LARGE SCALE MOLECULAR DYNAMICS SIMULATION OF MOLTEN SALTS

Yoshihiro Okamoto, Shigeru Ishizuki and Toru Ogawa

Japan Atomic Energy Research Institute (JAERI)
Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, JAPAN

ABSTRACT

A vectorized molecular dynamics code was parallelized to handle a larger system consisting of more than 10000 ions. In the parallelization, ions in a basic cell were divided in equal parts into each processing element, PE, of the supercomputer. The parallelization made possible to calculate physical properties with increased accuracy. Effects of the parallelization were checked in the MD simulation of molten UC13 having a medium-ranged structural order and molten NaCl-KCl-CsCl ternary mixture.

INTRODUCTION

We have calculated structure and physical properties of molten salts by a molecular dynamics (MD) simulation using supercomputers (1-3). A vector supercomputer (VP2600: Fujitsu Corporation) had been used to calculate some properties such as the shear viscosity and the electrical conductivity. Recently, a vector-parallel supercomputer VPP500 system (Fujitsu Corporation) was introduced at JAERI. Initially, we had used it only as a vector supercomputer (not as a parallel computer). Number of ions treated in the calculation has been limited less than 2000 in non-parallel computation, since large memory space was used for highly-leveled vectorization. This size is clearly insufficient in calculations of a mixture containing many kinds of elements and species having a medium-ranged structural order. In the present work, the MD code was parallelized to achieve faster and larger calculation. For examples, MD simulations of molten UC13 having a medium-ranged structural order and molten NaCl-KCl-CsCl systems containing four kinds of ions were performed by using larger systems.
PROCEDURE

In the parallelization, ions in a basic cell were divided in equal parts into each processing element, PE, of the supercomputer. The PE can be regarded as a supercomputer with single CPU. Each PE is connected by cross-bar network (400MB/s) with other PEs. Our already vectorized MD code had made possible to accumulate a million time steps data for 1000 ions system at the supercomputer VPP500 in JAERI. In this code, however, a large memory space proportional to square of total number of ions is used for high vectorization. This space limits the number of ions (less than 2000 ions) in the case of high-speed calculation.

Major problem at parallelization of our code in the VPP500 system was the memory access beyond a PE, since the VPP500 system has a distributed-memory architecture. Memory access beyond a PE (400MB/s) is extremely slower than that of local memory in PE. However, memory access beyond a PE cannot be avoided to calculate long-ranged force (Coulombic interaction). We solved this problem by saving the information on all ions in a global memory. Then memory access beyond a PE is minimized.

In the present work, MD calculations for molten KCl, UCl₃ and NaCl-KCl-CsCl were performed by using vectorized and vectorized-parallelized codes. For molten KCl, six kinds of systems containing 216, 1000, 1728, 5832, 17328 and 27000 ions were calculated by using non-parallel and three kinds of parallel (PE=2, 3 and 4) computations. Three kinds of calculation, that is, 1000 ions system by non-parallel, 5832 ions system by 4PE parallel and 27000 ions system by 16PE parallel were carried out for molten UCl₃. Pair potentials used in the calculations were Tosi-Fumi potential (3) for molten KCl and molten NaCl-KCl-CsCl mixtures, and potential proposed by our group in ref. (1) for molten UCl₃.

RESULTS AND DISCUSSION

Effects of parallelization

Fig. 1 shows the ratio of CPU time of parallel computations to non-parallel one for a MD time step for molten KCl. If ideal parallelization is completed, half and quarter values must be obtained for 2 and 4 PE calculations, respectively. It can be clearly seen that smallest system with 216 ions is not suitable for parallelization, since performance became poor in spite of parallelization. In addition, the parallelization did not work effectively for a system with 1000 ions we have been typically used at
non-parallel computations. They were due to lowering of vectorization effect by parallelization because number of ions in each PE decreases by parallelization and length of vectorization loop also decreases. Parallelization cannot compensate such a poor vectorization. To obtain merit of the parallelization, we should use at least 5000 ions system for 4PEs computation. Large systems beyond 10000 ions showed almost ideal results.

Fig.2 shows comparison of CPU time per MD step for calculation of molten UCl₃ based on 8000 ions system. These results imply that parallel computation is essential for practical calculation of such a large system.

**Molten UCl₃**

Partial correlation functions $G_{UCl}(r)$ of molten UCl₃ calculated at the VPP500 are shown in Fig.3. In molten UCl₃, U⁴⁺ ion is octahedrally surrounded by six Cl⁻ ions like many molten rare earth trichlorides(1,2). From X-ray diffraction analysis(1), we have confirmed that there is a medium-ranged structural order in the melt. It can be considered that this order is based on network ordering of the octahedra (UCl₆)³⁺ since sharing of a Cl⁻ ion from two U⁴⁺ ions are necessary to compensate lack of Cl⁻ ion in view of the chemical stoichiometry. The result from the 1000 ions system in the Fig.3 shows significant meaningful oscillation around 1.7nm. For precise calculation of reciprocal fourier transform of $G_{UCl}(r)$ function, value of the function at larger r region should be close to 1 to avoid a termination effect. Therefore, the 1000 ions system is not enough to discuss the medium-ranged structure order. There is no meaningful oscillation around cut-off distance for the 8000 ions system by 4PEs and the 27000 ions system by 16PEs. Thus we may expect more precise transformation for the 8000 and 27000 ions systems.

Fig.4 shows X-ray reduced intensity functions for experimental and three computational systems corresponding to the Fig.3. Standard deviations of the calculated functions from the experimental value are listed in the figure. It can be seen clearly that larger systems (N=8000 and 27000) gave better agreement with the experimental result.

**Molten NaCl-KCl-CsCl mixture**

Larger system in the MD simulation is expected to have an advantage in case of multicomponent systems such as NaCl-KCl-CsCl systems. Six kinds of compositions were calculated by using 1000 ions systems. Compositions and number of each ion are listed in Table 1. In addition to the 1000 ions systems, larger systems for 10 and 5%NaCl compositions containing 8000 ions were calculated by the parallel technique.
Fig. 5 shows partial RDF of Na-Na pair for composition of 45, 30, 20, 10 and 5% NaCl. These functions were deduced from accumulation of 5000 MD steps data. In all the functions, there are significant oscillation around the cut-off distance of 1.65-1.85 nm. It suggests that a larger system should be used in the simulation. In the system containing only 5% NaCl (only 25 ions in the system of total 1000 ions), shape of the function is not stable at all. Fig. 6 (a) and (b) show the PRDF of Na-Na pair obtained from the 8000 ions systems for 10% and 5% NaCl. The functions converged to 1.0 around cut-off distance and their curves are more smooth compared with the results of N=1000 systems. It is a clear illustration of the advantage of the larger systems in structural analysis.

CONCLUSION

The MD simulation code we have used for the calculation of structure and physical properties of molten salts has been parallelized to handle a larger system with more than 10000 ions. The parallelization is not effective for small system less than 1000 ions because of decreasing effect of the vectorization. To evaluate the medium-ranged structure order in molten UC13, we should use a larger system more than 10000 ions. Also for the multicomponent system, the calculation with a larger system gave more precise information.

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Table 1 Composition and number of ions in NaCl-KCl-CsCl ternary systems

(1000 ions systems) NaCl:KCl:CsCl

| Composition | Na   | K    | Cs  | Cl  |
|-------------|------|------|-----|-----|
| 45:45:10    | 225  | 225  | 50  | 500 |
| 30:30:40    | 150  | 150  | 200 | 500 |
| 20:20:60    | 100  | 100  | 300 | 500 |
| 10:10:80    | 50   | 50   | 400 | 500 |
| 5:5:90      | 25   | 25   | 450 | 500 |

(8000 ions systems) NaCl:KCl:CsCl

| Composition | Na   | K    | Cs  | Cl  |
|-------------|------|------|-----|-----|
| 10:10:80    | 400  | 400  | 3200| 4000|
| 5:5:90      | 200  | 200  | 3600| 4000|

Fig.1 CPU time ratio in parallel computations (N=number of ions in basic cell)

Fig.2 CPU time per a MD step for some kinds of computers for molten UCl₃ (8000 ions system)
Fig. 3 Partial radial distribution function $G_{UL}(r)$ in molten UC$_3$.

Fig. 4 X-ray reduced intensity $Q_i(Q)$ of molten UC$_3$ (S.D. - standard deviation).

Fig. 5 Partial RDF of Na-Na in molten NaCl-KCl-CsCl mixtures by 5000 MD steps accumulation.

Fig. 6 Partial RDF of Na-Na in molten NaCl-KCl-CsCl mixtures.