right) - \frac{C_{ij}}{r^6}, \quad (1)$$

where  $r$  is the distance between the ions  $i$  and  $j$  and  $q_i$  is the ionic charge ( $-1$  for  $\text{Cl}^-$  and  $+2$  for  $\text{Zn}^{2+}$ ) and  $C_{ij}$  is a coefficient in the short-range Van der Waals attraction. The exponentially decaying repulsive term is composed of  $\sigma_{ij}$ ; the sum of ionic radii,  $b_{ij}$  which is a hardness parameter [6], and  $\rho$  which is a constant.

The parameters we have generated for the short-range interaction, as well as parameters from other studies, are presented in table I. (The parameters used by us, Woodcock et al., Gardner and Heyes and Hirao et al. are referred to as KDR, WAC, GH and HS, respectively.) In generating a satisfactory set of parameters we have retained the hardness parameter of Woodcock et al. We have also kept the same  $\rho$  as in ref. [6] except for the  $\text{Zn}^{2+}$  interactions (see table I) in order to reduce the Coulomb repulsion between the  $\text{Zn}^{2+}$  cations. In view of the qualitative analysis by Ballone et al., we reasoned that a modification of the Woodcock potential, with main emphasis on reduction of the strong Coulomb repulsion between the Zn–Zn ions, would result in successfully simulating the experimental liquid structure by MD. Woodcock et al. had attributed the large difference in their computed cohesive energy to the absence of Van der Waals contributions. Indeed, Van der Waals contributions tend to be large in the presence of  $d^{10}$  cations. Therefore, contrary to using dielectric screening to decrease the ionic repulsion, as suggested by Ballone et al., we have tried to reduce the Coulomb repulsion between the Zn–Zn ions by introducing a Van der Waals attraction component to the short-range Zn–Zn interaction. A proper combination of the repulsion and attraction components results in effectively bringing the Zn–Zn correlation distance closer to the Cl–Cl distance as observed experimentally. Moreover, it has to be noted that our choice of ionic radii does not obey the additivity rule:  $\sigma_{+-} = \frac{1}{2}(\sigma_{+-} + \sigma_{--})$ .

Table I

The parameters of the rigid ion potentials used in modelling molten  $\text{ZnCl}_2$ . WAC, GH, HS, KDR refer to Woodcock et al. [5], Gardner et al. [6], Hirao et al. [14] and the present paper, respectively.

Parameters	WAC	GH1	GH2	GH3	HS	KDR	Units
$q_i$	-2	+2	+1.5	+1.25	-2	+2	$e$
$q$	-1	-1	0.75	-0.625	-1	-1	$e$
$b_{i+}$	0.190	0.285	0.190	0.190	0.19	0.19	$10^{-10}$ J
$b$	0.143	0.238	0.143	0.143	0.19	0.143	$10^{-10}$ J
$b_i$	0.166	0.261	0.166	0.166	0.19	0.166	$10^{-10}$ J
$\sigma_{i+}$	2.860	2.860	2.860	2.860	2.660	4.047	$\text{\AA}$
$\sigma$	3.356	3.356	3.356	3.356	3.356	3.842	$\text{\AA}$
$\sigma_i$	3.108	3.108	3.108	3.108	3.008	2.973	$\text{\AA}$
$\rho$	0.34	0.34	0.34	0.34	0.34	0.34*	$\text{\AA}$
$C_{i+}$	0.0	0.0	0.0	0.0	0.0	6.90	$10^{-16}$ J $\text{\AA}^6$
NT	8000	-	-	-	4000	8500	

\*  $\rho_{i+} = \rho = 0.34$  except  $\rho_{i+} = 0.3$ . All the values for the parameters used in the KDR and HS potentials were obtained by taking  $z_1 = 0$ ,  $z_2 = -1$  and  $n = 8$  for simulations at constant pressure.

NT is the total number of MD integration steps.

The model has been studied with an MD algorithm allowing for changes in shape and volume of the simulation cell, under periodic boundary conditions [8]. The addition of these degrees of freedom is essential for the study of small systems in the liquid state in which volume fluctuations play a decisive role.

In the constant stress MD formulation, three variable vectors,  $\mathbf{e}_1$ ,  $\mathbf{e}_2$  and  $\mathbf{e}_3$  forming a  $3 \times 3$  matrix  $\mathbf{H}$ , are necessary to describe the planar boundaries of the simulation cell. The volume of the cell is given by  $\Omega = \mathbf{e}_1 \cdot (\mathbf{e}_2 \times \mathbf{e}_3)$ . The position  $\mathbf{r}_i$  in a fixed Cartesian coordinate system may be expressed in the variable coordinate system as  $s_i = \mathbf{H}^{-1} \mathbf{r}_i$ .

The edges of the simulation cell are driven by the imbalance between an externally applied stress  $\boldsymbol{\sigma}$  and the internal stress tensor. The Hamiltonian governing the equations of motion of the system under constant stress  $\boldsymbol{\sigma}$  is written as

$$H = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 + \sum_{i>j} \phi_{ij}(r_{ij}) + \frac{1}{2} W \text{Tr}(\dot{\mathbf{H}}^T \dot{\mathbf{H}}) + \text{Tr}\{\boldsymbol{\sigma} \boldsymbol{\varepsilon}\} \Omega_0. \quad (2)$$

Where  $\dot{\mathbf{H}}$  stands for the time derivative of  $\mathbf{H}$ .  $\mathbf{H}^T$  and  $\text{Tr} \mathbf{H}$  are the transpose and trace of the matrix  $\mathbf{H}$ , respectively. The total energy is the

sum of the kinetic and potential energies of the set of particles, the kinetic energy of the borders of the simulation cell to which is artificially assigned a mass  $W$ , and the elastic energy, for which  $\Omega_0$  is the volume of the reference system used to measure the small strain  $\boldsymbol{\varepsilon}$ . The parameter  $W$  has the dimension of mass and can be visualized as the mass of the boundaries of the simulation cell. Average quantities calculated along the trajectories generated with the above Hamiltonian are independent of the mass of the borders while dynamical properties such as viscosity are not.

We have used an extension of the constant stress molecular dynamics formalism of Parinello and Rahman [8] to simulate assemblies of particles interacting through long-range Coulombic potentials [9]. The simulation of ions involves the summation of the Coulombic energy potential and forces between all pairs. The long-range nature of these interactions yields very slowly converging series. An extension to triclinic cells of the Ewald summation method is incorporated into the MD algorithm to accelerate the convergence.

All simulations in this study have been performed with the following set of conditions: the MD integration time step used was  $0.65 \times 10^{-14}$  s, the chosen temperature  $T$ , was 1200 K

and the pressure  $P = 1$  atm. The number of ions in the MD cell was 324 (216 anions and 108 cations).

#### 4. Results and discussion

Simulations using Woodcock et al.'s model and Hirao et al.'s model were performed to assess the effect of these potentials under constant pressure conditions. The results of these simulation; of simulations under constant volume conditions reported by GH and experimentally obtained values for the interionic distances, volume and total energy are tabulated in table II. The partial radial distribution function of the WAC system obtained under constant pressure are similar to the constant volume simulation results reported by Woodcock et al. (see fig. 1a). The results give a value of 4.3 for the coordination of unlike ions, with a distribution that is to a larger extent four-fold (75%) and five-fold (23%) with negligible amount of six-fold coordination. The partial radial distribution functions obtained using Woodcock's potential give 2.4 Å, 3.85 Å and 4.7 Å as the first neighbour distances for Zn–Cl, Cl–Cl and Zn–Zn, respectively. Furthermore, the ratio  $r_{\text{Cl-Cl}}/r_{\text{Zn-Cl}} = 1.60$ , and  $r_{\text{Zn-Zn}} = 2(r_{\text{Zn-Cl}})$ . The structure of the liquid simulated with the WAC potential is constituted

predominantly of  $\text{ZnCl}_4^{2-}$  tetrahedra sharing vertices with a Zn–Cl–Zn angle of  $180^\circ$ . Moreover, the WAC potential yields a peak at 5.7 Å for the  $g_{+-}$  partial radial distribution function, but no additional features are perceived in the range 4.36 Å to 5.0 Å. A calculation of the second nearest-neighbour Zn–Cl distances for the linearly linked tetrahedra gives a value of 5.75 Å as the distance of closest approach. The linear arrangement of the Zn–Cl–Zn triplet is the origin of the erroneous Zn–Zn correlation of 4.7 Å seen in the WAC potential. This first Zn–Zn distance in the radial distribution function is in excess of more than 23% of the experimental value.

The high Zn–Zn repulsion in the potential is mainly responsible for this large value as indicated by Ballone et al. Another consequence of the strong Coulomb repulsion is also reflected in the high energy values ( $-2170$  KJ/mol). In addition, the  $180^\circ$  bond angle for the Zn–Cl–Zn indicates an open liquid structure, which explains the large values of volume of the system.

In the case of the modified potential reported by Hirao et al., however, the results of our simulation seemed to be contrary to what these authors have reported. The simulation at constant pressure indicates a Zn–Zn correlation distance of 4.5 Å as opposed to 3.9 Å as claimed by Hirao et al. The structure of the liquid obtained

Table II

Comparison of structural parameters, values of energy and volume at  $T = 1200$  K of the WAC [5], GH [6], HS [14], Ballone et al. [7] and KDR (this paper) models. The experimental values for the radial distribution function and coordination numbers were obtained from ref. [3] while the values for the total energy and the molar volume were obtained from ref. [15].

Potential	$r_{+-}$ (Å)	$n_{+-}$ (Å)	$r_{++}$ (Å)	$n_{++}$ (Å)	$r_{--}$ (Å)	$n_{--}$ (Å)	Total energy (KJ/mol)	Total volume ( $\text{cm}^3/\text{mol}$ )
WAC*	2.40	4.3	3.85	8.9	4.7	5.1	-2170.0	81.6
GH1**	2.70	–	3.70	–	4.9	–	-1993.0	61.0
GH2**	2.60	–	3.70	–	4.9	–	-1060.0	61.0
GH3**	2.80	–	3.80	–	5.0	–	-672.0	61.0
HS*	2.30	4.1	3.70	7.8	4.5	4.5	2270.0	77.0
Ballone et al.	2.27	4.4	3.74	10.7	4.0	4.6	–	–
KDR*	2.30	4.6	3.60	10.5	3.8	5.7	-2442.3	85.3
Exp. for liquid ZnCl <sub>2</sub>	2.29 $\pm 0.02$	4.3 $\pm 0.02$	3.71 $\pm 0.02$	8.6 $\pm 0.05$	3.8 $\pm 0.01$	4.7 $\pm 0.8$	-2604.0	61.0

\* Values obtained with simulations performed at constant pressure of 1 atm.

\*\* Values obtained from ref. [6] wherein simulations were performed at a constant volume of  $61 \text{ cm}^3/\text{mol}$ .

using the potential of Hirao et al. [14] is very similar to that of the WAC model. The values of 2.3 Å and 4.5 Å for the first distance of approach for Zn–Cl and Zn–Zn suggest that the liquid structure is described by linearly linked tetrahedra, identical to that predicted by WAC. Nevertheless, the coordination number of 4.1 for the unlike ions, the value of 77 cm<sup>3</sup>/mol for the volume and the value of –2270 KJ/mol for the energy represent an improvement over the WAC study. There was also very good agreement of the Zn–Cl and Cl–Cl first neighbour distance with experiment similar to the WAC potential.

Gardner and Heyes made a detailed analysis of the effect of changes in the interionic potential on the structure of molten ZnCl<sub>2</sub> by varying the hardness parameters and the ionic charges. The three different variations in the potentials they have studied (represented as GH1, GH2 and GH3), and the values of internal energy as well as the first interionic distances of their models are presented in table II. The potential GH1 consisted of more repulsive short range terms than WAC. Consequently they obtain drastic increments in the position of the  $g_{++}$  and  $g_{-}$  peaks in the radial distribution function. The other two potentials namely GH2 and GH3, which correspond to variations in the ionic charges of the species, however, are shallower than the WAC potential and do not contribute to any improvements in the structure. They report that the potentials GH1, GH2 and GH3 generate less cohesively bound liquids resulting in larger values for the positions and increased spreading of the peaks. They also observed an increase in the internal energy of the system to an unrealistically large value of –672 KJ/mol, as they varied the potential from GH1 to GH2.

Ballone et al.'s analysis suggest that in addition to screening of the ionic charges by a dielectric constant, within a context of effective pair potentials, a very sharp rise of the zinc–zinc repulsion near the measured value of  $r_{Zn-Zn}$  was also necessary to realistically model ZnCl<sub>2</sub> liquid. They evaluated the constants in the screening function from refractive index data on ZnCl<sub>2</sub> and made reasonable estimates for the screening

length to yield the exact value of  $r_{Zn-Zn}$ . Ballone et al.'s qualitative predictions of the coordination numbers and the pair radial distribution functions are also tabulated in table II. Their predictions obtained by incorporating Coulomb screening of the Zn–Zn interaction are in very good agreement with the experimentally determined values.

The combination of the attraction and the repulsion terms in our potential is important for obtaining the correct Zn–Zn distance. Moreover, introduction of an attractive Van der Waals term also results in a cation–cation coordination of 5.7, anion–anion coordination of 10.5 and anion about cation coordination of 4.6 with a distribution ranging from 4 to 6 for  $n_{Zn-Cl}$ , 4 to 14 for  $n_{Cl-Cl}$  and 5 to 7 for  $n_{Zn-Zn}$ . These coordination numbers lie within the upper limit of the experimental range. However, it may be noted that the experimental partial radial distribution functions are obtained from the total partial structure factors by arbitrarily fixing one to begin with and allowing for variation in any one of the partial structure factors as the other two are held constant [3, 4]. Hence, the extent of error can, perhaps, never be exactly predicted.

The distribution of coordination numbers in the liquid simulated using our potential is 53% tetrahedral coordination, 31% five-fold coordination and 16% six-fold coordination. These percentages show that the system is predominantly tetrahedrally coordinated with a combination of pentahedral and octahedral coordinations. An examination of the coordination of the particles within the simulation cell clearly show that the different polyhedra are uniformly distributed throughout the simulation cell. There is no preference for any cation to have a particular unlike ion coordination near the borders or in the central region of the simulation cell. Therefore, ruling out any artifact which may have arisen from the periodic boundary condition. Nevertheless, there is good agreement between the partial radial distribution function of our model and the experimentally obtained functions (see table II).

Figs. 1a–c show plots of radial distribution function for the WAC, our (KDR) potential and for the experimental functions of molten ZnCl<sub>2</sub>

at 1200 K, respectively. The experimental values for the unlike ion coordination and the relatively broad peak in the range 4.5 to 5.6 Å (see fig. 1c) for the plot of the experimental functions suggests the presence of some five and six fold coordination in the zinc chloride structure studied by Enderby et al. [3]. Examination of the  $g_1$  partial radial distribution function in fig. 1b shows the major peak, corresponding to the first nearest-neighbour distance at 2.3 Å, which is consistent with the experimental minimum distance of approach for chlorine ions about zinc ions. However, the unlike ion radial distribution function exhibits additional features beginning with a plateau at 4.4 Å, followed by a more prominent peak at 5.6 Å.

Fig. 1b gives values of 3.8 Å and 3.6 Å for the first nearest-neighbour distances for the like zinc and chlorine ion pairs respectively. A ratio of  $r_{\text{Cl-Cl}}/r_{\text{Zn-Cl}} = 1.57 \sim \sqrt{8/3}$  is in good agreement with the ratio of 1.62 observed by Brigginn and Enderby [3], suggesting that our model consists primarily of  $\text{Zn}^{2+}$  ions occupying tetrahedral sites provided by the  $\text{Cl}^-$  ions. Further, it can be seen that  $r_{\text{Zn-Zn}} < 2(r_{\text{Zn-Cl}})$ , which is characteristic of  $\text{ZnCl}_4^{2-}$  tetrahedra sharing corners with Zn-Cl-Zn angles  $< 180^\circ$ . An estimated bond angle of  $111.2^\circ$  is in excellent agreement with the observation by Biggin and Enderby [3].

This arrangement of the  $\text{Zn}^{2+}$  and  $\text{Cl}^-$  ions satisfactorily explains the Zn-Zn first correlation distance of 3.8 Å. A calculation of the second nearest-neighbour distances for the tetrahedrally coordinated  $\text{Zn}^{2+}$  ions gives a value of 4.3 Å for the closest second neighbour distance and 5.55 Å for the farthest second neighbour distance. Similarly, conservative estimates for the closest and farthest second nearest-neighbour distances for tetrahedra sharing corners with pentahedra and octahedra as well as for edge sharing pentahedra and octahedra give values of 4.5 Å and 5.69 Å, respectively. It can also be conjectured that a slightly smaller distance of approach for the Cl-Cl ion pair (3.6 Å) may be responsible for the presence of a significant number of sixfold coordinated cations. A large fraction of six fold coordination may explain the accentuated peak near 5.6 Å.

The advantages of the present model over the WAC and other related models can be seen from the exact prediction of the Zn-Zn distance of approach, and the Zn-Cl-Zn bond angle of  $111.2^\circ$ . The reduction of the extent of Zn-Zn repulsion has successfully brought the cations closer and therefore reduced the Zn-Cl-Zn bond angle. However, this modification creates an unreasonably large amount of five- and six-fold coordination which is thought to be a consequence of the shorter Cl-Cl distance. The accomodation of the fivefold and sixfold coordination necessitates that the structure be "defected" resulting in an equilibrium volume larger than expected. The open structure of our model, however, does not affect the total internal energy of the system to a large extent. Table II shows the values for the energy. Our model results in good agreement with the experimental values for the energy as compared to the values obtained by using the WAC potential. This suggests that the total energy is largely controlled by the short range structure, rather than the global arrangement of basic polyhedra.

The MD simulations of the liquid we have performed require long equilibration times providing for 15% volume fluctuations. These fluctuations are however, not accompanied by any substantial changes in the chlorine coordination about the zinc. This observation appears to be a consequence of the network nature of the liquid. The individual motion of ions being brought about by an overall change in the orientation of the network due to steric restrictions rather than movement by ionic jumps. Evidence for such a network arrangement has been brought to light recently by Magazu et al. [13]. They have used photon correlation spectroscopy to analyze the relaxation processes in molten  $\text{ZnCl}_2$ . They observed an anomalous expansion across the melting point which is characteristic of a viscoelastic polymeric network.

An increase in the mass of the borders of the simulation cell,  $W$ , would result in a higher viscosity of the melt and larger relaxation times. Further simulations using the KDR potential were performed with a larger  $W$ . This latter condition more closely models a small volume of

liquid embedded in a much larger volume of more viscous liquid. It was observed that a ten fold increase in the mass of the borders reduces the volume fluctuations to 0.25% of the average volume. This behavior is believed to be related to the network nature of the liquid, wherein increasing  $W$  causes for an increase in the steric restrictions. These restrictions, in turn reducing the mobility of the basic polyhedra, and thus the fluctuations in the volume.

#### 4. Conclusions

The KDR potential developed in this work gives a more realistic representation of the  $\text{ZnCl}_2$  melt than previous models. The  $\text{Zn}^{2+}$  ions are predominantly tetrahedrally coordinated along with some fivefold and sixfold coordination. The model shows good agreement with the experimental partial radial distribution functions and the total internal energy. It is shown that despite the partial covalent nature of the Zn-Cl bond, it is possible to use purely rigid ionic models to describe the structure and properties of  $\text{ZnCl}_2$  contrary to the opinion expressed by Desa et al. [4]. Lastly, our work certainly provides impetus on the use of this model in further MD simulations of  $\text{ZnCl}_2$  glass. Studies on the structure of the vitreous state of  $\text{ZnCl}_2$  and effects of cooling rate on the glass transition are in progress [11].

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