PRECISE ANALYSIS OF THE PAIR DISTRIBUTION FUNCTION OF MOLTEN LITHIUM BROMIDE BY THE MD SIMULATION METHOD

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Molecular dynamics simulations of molten lithium bromide were performed using the Born-Mayer-Huggins type pair potentials under the NEV ensemble. The side length of the unit cell was taken based on the experimental density data. The partial pair distribution functions g(r) were examined precisely around 850 K, 1000 K, 1200 K and 1500 K. The first peak position of the g(r) function of the Li-Br interaction shifts to the shorter distance, on the other hand, those of the Li-Li and Br-Br interactions shift to the longer distances with increasing the temperature. The second peak positions, the third peak positions, the first minimum positions, the second minimum positions, and the third minimum positions of the three kinds of the interaction all shift to the longer distances with increasing the temperature.

INTRODUCTION

The structural studies of molten lithium bromide were carried out by the x-ray diffraction method (1, 2). The mass effect has been investigated by the molecular dynamics simulation method (3). The static and dynamic properties of molten lithium bromide at 1000 K and 1500 K has been compared at the CAMSE' 90 symposium (4). At this present work the molecular dynamics calculation method was applied to this salt at four temperature conditions in order to see how does the structure change on increasing the temperature by examining the g(r) function precisely.

METHOD

216 Li ions and 216 Br ions were placed in the cubic cell. The side length of the cell was taken assuming that the molar volumes of lithium bromide are 34.6 cm$^3$ at 850 K, 36.0 cm$^3$ at 1000 K, 38.0 cm$^3$ at 1200 K, and 41.6 cm$^3$ at 1500 K, based on the experimental density data.
The periodic boundary condition was introduced to avoid the boundary problems and the Ewald method (5) was employed in the calculation of the coulombic force. The Born-Mayer-Huggins type potential functions with the Tosi-Fumi parameters (6) were used in the simulation.

\[
V_{ij} = \frac{Z_i Z_j e^2}{4\pi \varepsilon_0 r} + (1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}) \exp\left[\frac{\sigma_i + \sigma_j - r}{\beta}\right] - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}
\]

where \(Z\) is an ionic charge number, \(e\) the elementary charge, \(\varepsilon_0\) the permittivity of vacuum, \(n\) the number of the electrons in an outermost shell, \(b\) a repulsion parameter, \(r\) a softness parameter. The time step of the simulation was taken to be 4 fs and the at the first stage of the simulation a NTV ensemble at each temperature was settled for several thousand steps with a method slightly different (7) from that of Woodcock (8). After the NEV ensemble and the subsequent calculation have reached the equilibrium, the collection of the data was begun. The present data analyses were made from the last 12,000 steps, it corresponds to 48 ps.

RESULT AND DISCUSSION

Figure 1 represents the partial pair distribution functions of the Li-Br interaction at four temperatures. The solid line shows the \(g(r)\) at 850 K. As shown in Fig. 1 the first peak position shifts to the shorter distance with increasing the temperature. On the other hand the second and the third peak position both shift to the longer distances with increasing the temperature. Figures 2 and 3 show the partial pair distribution functions of the Li-Li and Br-Br interactions, respectively. All peak positions shift to the longer distances with increasing the temperature.

In order to compare the peak profile of the pair distribution functions at various temperatures more precisely, we name the characteristic point of the \(g(r)\) function so as that \(R_i^1\), \(r_{M1}\) and \(r_{Mj}\) give the distances in pm where for the \(i\)-th time the \(g(r)\) crosses unity, have a maximum value and a minimum value, as shown in Fig. 4. Numerical values of the characteristic points of the pair distribution function are tabulated in Table 1. It is noticed that the \(R_i^1\) value of the Li-Br interaction shifts to the shorter distance with increasing the temperature. On the other hand the \(R_i^1\) value of Li-Li interaction shifts to the longer distance, and furthermore the \(R_i^1\) value of the Br-Br interaction has no change with increasing the temperature. It is clearly recognized that the first peak position \(r_{M1}\) of the Li-Br interaction
shifts to the longer distance with increasing the temperature. While those of the Li-Li pair and Br-Br pair have the tendency toward longer distances. The $R_2$ values for the Li-Br pair, the Li-Li pair and the Br-Br pair all shift to the longer distances with increasing the temperature. The characteristic values of the $g(r)$ beyond the $R_2$ point, $r_m$, $R_2$, $r_m$ values for three kinds of the interactions shift to the longer distances with increasing the temperature. The first peak heights for three kinds of the interaction become lower and lower and the first minimum heights become higher and higher as the temperature increases as shown in Table 1.

The coordination numbers for the three pairs at four temperatures are listed in Table 2. With increasing the temperature, the coordination numbers of three pairs decrease. It is now under examination that the coordination structure changes or not by the angular correlation function. And I would like to mention that the molecular dynamics simulation under the constant volume condition is now going on whether the volume effect or the temperature effect does cause these phenomena.

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Table 1. Characteristic Values of the Pair Correlation Functions $g(r)$. $R_i$, $r_{M_1}$ and $r_{m_1}$ are the distances in pm where for the $i$th time $g(r)$ crosses unity, has a maximum and a minimum, respectively.

|       | $R_1$ | $r_{M_1}$ | $R_2$ | $r_{m_1}$ | $R_3$ | $r_{M_2}$ | $R_4$ | $r_{m_2}$ | $R_5$ | $g(r_{M_1})$ | $g(r_{m_1})$ |
|-------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-------------|-------------|
| 850 K | Li–Br | 210       | 241   | 300       | 368   | 498       | 581   | 661       | 737   | 834         | 3.69        |
|       | Li–Li | 340       | 399   | 490       | 565   | 668       | 742   | 838       | 916   | 1003        | 1.85        |
|       | Br–Br | 348       | 395   | 484       | 560   | 668       | 744   | 833       | 909   | 1003        | 2.24        |
| 1000 K| Li–Br | 208       | 239   | 302       | 375   | 501       | 582   | 665       | 741   | 841         | 3.79        |
|       | Li–Li | 341       | 402   | 494       | 571   | 674       | 749   | 844       | 920   | 1012        | 1.78        |
|       | Br–Br | 348       | 401   | 487       | 569   | 673       | 754   | 841       | 913   | 1010        | 2.16        |
| 1200 K| Li–Br | 205       | 237   | 304       | 380   | 507       | 585   | 673       | 754   | 853         | 3.57        |
|       | Li–Li | 342       | 405   | 499       | 576   | 680       | 757   | 853       | 932   | 1025        | 1.70        |
|       | Br–Br | 348       | 399   | 494       | 572   | 681       | 755   | 849       | 927   | 1025        | 1.99        |
| 1500 K| Li–Br | 201       | 235   | 307       | 385   | 513       | 588   | 683       | 761   | 866         | 3.48        |
|       | Li–Li | 344       | 411   | 506       | 583   | 688       | 770   | 867       | 948   | 1041        | 1.61        |
|       | Br–Br | 348       | 404   | 500       | 577   | 691       | 763   | 865       | 944   | 1039        | 1.85        |
Table 2. The Coordination numbers $n(r)$. $R_i$ and $r_{mi}$ are the distances in pm
Where for the ith Time $g(r)$ Crosses Unity, Has a Minimum Value, Respectively.

| Temperature | Li—Br | Li—Li | Br—Br | Li—Br | Li—Li | Br—Br |
|-------------|-------|-------|-------|-------|-------|-------|
| 850 K       | 3.2   | 9.1   | 9.1   | 3.1   | 8.8   | 8.8   |
|             | 4.2   | 12.6  | 12.4  | 4.2   | 12.4  | 12.3  |
| 1000 K      | 3.0   | 8.5   | 8.5   | 3.0   | 8.5   | 8.5   |
|             | 4.1   | 12.0  | 11.9  | 4.1   | 12.0  | 11.9  |
| 1200 K      | 2.8   | 7.9   | 7.8   | 2.8   | 7.9   | 7.8   |
|             | 3.9   | 11.4  | 11.1  | 3.9   | 11.4  | 11.1  |
| 1500 K      |       |       |       |       |       |       |
|             |       |       |       |       |       |       |
Figure 1. The Partial Pair Distribution Function $g(r)$ of the Li-Br Interaction at Four Temperatures.

- 850 K
- 1000 K
- 1200 K
- 1500 K

Figure 2. The $g(r)$ of the Li-Li Interaction.

- 850 K
- 1000 K
- 1200 K
- 1500 K

Figure 3. The $g(r)$ of the Br-Br Interaction.

- 850 K
- 1000 K
- 1200 K
- 1500 K

Figure 4. The Characteristic Names of the Pair Distribution Function.