STUDY OF BICOMPONENT MOLTEN SALTS
BY THE CONTACT MELTING METHOD

P.F. Zilberman, A.N. Chernikov, V.S. Znamensky, E.A. Goncharenko, Y.I. Skaev

Institute of Informatics and Problems of Regional Development
GIS Department, Armand Str. 37a, Nalchik 360000, Russia

ABSTRACT

Contact melting of molten salts was studied by computer modeling using the molecular dynamics method. The following properties of molten salt systems were described: diffusion coefficients, partial radial distribution functions, normalized velocity autocorrelation functions. Different forms of interionic potential were compared.

INTRODUCTION

Phenomenon of formation and growing of liquid phase in the contact zone of heterogeneous crystals at the temperature lower than the melting temperature of each crystal is called contact melting. Contact melting is widely used in various engineering processes and in physical chemistry analysis. It is successfully used to produce permanent joints, construction materials, alloys and chemical compounds. Contact melting serves in constructing fusibility diagrams and in simplifying investigations of diffusion processes. In particular, it allows one to easily determine inter-diffusion and partial diffusion coefficients.

Wide use of contact melting both in industrial and scientific purposes demands its microlevel thorough research for a wide set of ionic crystals. Finding out the basic laws of the phenomenon in different alcali-halid systems lets us widen its application fields and our knowledge of microlevel properties of processes taking place in homogenous and heterogeneous surroundings.

The problem of contact melting research on a nanometer-size scale is interesting for scientists engaged in studying this phenomenon. The basic questions are: what occurs in the contact region and how ions or atoms move there? Understanding the atomic processes at the interface zone of two solids brought together at high temperature, is central to many technological problem, including soldering, and coagulation. We have applied a method of numerical simulation to find the answers to these questions - a molecular dynamics (MD) method. The computer simulation gave a series of interesting results, from a physics point of view. Simulations can show which ions interact more strongly, which ions interact more weakly, what happens, if diverse crystals are in contact, which ions will strengthen the interaction, and which will ease interactions.
METHOD DESCRIPTION

The molecular dynamics method is based on the solution of the classical system of Newton equations

\[
\frac{d}{dt} m_i \frac{dr_i}{dt} = p_i, \quad \frac{dp_i}{dt} = \sum_{j \neq i} F(r_{ij})
\]  

[1]

describing movement in a system of N particles placed into a cell, for example a cube with side length L, which is chosen considering ionic radius and the number of particles in the system. The equations are approximated by a suitable numerical scheme which error can be made as little as we wish and it's decrees is limited only by the computer speed and amount of memory. One of the most commonly used is the velocity form of Verlet algorithm:

1. Define coordinates at step 1.
2. Define velocities at step 1.
3. Calculate coordinates at step n+1:

\[
r_i^{n+1} = r_i^n + h v_i^n + \frac{h^2}{2m} F_i^n
\]  

[2]

4. Calculate velocities at step n+1:

\[
v_i^{n+1} = v_i^n + \frac{h}{2m} (F_i^{n+1} + F_i^n)
\]  

[3]

The exact values of the starting conditions are not always known. In order the system to reach the desired energy reasonable starting conditions are implemented. After that energy is given to or taken away from the system. This procedure is repeated until the system reaches the desired state. Such actions may cause significant velocity changes. That is why the system is given some time after that to become stable. So the algorithm described is as follows:

1. Integrate the movement equation at the current time step.
2. Calculate kinetic and potential energies.
3. If the full energy of the system differs from the desired value, change velocities.
4. Go on with step 1 until the system becomes stable.

In our modeling we assume that interionic interaction can be described by Fumi-Tosi potential:

\[
U_{ij}(r) = Z_i Z_j \frac{e^2}{r} + B_{ij} e^{-\sigma r} - C_{ij} \frac{D_{ij}}{r^6} - \frac{D_{ij}}{r^8}
\]  

[4]

where \(C_{ij}, D_{ij}\) - Van der Vaals coefficients of Mayer.
Table 1. Van der Vaals coefficients of Mayer. Units: $C_i$ in units of $10^{12}$ erg A$^6$, $D_{ij}$ in units $10^{12}$ erg A$^8$

|       | $C_{++}$ | $C_{-}$ | $C_{-}$ | $D_{++}$ | $D_{-}$ | $D_{+}$ |
|-------|----------|----------|----------|----------|----------|----------|
| NaF   | 1.68     | 16.5     | 4.5      | 0.8      | 20.0     | 3.8      |
| NaCl  | 1.68     | 116.0    | 11.2     | 0.8      | 233.0    | 13.9     |
| NaBr  | 1.68     | 196.0    | 14.0     | 0.8      | 450.0    | 19.0     |
| NaI   | 1.68     | 392.0    | 19.1     | 0.8      | 1100.0   | 31.0     |
| KF    | 24.3     | 18.6     | 19.5     | 24.0     | 22.0     | 21.0     |
| KCl   | 24.3     | 124.5    | 48.0     | 24.0     | 250.0    | 73.0     |
| KBr   | 24.3     | 206.0    | 60.0     | 24.0     | 470.0    | 99.0     |
| KI    | 24.3     | 403.0    | 82.0     | 24.0     | 1130.0   | 156.0    |

For the short-range repulsive terms the following assumptions are made:

1) for any crystal $\alpha_{+-} = \alpha_{++} = \alpha_{--} \equiv \frac{1}{\rho}$, but the value of $\rho$ is different for different crystals;

2) the constants $B_{ij}$ are calculated as follows:

$$B_{ij} = \beta_{ij} b \rho \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j}$$  \[5\]

where $b = 0.338 \times 10^{-12}$ erg is constant for all crystals, $\sigma_i$ and $\sigma_j$ - ionic radii; $\beta_{ij}$ - Pauling factors:

$$\beta_{ij} = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}$$  \[6\]

$n_i, n_j$ - number of electrons in outer shells.

In order to get rid of the limitations of the particle movement trajectories the periodic boundary conditions were used. It is assumed that the cell under study is surrounded by the cells of the same size. When a particle leaves the cell it is supposed that the particle enters it from the opposite side with the same speed. The cell is divided into two parts by an imaginary boundary. One part is filled by ion combination of the first type and another one - by ion combination of the second type. Initially ions of Na+, K+, A' are placed into nodes of cubic lattice so that the closest neighbors of each ion are ions of the opposite charge. Ions of Na' and K' are placed into the opposite sides of the cell. This imitates contact of two salts.

A software complex was developed for MD-modeling of ionic crystals contact melting. Personal computers permit one to study temperature dependencies of the ionic crystal and melt characteristics in a boundary zone. Analysis has shown, that the MD-method permits one to evaluate the system characteristics using a modern personal computer with arithmetic coprocessor. The method accuracy is increased with application of more high-speed computers by means of expansion of a calculation base for statistical processing.
Different ion numbers \( N \) were used in modeling. The results showed that when \( N \geq 64 \) with the increase of \( N \), values of the calculated system parameters are very close at the same modeling conditions. For example, deviation of diffusion coefficient was 15%.

RESULTS

This method lets achieve coordinates and velocities of moving particles and then by the statistical processing obtain thermodynamic, kinetic and structural description of the system under study. In this work we show the results of molecular dynamic studies of common-anion (common-kation) systems obtained by the contact melting. Different configurations and ion ensembles were modeled which allowed to study both the system as a whole and each of its components separately. KF-NaF, NaCl-KCl, KBr-NaBr, NaI-KI systems were studied at the temperatures of 400K-1200K. Comparison of the numeric modeling results with the experimental facts of contact melting and radio-active isotopes leads to the conclusion that there is agreement of the calculated and experimental values. Structural and kinetic features of systems with different anion and kation composition were studied.

Results achieved at different temperatures were exposed to mean square approximation in order to obtain dependencies of the system parameters on the temperature. This is how the exponent multipliers and energies activation of diffusion were calculated.

Potential choice.

Poling potential was also used in modeling in the following form:

\[
U_0(r) = \frac{e^2}{4\pi\varepsilon_0 r} \left[ \frac{\text{sgn}(q_i,q_j)}{p} \left( \frac{\sigma_i + \sigma_j}{r} \right)^p \right]
\]

[7]

where \( q_i \) – ionic charge; \( \sigma_i \) – ionic radius; \( p=8 \) defines the strength of repulsive part of potential; \( e \) – electron charge.

Application of Poling method allows to get activation energy closer to experimental values than of other methods while Fumi-Tosi potential gives better exponent multipliers. Besides, it was observed that application of Poling potential lets achieve correlation of diffusion coefficients for Na, K, Cl closer to experimental values. At the same time we should note that error of diffusion coefficients values received makes about 10%, while experimental error is much lower and equals to 15-20%.

Diffusion coefficients.

It was found out that independently on potential choice, diffusion coefficients grow exponentially:
Analysis of penetrating ion trajectories showed that ions situated in the contact zone at the initial stage are much more mobile than those in the homogeneous surroundings. These causes easy formation of ion grouping. It is possible that these groups cause further formation of liquid phase.

The research was conducted for NVT model at the temperature several degrees lower the melting point. The dependence of diffusion coefficient on anion ionic radius was obtained.

Table 2. Diffusion coefficients for Na⁺A⁻ - K⁺A⁻ were A⁻=F⁻, Cl⁻, Br⁻, I⁻. Units: 10⁻² cm²/s

|        | NaF-KF, T=1000K | NaCl-KCl, T=1000K | NaBr-KBr, T=880K | NaI-KI, T=850K |
|--------|-----------------|-------------------|------------------|----------------|
| Na⁺    | 1.71            | 1.837             | 1.974            | 2.32           |
| K⁺     | 1.2             | 1.38              | 1.856            | 3.27           |
| A⁻(Na) | 1.79            | 1.68              | 1.53             | 0.96           |

From the table above it may be concluded that diffusion coefficients of kations increase with the growth of effective ionic radius of anions and diffusion coefficients of anions decrease.

Partial radial distribution functions (PRDF).

Values achieved are typical for ionic melts.
Table 3. Values of partial radial distribution functions for Na⁺A⁻ - K⁺A⁻ were A⁻=F, Cl⁻, Br⁻, I⁻.

|          | NaF-KF | NaCl-KCl | NaBr-KBr | NaI-KI |
|----------|--------|----------|----------|--------|
| Na⁺-A⁻   | 8.1    | 8.0      | 6.3      | 5.8    |
| K⁺-A⁻    | 5.4    | 5.2      | 4.8      | 4.0    |

Analyses of these results shows that PRDF values for a pair of ions at the point or the first maximum are greater for ions with cation of smaller radius. Interionic distances in a melt are greater for systems with greater anion radius. PRDF for different temperatures were also obtained. For the 900 K melt temperature, parameters of PRDF (location of first nonzero value, location of first maximum, values of first maximum) are presented in table 4.

Table 4. Parameters of PRDF. Units: 10⁻¹⁰m.

| Na⁺-Na⁺ | Na⁺-Br⁻ | Br⁻-Br⁻ | Na⁺-K⁺ | K⁺-K⁺ | Na⁺-Cl⁻ | Br⁻-Cl⁻ | K⁺-Cl⁻ | Cl⁻-Cl⁻ |
|---------|---------|---------|--------|-------|---------|---------|--------|---------|
| Loc. of | 3.30    | 2.78    | 4.14   | 3.72  | 2.99    | 3.93    | 2.67   | 4.03    | 2.99    | 3.82    |
| the first |         |         |        |       |         |         |        |         |         |         |
| nonzeros |         |         |        |       |         |         |        |         |         |         |
| Loc. of  | 11.2    | 3.22    | 6.17   | 6.49  | 3.71    | 6.49    | 3.11   | 5.75    | 3.74    | 5.96    |
| first    | 3       |         |        |       |         |         |        |         |         |         |
| maximum  |         |         |        |       |         |         |        |         |         |         |
| First    | 1.7     | 4.1     | 1.9    | 1.9   | 4.0     | 2.0     | 4.5    | 1.9     | 3.7     | 1.8     |

The location of the first nonzero value for ions of different types (anion-kation) is less than the location of the first nonzero value for ions of similar type (anion-anion, kation-kation). The values of the first maximum for ions of different types (anion-kation) are greater than the values of the first maximum for ions of similar types (anion-anion, kation-kation).

The values of the first maximum for ions of different types (anion-kation) for Na⁺-Cl⁻ is greater than for Na⁺-Br⁻, K⁺-Br⁻, K⁺-Cl⁻. The values of the first maximum for ions of similar types (anion-anion, kation-kation) for K⁺-K⁺ are greater than values of the first maximum for Na⁺-K⁺, Br⁻-Cl⁻, Br⁻-Br⁻, Na⁺-Na⁺.

Modeling conducted for various temperatures specified a significant extension of maximums for the first and the second coordinate spheres. Intensity of these maximums was reduced. It can also be noted that the position of the first maximum for a crystal is higher than that for melts, and with growth of temperature an insignificant increase is observed.

Normalized velocity autocorrelation functions.

The normalized velocity autocorrelation functions were calculated for ionic systems in the boundary zone during contact-melting modeling. An oscillation part is typical for velocity autocorrelation functions of ionic systems, as well as for liquid metals. With temperature increase the function becomes more gently growing. We used the following...
data as characteristic parameters for velocity autocorrelation functions: first passage times of the first minimum; value of the first minimum. For this system it was found: 1- Na 84 fs, Br 190 fs, K 135 fs, Cl 113 fs; 2 - Na 0.45, Br 0.30, K 0.43, Cl 0.45. Comparing molecular-dynamic experiments with one-component ionic systems by repeating some other known analyses, agreement of our results with the results of other authors was shown.

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