

## Monte Carlo Studies on Fused Salts

### I. Calculations for a Two-dimensional Ionic Model Liquid

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The possibility of using the Monte Carlo method for estimating the configurational thermodynamic properties of fused salts has been considered. The method has been tested by calculations on a two-dimensional model of molten sodium chloride. The behaviour of this Monte Carlo model has been discussed in conjunction with experimental data on melts. The calculations are seen to give reasonable results and it is concluded that the Monte Carlo method appears to be a promising approach to the study of the ionic liquids.

The Monte Carlo method was successfully applied 10 years ago for obtaining thermodynamic data on systems of molecules interacting with a Lennard-Jones potential.<sup>1</sup> To the knowledge of the authors no attempt has previously been made to extend this approach to molten salts, though recently some calculations on strong aqueous electrolytes have appeared.<sup>2</sup> Molten salt work has been discouraged presumably because of the long range of the coulombic forces together with the practical necessity of working with systems with a small number of ions and hence of small dimensions. The long range of the coulomb forces may not prove as serious as it might seem, however, since the forces tend to average out rapidly with distance. This is indicated by calculations of Madelung constants for crystalline systems. Provided that the overall charge balance is maintained, the first few closest interactions will suffice to obtain a good approximation to the true Madelung constant.<sup>3</sup>

The alternative method of "molecular dynamics" (or in our case "ionic dynamics") should also be considered. Whether this or the Monte Carlo method is the more advantageous is probably best seen when experience with both types of calculations has been obtained.

For reasons of computing time economy the present study was initiated with a hypothetical two-dimensional model system. It was hoped that calculations on this system would indicate if the Monte Carlo method could be expected to provide a useful approach to the study of fused salts.

#### EVALUATION OF THE ENERGY SUMMATION

The Monte Carlo computations were carried out on the UNIVAC 1107 computer. A program (in ALGOL) was written for the purpose. The method adopted is essentially that developed by Metropolis *et al.*<sup>4</sup> and used by Wood and Parker.<sup>1</sup> The original papers should be consulted for an account of the theory and procedure. A couple of modifications necessitated by the charge effects had to be introduced, however. These modifications consist mainly in keeping track of the kind of ion occupying each specified position, and in performing the energy summation over an equal number of anions and cations. The latter condition precludes the exclusion of interactions beyond one half the cell edge, such as was done for the earlier type of systems studied.<sup>1</sup> Instead a summation over all ions both in the fundamental Monte Carlo cell and in the repetition cells next to it had to be performed. To save computing time, only the energy change on going from one configuration to the next was calculated. The total configurational energy  $U$  was obtained by adding the energy changes  $\Delta U_k$ :

$$U = U_0 + \sum_k \Delta U_k \quad (1)$$

$U_0$  is the initial configurational energy and  $\Delta U_k$  is the configurational energy change on going from configuration No.  $k-1$  to No.  $k$ .  $U$  was from time to time calculated directly to ensure that errors did not accumulate. This procedure of course increased the required computing time relative to the case of molecules interacting with a Lennard-Jones potential.

The mathematical representation for the interaction potential between atoms  $i$  and  $j$

$$u_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + \frac{b_{ij} e^2}{r_{ij}^n} \quad (2)$$

it also less expediently computed than the Lennard-Jones potential (since it is necessary to evaluate  $\sqrt{r_{ij}^2}$  to obtain the coulomb potential). In the above expression  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $Z_i \cdot e$  and  $Z_j \cdot e$  are the charges on the ions  $i$  and  $j$ , respectively,  $b_{ij}$  is the Born-Landé repulsion coefficient and  $n$  a number ranging from 5 to 12 depending on the types of ions present.

Because of the above mentioned complications, the computing speed reckoned as accepted configurations (*i.e.* number of steps in the Markov chain) per hour, is actually lower in the work reported here than for the Lennard-Jones case calculated with an IBM 704 computer in 1957.<sup>1</sup> This can be seen from Table 1.

For the present study a quadratic two-dimensional face-centered lattice was used as the starting point. The ionic interaction was chosen to be that

Table 1. Speed of computation for various systems.

Potential	Number of atoms in basic cell	Number of configurations per hour	Dimension	Computer
Coulomb	16	22 500	2	UNIVAC 1107
	36	12 000	2	
	64	6 200	2	
	64	2 500	3	
L-J	32	19 000	3	IBM 704
	108	6 500	3	

expected from a system of sodium ions and chloride ions. The Born-Landé repulsion coefficient  $b_{ij}$  for a sodium chloride crystal was obtained from the following expression<sup>5</sup>

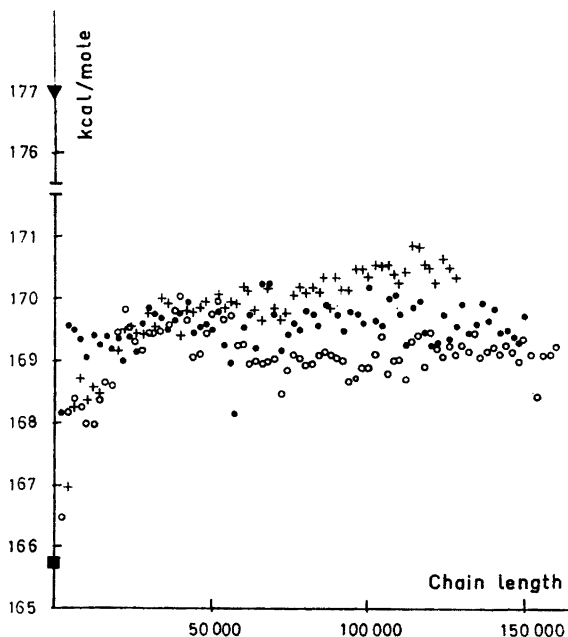
$$b_{ij} = \frac{r_0^{n-1} A}{n M} \quad (3)$$

For a three-dimensional sodium chloride crystal the interatomic equilibrium distance  $r_0$  is 2.81 Å,  $n$  (as defined in eqn. 2) is taken to be 8, the Madelung constant  $A$  is 1.748, and the corresponding Madelung term  $M$  for the repulsion term is 6.937. This gives a repulsion coefficient of 43.5 (Å<sup>7</sup>). This value for the repulsion coefficient is essentially representative for the sodium-chlorine interaction, the chlorine-chlorine and the sodium-sodium ion pairs contribute less to the repulsion term. The use of a common repulsion coefficient does not introduce a great error, however, since like ion encounters are relatively infrequent.

From eqn. 3 the equilibrium distance in a two-dimensional crystal of sodium chloride is found to be 2.65 Å by using 43.5 Å<sup>7</sup> for the repulsion coefficient and the appropriate Madelung constant for the two-dimensional crystal ( $A=1.614$  and  $M=4.279$ ).

The size of the Monte Carlo cell was chosen from the following considerations. The experimental density of fused sodium chloride at 1423°K is 1.366 g/cm<sup>3</sup>. A hypothetical expanded ideal crystal of the same density has a sodium-chlorine first neighbour distance of 3.29 Å. This distance should be reduced (by a factor of  $(4/6)^{1/2}$  (Ref. 5)) to 3.10 Å to conform with the two-dimensional nature of the system studied. The Monte Carlo cell edges are thus taken as even multiples of 3.10 Å. In addition a cell with edge length 6 times 2.81 Å was tried with the expectation that the system in this case would remain in the crystalline state.

In order to save computing time, the atoms were not permitted to approach each other closer than 2.20 Å. This effectively means a modification of the potential function in eqn. 2, setting  $U(r)=\infty$  when  $r < 2.20$  Å. With this additional restriction on the potential function it was found that only about 50 %



*Fig. 1.* Configurational energy in kcal/mole of the two-dimensional model of fused sodium chloride *versus* chain length in number of configurations.

The different points represent the average over only those configurations generated since the preceding point (2000 configurations).

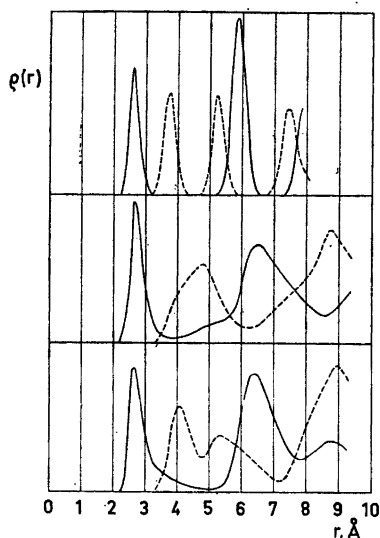
+ : 64 ions in the fundamental cell. ○ : 36 ions in the fundamental cell. ● : 16 ions in the fundamental cell. ■ : Lattice energy of expanded crystal. ▼ : Lattice energy of ideal crystal.

of the trial configurations were rejected by the test ensuring the Markov chain (where asymptotically each state recurs with a frequency proportional to the Boltzmann factor).

## RESULTS

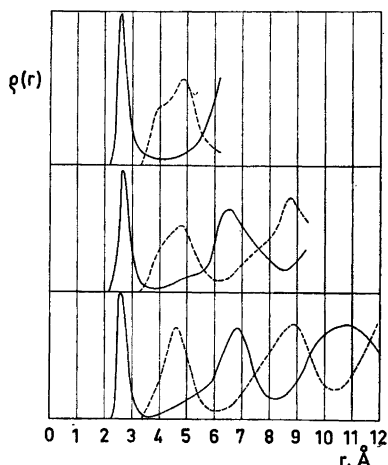
Fig. 1 gives the average of the energy over 2000 consecutive configurations as a function of chain length (*i.e.* number of configurations) for cells with 16, 36, and 64 ions in the fundamental cell. (Reference state: a gas of free ions.) The starting point for the chain is the ideal expanded crystal with closest cation-anion separation of 3.10 Å, having a lattice energy of 165.76 kcal/mole. The ideal crystal with 2.65 Å cation-anion separation correspondingly has a lattice energy of 176.97 kcal/mole and the molten salt values are seen to be intermediate.

The convergence is fair, though not entirely satisfactory for the largest cell. The three different cell sizes seem to result in somewhat different energy values. It is noteworthy that there appears to be an energy jump for the 36 ion cell between configuration number 54 000 and 60 000. This cell gives in the



*Fig. 2.* Radial distribution functions (RDF) versus the distance  $r$  of the two-dimensional model of sodium chloride. The RDF is defined at the distance  $r$  as the number of ions in the shell between  $r - 0.05$  Å and  $r + 0.05$  Å. The fully drawn curves give the cation-anion distribution and the dashed curves give the cation-cation or the equal anion-anion distribution. The number of ions in the fundamental cells is 36 in all cases.

1. The upper curve gives the RDF for the crystalline state as an average over the first 28 000 configurations (normalized to 14 000 configurations). The ordinate values should be multiplied by two to be comparable with the two lower curves. 2. The middle curve gives the RDF for the fused model as an average over the configuration range 20 000–54 000 (normalized to 28 000 configurations). 3. The lower curve gives the RDF for the fused model as an average of the 28 000 configurations in the configuration range 88 000–116 000.



*Fig. 3.* Radial distribution functions (RDF) versus the distance  $r$  of two-dimensional model of fused sodium chloride. The RDF is defined at the distance  $r$  as the number of ions in the shell between  $r - 0.05$  Å and  $r + 0.05$  Å. The fully drawn curves give the cation-anion distribution and the dashed curves give the cation-cation or the equal anion-anion distribution.

1. The upper curve gives the RDF as an average over the configuration range 16 000–122 000 (normalized to 28 000 configurations) for a model with 16 ions in the fundamental cell. 2. The middle curve gives the RDF as an average over the 28 000 configurations in the configuration range 88 000–116 000 for a model with 36 ions in the fundamental cell. 3. The lower curve gives the RDF as an average over the 28 000 configurations in the configuration range 54 000–82 000 for a model with 64 ions in the fundamental cell. The three distribution curves are drawn to the same relative scale.

region from configuration number 20 000 to 54 000 almost the same energy as the two other cell sizes, but a different internal energy above configuration number 60 000. This jump is associated with what appears to be a transition of some kind. The two lower curve pairs in Fig. 2 show the radial distribution functions for the 36 ion melt before and after the jump. It is seen that after the jump the radial distribution function has approached that of the crystalline state. This follows from a comparison with the upper curve pair in Fig. 2, which shows the results of the Monte Carlo calculations for the smaller

crystalline cell with edge length  $6 \times 2.81 \text{ \AA}$ . The direction of the jump away from the ideal crystal energy, is puzzling but may be due to the formation of a pseudopolycrystalline state with voids.

Fig. 3 shows the effect of cell size on the radial distribution curves. It is obvious that the cell size does not greatly effect the appearance of the radial distribution curves within a distance of one half of the cell edge.

From the radial distribution functions in Figs. 2 and 3 it is seen that the changes upon melting may be summarized as follows:

*The anion-cation distribution.* 1. The first peak at  $2.65 \text{ \AA}$  is not significantly shifted on going from the crystal to the melt, but it is diminished in size. The effect corresponds to a reduction of the coordination number from 4 in the crystal to an average value close to 3 in the melt. 2. The second peak is displaced from  $5.9 \text{ \AA}$  in the crystal to  $6.5 \text{ \AA}$  or  $6.8 \text{ \AA}$  for the 36 and 64 ion melt, respectively. The peak is considerably broadened in the melt.

*The cation-cation distribution* (equivalent with the anion-anion distribution). 1. The first two peaks of the crystal at  $3.7 \text{ \AA}$  and  $5.2 \text{ \AA}$  appear to merge to a single broad peak around  $4.6 \text{ \AA}$  in the melt. This merger is perfect in the 64 ion melt, but for decreasing cell size the peak shows an increasing tendency to split (Fig. 3). 2. The third peak of the crystal at  $7.4 \text{ \AA}$  is shifted to around  $8.8 \text{ \AA}$  in the melt.

These effects may be compared with observations on real fused salts. A comparison with the representative case of molten lithium chloride will be made. Lithium chloride has been chosen for the following reasons. The cation-anion closest equilibrium distance in crystalline lithium chloride at the melting point,  $2.66 \text{ \AA}$ ,<sup>6</sup> is quite close to that of the hypothetical two-dimensional sodium chloride crystal. Molten lithium chloride has been studied both by X-ray diffraction and neutron diffraction.<sup>6</sup> Assuming that the cation-cation distribution in the melt is identical with the anion-anion distribution, it is possible to obtain separately the distribution of opposite charged particles and of equally charged particles by combining the X-ray and neutron data. A separation by an approximate method has been effected, and the result is shown in Fig. 4. The position and frequency of various distances in the

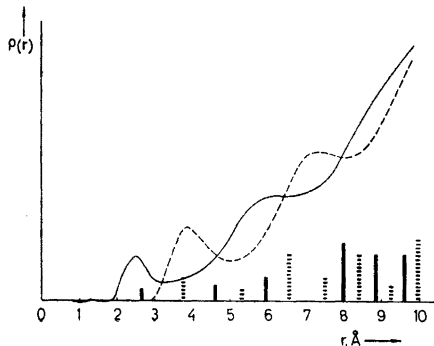


Fig. 4. Radial distribution functions (RDF) versus the distance  $r$  for different types of separations in molten LiCl calculated from experimental RDF's of Levy, Agron, Bredig and Danford.<sup>6</sup> The fully drawn curve gives the cation-anion distribution and the dashed curve gives the anion-anion distribution or the assumed equivalent cation-cation distribution. For comparison the equilibrium distances in crystalline LiCl at the melting point is indicated in the figure as bars. Solid bars give cation-anion equilibrium distances and dashed bars give cation-cation equilibrium distances. The height of the bars indicate the number of ions in the different shells. By comparison with the upper curve in Fig. 2, the space diagonal separations are easily identified.

crystal at the melting point is also indicated in the figure. Some of the features exhibited by the Monte Carlo two-dimensional system are seen to have counterparts in the real molten salt.

The first peak in the anion-cation distribution of the molten salt is shifted on melting to 2.45 Å (from 2.66 Å in the crystal) whereas no significant shift was observed in the Monte Carlo results. The peak area and thus the average coordination number is reduced from 6 to between 4.0 and 3.5, as compared with a reduction from 4 to 3 for the two-dimensional system.

The second peak of the cation-anion distribution occurs around 6 Å in the molten salt *vs.* 6.5 Å to 6.8 Å in the two-dimensional systems. This discrepancy may be accounted for by the presence of "space diagonal separations" not existing in the two-dimensional case. The crystalline three-dimensional salt has a space diagonal cation-anion distance at 4.6 Å and undoubtedly the related distances in the molten salt will contribute to a shift of the 6.5 Å to 6.8 Å peak of Fig. 3 to lower values.

The first peak of the cation-cation distribution or anion-anion distribution occur at 3.85 Å in the molten salt *vs.* 3.76 Å in the crystal.<sup>6</sup> The corresponding shift is larger in the two-dimensional case, from 3.7 to 4.6 Å. This is understandable from the difference in geometry since the two crystalline peaks at 3.7 Å and 5.2 Å occur with equal frequency for the two-dimensional crystal whereas in the three-dimensional crystal the shorter distance is twice as frequent as the longer. The second peak of the equal charge distribution occurs for 7.3 Å in the melt as compared with 8.8 Å in the two-dimensional case. This may again be understood by observing the presence of a frequent space diagonal at 6.5 Å in the three-dimensional crystal, not occurring in the two-dimensional crystal.

Apart from the effect of space diagonals, the two-dimensional and the three-dimensional distribution curves differ by the fact that the former are proportional to  $r$  and the latter to  $r^2$  (for large values of the interatomic distance  $r$ ). If these differences are taken into account, there appears to be some degree of correspondence between the two-dimensional Monte Carlo results (Fig. 3) and the experimentally determined radial distribution curves for molten alkali halides (Fig. 4). It is therefore concluded that the work with Monte Carlo models might profitably be extended to three-dimensional systems. Work on a three-dimensional ionic model liquid is now in progress.

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