VISUAL SIMULATION OF MOLTEN Li$_2$BeF$_4$
BY MOLECULAR DYNAMICS

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Abstract
A new computer "visual simulation" which efficiently uses coordinates and velocities to represent structure and ionic motion in liquids is presented. As an initial try, visual simulation using molecular dynamics was applied to molten Li$_2$BeF$_4$ and LiBeF$_3$ to clarify the salts' liquid structure and their ionic dynamics. New information about liquid structure and ionic dynamics was obtained from the simulation as follows. There are many clusters such as monomers (BeF$_4^{-}$) and dimers (Be$_2$F$_7$) in molten Li$_2$BeF$_4$. On the other hand, there is a network structure in molten LiBeF$_3$. The diffusion coefficient of F ions in molten Li$_2$BeF$_4$ is larger than that of molten LiBeF$_3$. This is explained by the differences in liquid structure between the two salts.

1. Introduction
It has been 15 years since the application of the results of computer simulation of simple liquids [1] to molten salts has begun. During these 15 years, computer simulations have largely contributed to the development of molten salts chemistry by giving new information and interpretation about structure and transport phenomena in liquids [2] [3].

However, previous computer simulations do not fully utilize their output data, which consists of coordinates and velocities of all the particles in the system. Therefore, in this work, a new computer "visual simulation", which efficiently uses coordinates and velocities to represent structure and ionic motion in liquids is presented.

Previously, limited graphical representations were created,
such as stereoscopic figures of liquid structures or trajectory figures of atomic motion projected on a plane by wire frame models. But it was difficult to produce a more realistic animation of structure and ionic motion in a liquid by three dimensional computer graphics with shading and highlights [4] because of limitations in computer technology. Recent developments in computer technology, such as a supercomputer capable of performing hundreds of millions of floating point operations per second (MFLOPS) and high speed graphics technology now enables us to produce these kinds of animated films.

As an initial try, visual simulation using molecular dynamics was applied to molten Li$_2$BeF$_4$ and LiBeF$_3$ to clarify the salts' liquid structure and their ionic dynamics.

2. Molecular Dynamics Simulations

Molecular dynamics simulations were performed under the conditions shown in table one. An initial configuration of 150 Li$_2$BeF$_4$ molecules (or 210 LiBeF$_3$ molecules) was taken from a crystal structure. The temperature of the system was increased to the desired temperature by making small, random velocity changes during the first 10000 integral time steps in the trajectories, which were then continued for a total of 20ps (20000 integral time steps). The computation time per time step was about 0.48 seconds on the FACOM VP-200 supercomputer (570 MFLOPS). This computation speed was 15 times faster than that of the current fastest general purpose computer, the FACOM M380 (9 MFLOPS).

The forces on the ions were calculated from the Born-Mayer-Huggins function. The parameter of the repulsion term adopted the Busing's values (model 2) which were determined for crystal Li$_2$BeF$_4$ [5]. The coulombic force term on ions was calculated using Ewald's summations ($R_{\alpha} = L/2$, $n < 27$, $\alpha \cdot L = 6$, where $L$ is the edge length of the cubic box).

3. Visualization of Liquid Structure and Ionic Motion

Liquid structure and ionic motion in the molten Li$_2$BeF$_4$ and LiBeF$_3$ was visualized by means of the painter's algorithm and trapezoidal approximation, as well as other high speed graphics techniques incorporating shading and highlights (see [4]), using the three dimensional coordinates of the ions in the cubic box at each integral time step. A snapshot of the liquid structure of molten Li$_2$BeF$_4$ is shown in figure one. Video tapes of ionic motion in molten Li$_2$BeF$_4$ and LiBeF$_3$ were produced using the computer system described in figure two.
4. Results and Discussion

4.1 Pair Correlation Function

In table two, the first peak positions are shown together with the corresponding experimental values by Vaslow and Narten [6]. Though the peak positions obtained by molecular dynamics are shorter than the experimental ones by 0.03-0.06 angstroms, the agreement between molecular dynamics results and the experimental ones are very good.

In figures three and four, the pair correlation functions for unlike ion pairs and like ion pairs are shown together with their corresponding running coordination numbers. There are no observed differences between the pair correlation functions for unlike pairs for molten Li\textsubscript{2}BeF\textsubscript{4} and for LiBeF\textsubscript{3}. However, in the case of the functions for like ion pairs (F-F pairs, Be-Be pairs), the second peak position of the pair correlation function in Li\textsubscript{2}BeF\textsubscript{4} is shifted by 0.02nm to the right. These facts suggest that the liquid structure over a long range for Li\textsubscript{2}BeF\textsubscript{4} differs from the structure for LiBeF\textsubscript{3}.

4.2 Coordination Number

In figure five, the distribution function of the number of F ions located around Be ions with radius $R_n$ (where $R_n$ is the distance where a pair correlation function crosses unity after the first peak, as in table three) is shown. The average value is 3.86 in molten Li\textsubscript{2}BeF\textsubscript{4} and 3.85 in molten LiBeF\textsubscript{3}. The proportion of coordination number 4 is 80 percent for both Li\textsubscript{2}BeF\textsubscript{4} and LiBeF\textsubscript{3}. In figure six, the distribution function of the number of Be ions located around F ions with $R_n$ is shown. The proportion of coordination number 2 is 16% in Li\textsubscript{2}BeF\textsubscript{4} and 35% in LiBeF\textsubscript{3}. The proportion of coordination number 1 is 66% in Li\textsubscript{2}BeF\textsubscript{4} and 58% in LiBeF\textsubscript{3}. These facts suggest that there are monomers (BeF\textsubscript{4}) in molten Li\textsubscript{2}BeF\textsubscript{4} but that in the case of LiBeF\textsubscript{3} a network structure exists.

4.3 Angular Distribution

For a more detailed description of the short-range structure, an angular distribution function [7] is defined as

$$P(\theta) = \frac{n(\theta)}{\int_0^{2\pi} n(\theta) d\theta}$$

where $n(\theta)$ is the number of ion pairs located around an ion within $R_n$ at an angle of $\theta$. In figure seven, the angular distribution functions around a Be ion are shown. The angle of F-Be-F distributes sharply about a center of 104 degrees, which is close to the central angle of a regular tetrahedron. This suggests that F ions coordinate around Be ions in a regular tetrahedron arrangement. The angle of Be-Be-Be widely distributes around a center of 100 degrees, which is close to the vertex angle of a pentagon (108 degrees).
4.4 Rings and Clusters

For a more detailed description of the long range structure, topological analysis was performed. The "ring" shown in figure eight is defined as the minimum circle formed by Be-F pairs which are connected with a distance of 0.22nm. For example, a 3-membered ring consists of three Be ions and three F ions. The "cluster" showing in figure nine is defined as an ionic complex that is formed by Be-F pairs also connected within 0.22nm where, in this case, F ions on the outside of the complex connect to only one Be ion.

In table four, the number of rings existing in a basic cell are shown. These numbers were averaged over 150 ensembles at 0.02 picosecond intervals. In molten Li₂BeF₄, the 5-membered ring is most populous. The largest ring is a 30-membered one. There are, in all, about 19 rings in molten LiBeF₄. These analyses were confirmed by the use of computer graphics.

In figure 10, pictures of rings existing in molten LiBeF₄ are shown. On the other hand, there are few rings in molten Li₂BeF₄. It was observed, by using computer graphics, that the network structure disappears in the case of Li₂BeF₄. In table five, the number of clusters in a basic cell is shown. There are about 14 monomers (BeF₄⁻) and about 5 dimers (Be₂F₇⁻) in molten LiBeF₄. However, in molten Li₂BeF₄ there about 40 monomers and 14 dimers, as many as 3 times as in molten LiBeF₄.

It was observed that there are many clusters in molten Li₂BeF₄ by computer graphics. In figure 11, pictures of clusters in molten Li₂BeF₄ are shown.

4.5 Diffusion Coefficient

In table six, the diffusion coefficients of each ion at 1120 degrees K, obtained from mean square displacement, are shown together with their corresponding experimental results [8]. The diffusion coefficients in molten Li₂BeF₄ are larger than those for molten LiBeF₄. This can be explained from the differences in liquid structure between molten Li₂BeF₄ and LiBeF₄. That is, there are network structures in molten LiBeF₄, but in molten Li₂BeF₄ there are many clusters but few network structures. To make sure that a small complex of ions moves more easily than a large one, the mean square displacements of Be ions and F ions, which are members of monomers (BeF₄⁻), and one of Be ions and F ions which are not members of monomers were calculated. In figure 12, the mean square displacements of Be ions and F ions in molten LiBeF₄ are shown. The displacements of Be and F ions which are members of monomers are larger than ones which are not members of monomers. This proves that a small complex moves more easily than
a large complex. In figure 13, the mean square displacements of Be ions and F ions in molten Li$_2$BeF$_4$ are shown. Though the displacements of the ions which are monomer members are larger than one which are not, the differences are not remarkable. This is explained from the fact that 30 percent of all Be ions in a basic cell of Li$_2$BeF$_4$ are the members of monomers, and network structures are few.

4.6 Relative Velocity Auto Correlation Function

To clarify the ionic dynamics in molten Li$_2$BeF$_4$ and LiBeF$_3$, an auto-correlation function of relative velocity (RVAF) between a central ion and ions located around that ion with $R_n$ was calculated.

In figure 14, relative velocity auto-correlation functions for Be-Be pairs are shown. In the same figure, $V_r$ is the relative velocity, $V_t$ is the transverse component of $V_r$ ($V_t = u_r \times V_r$, where $u_r$ is the unit direction vector from a central ion to the surrounding ion), and $V_l$ is the longitudinal component of $V_r$ ($V_l = u_r \cdot V_r$). Though the longitudinal part of the RVAF in molten Li$_2$BeF$_4$ vibrates, in its cosine form, with a period of 0.04ps over 0.4ps, LiBeF$_3$ deforms over 0.12ps. This is consistent with the fact that 26 percent of all Be ions in the basic cell of molten Li$_2$BeF$_4$ are member of dimers (Be$_2$F$_7$). In the case of LiBeF$_3$, 54 percent of all Be ions in the basic cell are members of dimers (Be$_2$F$_7$). This suggests that Be$_2$F$_7$ with a lifetime over 0.4ps exists in molten Li$_2$BeF$_4$, and the dimer vibrates in stretching mode.

In figure 15, RVAFs for Be-F pairs are shown. A remarkable difference between the longitudinal part and the transverse part of the RVAF is not observed. Their correlation is weaker than that for Be-Be pairs. This suggests that F ions located around Be ions may rotate around the Be ions. To observe such a motion, a videotape of ionic motion was produced using the computer system described in figure one. This video tape will be shown at the 5th International Symposium on Molten Salts.

5. Conclusion

We have presented the first visual simulation of molten salts Li$_2$BeF$_4$ and LiBeF$_3$. The information about the liquid structure and dynamics behavior of the salts obtained from the visual simulation was as follows.

(1) There are many clusters such as Be$_4^+$ and Be$_7^-$ in molten Li$_2$BeF$_4$. 50 percent of all Be ions in the basic cell are members of monomers and dimers.
(2) There are network structures in molten LiBeF₃. Five-membered rings comprise the most abundant of these in the basic cell, numbering about six. 60 percent of all Be ions in the basic cell are the members of rings. On the other hand, only 11 percent of all Be ions in the basic cell are members of monomers or dimers.

(3) The diffusion coefficient of F ions in molten Li₂BeF₄ is larger than that for LiBeF₃. This is consistent with experimental results and is due to the difference in liquid structure between molten Li₂BeF₄ and LiBeF₃.

We think that there are still a few problems to solve, as follows:

(1) It is necessary to refine the pair potential function and its parameters to provide better agreement with experimental results, including a discussion of the failure in the pair potential [9].

(2) It is necessary to develop techniques which more effectively and clearly demonstrate the characteristics of ionic motion in a liquid.

If these problems are resolved, visual simulation can serve to help understand the dynamical behavior and various properties of liquids at any temperature and pressure. For example, the results of this work may be applied to silicates because of the similarity between MgO-SiO₂ systems and LiF-BeF₂ systems [10].

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• Ensemble ------ micro canonical system

• Number of ions in the basic cell
  Li$_2$BeF$_4$ --- 1050 ions (300Li,150Be,600F)
  LiBeF$_3$ --- 1050 ions (210Li,210Be,630F)

• Size of the basic cell

| Liquid  | Temp/K | L / nm | $\rho$ / g-cm$^3$ |
|---------|--------|--------|-----------------|
| Li$_2$BeF$_4$ | 673  | 2.31003 | 2.064 |
|         | 873  | 2.34257 | 1.979 |
|         | 1120 | 2.38183 | 1.874 |
| LiBeF$_3$  | 828  | 2.30590 | 2.009 |
|         | 873  | 2.31436 | 1.987 |
|         | 1120 | 2.36315 | 1.866 |

$L$ is the edge length of a basic cell.

Table 1 Conditions of Molecular Dynamics simulations.

| Pair     | Li$_2$BeF$_4$ : 828 K | LiBeF$_3$ : 673 K |
|----------|------------------------|-------------------|
| Li-Li    | 0.296 (-----)          | 0.292 (-----)     |
| Be-Be    | 0.312 (-----)          | 0.308 (-----)     |
| F-F      | 0.252 (0.256\*)       | 0.252 (0.256\*)  |
| Li-Be    | 0.306 (-----)          | 0.310 (-----)     |
| Li-F     | 0.178 (0.185\*)       | 0.180 (0.185\*)  |
| Be-F     | 0.154 (0.158\*)       | 0.156 (0.158\*)  |

Table 2 Mean distances of ion pair in molten Li$_2$BeF$_4$ and LiBeF$_3$.

(*) F.Vaslow and A.H.Narten, J.Chem.Phys., 59 (1973) 4049
Fig. 1 Snapshot of molten Li$_2$BeF$_4$ by computer graphics; the small balls are Be ions, the medium ones are Li ions, the big ones are F ions, the sticks join Be ions and F ions where their separation is within 0.22 nm.

Fig. 2 Computer system configuration for Visual Simulation.
Fig. 3 Pair correlation functions and running coordination numbers of unlike ion pairs in molten Li$_2$BeF$_4$ and LiBeF$_3$. 
Fig. 4 Pair correlation functions and running coordination numbers of like ion pairs in molten Li2BeF4 and LiBeF3.
Table 3  Upper limit distances (Rn) of nearest neighbor of ion pair.

| ion pair | LiBeF₃  | Li₂BeF₄ |
|----------|---------|---------|
| Li-Li    | 0.365   | 0.362   |
| Be-Be    | 0.338   | 0.337   |
| F-F      | 0.300   | 0.328   |
| Li-Be    | 0.360   | 0.361   |
| Li-F     | 0.220   | 0.221   |
| Be-F     | 0.187   | 0.187   |

Fig. 5  Distribution functions of the number of F ions located around Be ion within Rn.

Fig. 6  Distribution functions of the number of Be ions located around F ion within Rn.
Fig. 7 Distribution function of angle around Be ion
\( \triangle: \text{Li}_2\text{BeF}_4, \quad \circ: \text{LiBeF}_3 \)
Fig. 8 Rings formed by Be-F pairs which are connected within a distance of 0.22 nm.

Fig. 9 Clusters formed by Be-F pairs connected within 0.22 nm where F ions on the outside of the complex connects to only one Be ion.

| Kind of Ring   | LiBeF₃ | Li₂BeF₄ |
|---------------|--------|--------|
| 2-membered ring | 0.36   | 0.58   |
| 3-membered ring | 1.48   | 0.26   |
| 4-membered ring | 3.24   | 1.18   |
| 5-membered ring | 6.02   | 0.52   |
| 6-membered ring | 2.44   | 0.007  |
| 7-membered ring | 1.48   | 0.0    |
| 8-membered ring | 0.63   | 0.0    |
| 9-membered ring | 0.78   | 0.0    |
| total          | 18.90  | 2.55   |

Table 4 The numbers of Rings existing in a basic cell.
| Kind of Cluster | LiBeF₃ | Li₂BeF₄ |
|----------------|--------|---------|
| BeF₄           | 13.70  | 39.30   |
| Be₂F₇          | 4.82   | 13.70   |
| Be₃F₁₀         | 2.05   | 5.14    |
| Be₄F₁₃         | 0.17   | 2.68    |
| total          | 22.50  | 66.70   |

Table 5 The numbers of Clusters existing in a basic cell.

| Temp. | ion  | Li₂BeF₄ | LiBeF₃ |
|-------|------|---------|--------|
| 1120 K| Li   | 6.1×10⁻⁹| 4.7×10⁻⁹|
|       | Be   | 2.6×10⁻⁹| 1.5×10⁻⁹|
|       | F    | 3.9×10⁻⁹| 2.4×10⁻⁹|
| 900 K | F (exp.*) | 3.0×10⁻⁸| 3.0×10⁻⁸|

* Ref. [8]

Table 6 The diffusion coefficients (m²s⁻¹) of each ion at 1120 K obtained from their corresponding mean square displacements together with the experimental results at 900 K.
Fig. 10 Pictures of Rings existing in molten LiBeF3: the small balls are Be ions, the big ones are F ions.
Fig. 11 Pictures of Clusters existing in molten Li2BeF4: the small balls are Be ions, the big ones are F ions.
Fig. 12 The mean square displacements of ions in molten LiBeF₃.

Fig. 13 The mean square displacements of ions in molten Li₂BeF₄.

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Fig. 14 The relative velocity autocorrelation function for Be-Be pair.
Fig. 15 The relative velocity autocorrelation function for Be-F pair.