Preliminary Results of a Molecular Dynamics Simulation of Potassium Bromide

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Molecular dynamics simulation program (MDIONS/III) has been used to simulate potassium bromide at a density of 3910.8 kg m\(^{-3}\) and an average temperature of 958 K. Born-Mayer-Huggins form of pair-potential, using Tosi-Fumi parameters from the solid state properties, has been applied to estimate the interaction potentials, the Coulomb interaction having been evaluated using Ewald's method. Radial distribution functions have been calculated and compared with the results of Monte Carlo simulation.

Since the pioneering work of Woodcock and Singer\(^1\) on the Monte Carlo (MC) simulation of ionic salts, there has been considerable progress in this direction\(^2\)–\(^5\). Though the MC technique was the first to be applied to ionic systems, the molecular dynamics (MD) studies\(^6\)–\(^10\) of the same have far exceeded the MC studies. The MC and MD simulation data on alkali halides show that of the various interionic pair-potentials tested\(^11\)–\(^15\), the Born-Mayer-Huggins (BMH) potential,

\[
\phi_{ij}(r) = A_{ij} \exp \left[ B_{ij}(\sigma_{ij} - r) - C_{ij} r^{-6}\right] - D_{ij} r^{-8}(i,j = + or -) \quad (1)
\]

using the parameters proposed by Tosi and Fumi\(^16\) (BMH-TF) is still the most effective pair-potential for the simulation of ionic systems. The systematic discrepancies\(^6\) for diffusion coefficients and viscosities in MC results are possibly due to neglect of the polarization effects in these calculations. The influence of density and temperature on the thermodynamic properties of pure molten salts has also been reviewed\(^17\). However, the available data give only an incomplete picture of the behaviour of these salts.

In this paper the preliminary results of the application of a new MD simulation program based on the MDIONS package\(^18\) from the Collaborative Computational Project CCP5, to the simulation of potassium bromide are reported.

A brief account of the points most pertinent to the simulation of molten salts is given; the details of the technique can be found elsewhere\(^14\).

The model consists of a set of 216 particles (108 anions and 108 cations) in an elementary cubic box of side L. The system is made pseudoinfinite by translation of replicas of the parent cube in the three dimensions. Potential energy of the system is assumed to be pairwise additive. Non-Coulomb part of the interaction between a pair of ions of species i and j is calculated by a pair-potential of the form

\[
\phi_{ij}^{\text{non}}(r) = A_{ij} \exp \left[ B_{ij}(\sigma_{ij} - r) - C_{ij} r^{-6} - D_{ij} r^{-8}\right] \quad (2)
\]

The first term in Eq. (2) represents Born-Huggins exponential repulsion while second and third terms represent, respectively, the dipole-dipole and dipole-quadrupole dispersion energies. The polarization of the ions and the ion-dipole interactions are neglected.

Initially a random set of velocities and sodium chloride type lattice positions are assigned to the particles. By summing the potential \(\phi(r)\), the virial \(\text{virial} = \frac{1}{2} \sum_{i} \sum_{j} Z_i Z_j e^2 r^{-1}\) and the force

\[
f = - \frac{\partial \phi(r)}{\partial r} \quad (3)
\]

is transformed into two convergent series, one over the real space and the other over the reciprocal space, as

\[
\Phi_{\text{r}} = \Phi_{\text{r}} + \Phi_{\text{f}} \quad (4)
\]

\[
\Phi_{\text{r}} = \frac{1}{2} \sum_{i} \sum_{j} \sum_{h} \left\{ \text{erfc}(r) \frac{2 Z_i}{r} \right\}, \quad i \neq j \text{ if } h = 0 \quad (5)
\]

where \(\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} \exp(-u^2) du\).

\[
\Phi_{\text{f}} = \sum_{k} A(k) \sum_{i} \sum_{j} Z_i Z_j \cos |k.(r_i - r_j)| \quad (6)
\]

where,

\[
k = \frac{2\pi}{L}(l, m, n)
\]

and
$A(k) = \frac{2\pi}{L^2} \exp(-k^2/4\alpha^2)/k^2$

The parameter $\alpha$ is so chosen that complementary error function $erfc(\alpha r)$ decreases rapidly with $r$ to make it a good approximation which takes only the nearest images in the sum over $h$ and the computations to be truncated at $r_n$. For the reciprocal space sums (Eq. 6) a spherical cut-off in $k$-space is applied. The sum over $k$ becomes a sum over $l$, $m$ and $n$ with $(l^2 + m^2 + n^2) \leq k^2_{max}$. Forces can be obtained by differentiation of the respective energy terms. Once the total force on each particle has been found, the Newtonian equations of motion can be solved numerically for particular time step giving rise to a new configuration. A leapfrog algorithm is used for the integration between time steps. Temperature of the system at any step calculated as

$$T = \sum_i m_i v_i^2 / 3k_B N_\rho,$$

where $N_\rho$ is Avogadro’s number and $k_B$ the Boltzmann’s constant, can be adjusted by scaling the velocities.

The ‘experiment’ consists of two parts: (1) An equilibration period over which the system is advanced by about a thousand time steps. Temperature is kept close to the desired value by frequent scaling of the velocities. (2) The production run over which the micro-canonical ensemble averages of various properties are calculated as time averages. Instantaneous coordinates and velocities and pair-distance histograms for radial distribution function calculations are stored on a magnetic tape.

The total energy

$$U = N^\beta \left[ 3 N k_B \langle T \rangle + \langle \Phi \rangle \right]$$

is a conserved quantity and is used as a check of the accuracy of the numerical algorithm. Pressure is given by

$$\langle P \rangle = \frac{N}{N_j} \left( 2 N k_B \langle T \rangle - \frac{1}{3} \langle \psi \rangle \right),$$

where $\langle \rangle$ indicates time average.

The core-core partial radial distribution functions $(rdfs)$ $g_{ij}(r)$ are calculated as

$$g_{ij}(r) = \frac{V}{N_j} \frac{N(r, \Delta)}{4\pi r^2 \Delta}$$

where $V$ is the cell volume and $N(r, \Delta)$, the average number of particles of species $j$ at a distance between $(r - \frac{1}{2}\Delta)$ and $(r + \frac{1}{2}\Delta)$ from the reference particle. The pair-distance histograms are used for the purpose.

The present MD run for the simulation of potassium bromide near its melting point (1007K) consisted of 2500-real time steps of $8 \times 10^{-15}$s. At a density of 3910.8 kg m$^{-3}$ used for this run, the cubic unit cell had a side length of 2.1574 nm. The non-Coulomb interaction and the real space part of the Ewald sums were truncated at a cut-off distance $r_c = L/2 = 1.0787$ nm. Necessary long range corrections to potential energy and virial were made. The BMH-TF parameters$^3$ used for the run are given in Table 1. The $\alpha$ and $k_{max}$ values used for the calculations are $5.6/L$ and $3 \times 10^{-10}$m$^{-1}$ respectively.

After an equilibration run of 2000-time intervals† the average internal energy, temperature, pressure and radial distribution functions were calculated in the production run of 500 steps. The system required 48s of CPU time on an IBM 360/44 for advancing it by one time step. Full use of tables was made in the force calculations to affect time economy. In view of the heavy CPU time requirements the computations were done in single precision and were restricted to a rather short production run. Values of average properties for potassium bromide over 500 real time steps are:

- Potential energy $= -635 \pm 5$ kJ mol$^{-1}$;
- Virial $= 137 \pm 16$ kJ mol$^{-1}$;
- Kinetic energy $= 23.9 \pm 0.9$ kJ mol$^{-1}$;
- Total energy $= -612 \pm 5$ kJ mol$^{-1}$;
- Pressure $= -529 \pm 88$ MPa;
- Temp. $= 958 \pm 36$K.

(The root mean square fluctuations in various quantities are also included). It may be noted that negative pressures ($-529$ MPa in the present case) are not uncommon in computer simulation results. It can be seen that total energy fluctuates to an extent of 0.4 per cent, which is well within the accepted limits of simulation studies$^7$. However, it can be improved further if the force calculations are made in double precision. Our value of $-635$ kJ mol$^{-1}$ for internal energy of liquid potassium bromide at 958K can be compared with the experimental value$^3$ of $-596.1$ kJ mol$^{-1}$ at melting temperature (1007K). The difference can be attributed to the fact that at 958K potassium bromide is in a supercooled state.

The radial distribution function $g_{ij}(r)$ is the most important quantity in the description of equilibrium microstructure. For a pure salt the mean radial

<table>
<thead>
<tr>
<th>Table 1—Parameters of Born-Mayer-Huggins Pair-Potential for Potassium Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A/10^{-19}$</td>
</tr>
<tr>
<td>+ 0.4225</td>
</tr>
<tr>
<td>- 0.3380</td>
</tr>
<tr>
<td>- 0.2535</td>
</tr>
</tbody>
</table>

† Such a long equilibration run is justified as the final debugging of the programme was done simultaneously.
NOTES

Table 2—Position of First Peak \( (r_{\text{max}}) \) and Coordination Number \( (n) \) of MD- and MC-Generated Radial Distribution Functions for Potassium Bromide

<table>
<thead>
<tr>
<th>Function ( g(r) )</th>
<th>MD/MC simulation</th>
<th>( r_{\text{max}}/\text{nm} )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_+ (r) )</td>
<td>MD</td>
<td>0.325</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>MC*</td>
<td>0.32</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>MCb</td>
<td>0.325</td>
<td>6.0</td>
</tr>
<tr>
<td>( g_- (r) )</td>
<td>MD</td>
<td>0.487</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>MC*</td>
<td>0.48</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>MCb</td>
<td>0.475</td>
<td>12.8</td>
</tr>
<tr>
<td>( g_{\text{gt}} (r) )</td>
<td>MD</td>
<td>0.487</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>MC*</td>
<td>0.48</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>MCb</td>
<td>0.475</td>
<td>12.9</td>
</tr>
</tbody>
</table>

(a) Reference 3; (b) these values are for crystalline KBr.

Fig. 1—Radial distribution functions for potassium bromide at 958K [--- \( g_+ \); ---- \( g_- \); \( g_{\text{gt}} \) and \( g_{\text{gt}} \) ]

distribution function is given in terms of partial rdfs by the relation (11).

\[
g_{nm}(r) = \frac{1}{4}g_+(r)^2 \left[ g_+(r) + g_-(r) \right] \quad \text{... (11)}
\]

The partial rdfs and the mean radial distribution function \( g_{nm}(r) \) are shown graphically in Fig. 1 and the prominent features are summarized in Table 2. The rdfs provide information about the distances of the closest approach of ions in the spherical shells around them. In addition to the \( r_{\text{max}} \), the position of the first peak, the coordination numbers calculated by integration of the function \( 4\pi r^2 g_f(r) \) up to the first minimum are also included in Table 2. These values are compared with the corresponding data from MC simulations. In spite of the bad statistics expected of a short production run, the agreement between the two sets of values is good. These comparisons may be regarded as additional criteria for the reliability of the calculations.

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References