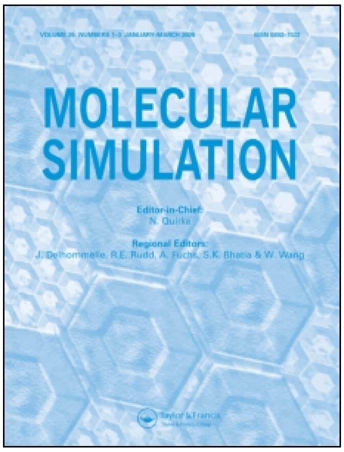

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MOLECULAR DYNAMICS STUDY OF BaB_2O_4 IN CRYSTALLINE AND MOLTEN STATES

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Structural aspects of BaB_2O_4 liquids have been investigated by the molecular dynamics simulation including the determination on the parameters of the interatomic potential applicable to BaB_2O_4 in both crystalline and molten states. The structure and physical properties of BaB_2O_4 crystals were successfully reproduced by the MD simulation for both α and β phases. The simulated interference function in the liquid state was also in good agreement with the experimental one. Several interesting features on the relaxation phenomena just after melting were reproduced by the simulation that the structure factors of simulated liquid maintain the characteristic features of the original crystal structure for more than 40ps after melting, and the variation of the number of rings formed by B-O bondings was found to increase after melting.

KEY WORDS: Barium borate, liquid structure, relaxation phenomena, molecular dynamics

1 INTRODUCTION

The composition of barium metaborate (BaB_2O_4) has two modifications for the crystal structure, high temperature (α) and low temperature (β) phases, and the β-BaB_2O_4 crystal is known to show the nonlinear optical property. A large, homogeneous single crystal of β-BaB_2O_4 is required for the purpose of the wavelength conversion of the laser beam into the ultra-violet regions. However, it is difficult to obtain a single crystal of β phase with good quality since the stability of α phase is preferred at the melting temperature, and thus several attempts have been made, for example, by adding some flux elements [1].

Onishi [2] and Itoh *et al.* [3] found that the β phase crystal can be grown by the direct Czochralski method from the melt prepared by a starting material of β phase by applying a large temperature gradient at the solid-liquid interface. Kôzuki and Itoh [4] investigated the relationship between the temperature of solid-liquid interface and the phase of the resultant crystal, and found that the β phase can be grown at 1321 K in the supercooled region which is considerably higher than the $\alpha-\beta$ transition temperature, 1193 K [5]. Kouta *et al.* [6] found that a single crystal of β phase cannot grow when the melt is heated up to about 100 K higher than the melting point. These facts are quite interesting in both scientific and engineering aspects, and several authors tried to explain them by using the Ostwald step rule

[4, 5] or by a hypothetical metastable state in the liquid just above the melting point [7]. However, there has been no theory or model which can explain all of the experimental result, and some further investigation is required for the better understanding of these phenomena on a microscopic level

The main purpose of this paper is to present the structural features of BaB_2O_4 liquid obtained from β phase crystal by using the molecular dynamics (MD) simulation, together with a parameter set of interatomic potentials applicable to BaB_2O_4 in both crystalline and liquid states. The detailed analysis on the difference between the properties of the liquids obtained from α and β phases will be reported elsewhere [8].

2 MOLECULAR DYNAMICS SIMULATION

In this study, we adopted the interatomic potential of the Born-Mayer-Huggins form which is widely used for the study of oxides given by,

$$\phi_{ij}(r) = f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) + \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r}, \tag{1}$$

where r is the separation between i and j species, ε_0 the dielectric constant, e the electron charge, a_i and b_i are the radius and softness parameters of ion i, Z_i the valence of ion i, and $f_0 = 6.947 \times 10^{-11}$ N. The values of the potential parameters will be given and discussed later.

The MD simulation for both crystalline and molten states was carried out on 4536 atoms by using the Verlet algorithm [9] with the time step of 2 fs. The MD basic cell was selected as a rectangular super cell of each crystal structure with the dimension of $4.34 \times 3.76 \times 3.92$ nm and $3.76 \times 4.34 \times 3.81$ nm for α and β phases, respectively. The periodic boundary conditions were applied to the MD basic cell, and the long range forces and energy were calculated by the Ewald sum method [9]. The simulation was started with random atomic velocities corresponding to 300 K followed by the initial relaxation period of 3600 steps at the atmospheric pressure. The simulation for the crystalline state was carried out at 300 K for 2500 steps. For the molten state, simulation was carried out at 1400 K for 20,000 steps after heating the β phase crystal from 300 K to 1400 K with the rate of 0.5 K/step. The ensemble of the simulation is the constant-*NPT* with Nosé's thermostat [10], and the cell dimension was controlled so as to maintain the total pressure of 10^5 Pa by using Andersen's method [11].

3 RESULTS

Interatomic Potentials and Crystal Structures of BaB_2O_4

The crystal structure of BaB_2O_4 was analyzed by Mighell [12] and Liebertz [13], and was found to have the space groups of $R\bar{3}c$ and $R3c$ for α and β phases, respectively. These structures are in close relation to each other that both crystals are constructed by stacking the pair of parallel, oppositely directed B_3O_6 groups (boroxol rings). The main difference between α and β phases appears in the cell dimensions and the sites of barium atoms [14].

We determined the potential parameters a_i, b_i, and Z_i applicable to BaB_2O_4 by using the following concepts; i) each element is assumed to be completely ionized, ii) values of the softness parameters, b_B and b_O, are assumed to be equal to Kawamura's ones [15] which is originally determined for Na_2O-B_2O_3 system, iii) values of the rest parameters, a_B, a_{Ba}, a_O, and b_{Ba} are selected so as to reproduce the stability of crystal structures under the melting point of each crystal phase. After checking the result of MD simulation with changing the values for a_i and b_i, we finally selected the parameter set as listed in Table 1. It may be noted that the present value of a_O for BaB_2O_4 slightly differs from the Kawamura's one for Na_2O-B_2O_3 system. By using our potential parameters, the atomic positions including the stacking sequence of boroxol rings and barium atom in each crystal were successfully simulated. In Table 2 are shown the comparison of positional parameters obtained by MD simulation and X-ray analysis [12, 14]. The agreement of the values of each atom is quite good for α phase. The general agreement is also maintained for β phase, however in this case, there were some small discrepancies due to the difference in the distance between the paired boroxol rings. The simulated structure has smaller distance between the boroxol rings by about 10% than the actual one. The authors consider such an error in detail is inevitable as far as we adopt the pairwise approximation for the atomic interactions.

Table 3 summarizes a comparison between the simulated and experimental [12–14, 16] values of density, thermal expansion, and bond lengths in the crystalline

Table 1 Interatomic potential parameters used in this study.

i	a_i/nm	b_i/nm	Z_i
O	0.1560	0.0085	−2.0
B	0.0720	0.0080	3.0
Ba	0.1545	0.0080	2.0

Table 2 Comparison of simulated and experimental (in parentheses) positional parameters of the atoms in each crystal. The notation of atoms and experimental values were taken from the literatures [12, 14].

α phase	x/a_{hex}	y/a_{hex}	z/c_{hex}
O(1)	0.165 (0.174)	0.196 (0.205)	0.0306 (0.0400)
O(2)	0.399 (0.405)	0.058 (0.059)	0.0363 (0.0365)
B(1)	0.965 (0.967)	0.179 (0.178)	0.0319 (0.0380)
Ba(1)	0.000 (0)	0.001 (0)	0.3459 (0.3498)
Ba(2)	0 (0)	0 (0)	1/4 (1/4)
β phase	x/a_{rho}	y/a_{rho}	z/a_{rho}
Ba	0.726 (0.738)	0.371 (0.373)	0.013 (0.019)
O(1)	0.510 (0.458)	0.644 (0.625)	0.434 (0.415)
B(1)	0.554 (0.543)	0.401 (0.373)	0.625 (0.589)
O(11)	0.711 (0.671)	0.566 (0.594)	0.282 (0.258)
O(2)	0.307 (0.359)	0.097 (0.144)	0.231 (0.220)
B(2)	0.194 (0.264)	0.111 (0.119)	0.337 (0.340)
O(21)	0.679 (0.779)	0.955 (0.926)	0.530 (0.495)

Table 3 Physical properties and structural parameters of BaB_2O_4 crystals calculated by MD simulation. Bond lengths of experiments are expressed in terms of the distribution range of the distances for rigorously classified atomic pairs, whereas those of MD simulation are represented by the mean distances and the deviations due to the thermal vibration. Noted is that the simulated pair correlation of Ba-NBO in β phase is strongly anisotropic.

	α phase		β phase	
property	exp.[12]	*MD*	exp.[13, 14, 16]	*MD*
density/g·cm^{-3} (300 K)	3.75 3.74	3.811	3.85 3.84	3.836
thermal expansion/10^{-5}K^{-1} (volume, 300 ~ 1000 K)	–	4.14	4.4	4.21
bond length/nm (300 K)				
B-BO*	.140 ~ .141	.139 ± .002	.138 ~ .142	.140 ± .002
B-NBO**	.132	.124 ± .002	.133	.123 ± .001
Ba-BO*	.308	.305 ± .006	.273 ~ .278	.276 ± .005
Ba-NBO**	.267 ~ .284	.272 ± .006	.261 ~ .303	.266 ~ .296

*Bridging oxygen
**Non-bridging oxygen

states. The agreement is quite good for each property for both α and β phases. The simulated values of density at the room temperature agree with the experimental data with the uncertainty of 2%, and the difference between α and β phases is also simulated properly. The bond lengths of each cation-oxygen pair are also found to agree with the experimental data within 0.01 nm. The thermal expansion is also reproduced properly for the β phase crystal, however the experimental data is not available for the α phase at the present time. It should be noted here the density in the present study is adjusted by using the total pressure only, and more rigorous treatment for the pressure control in the simulation [17] is required if the anisotropic thermal expansion reported by Eimerl *et al.* [16] is reproduced correctly.

Mean Structure of BaB_2O_4 Liquid

While heating the crystal in the simulation, the boroxol ring appears to be stable in the temperature range up to about 1100 K. The precise value of melting point cannot be estimated in this work because the free energy calculation is difficult by the conventional MD simulation. However, it may be worth describing from the present results with the heating rate of 0.5 K/step, that the meltings of both α and β phase crystals take place at about 1400 K which is close to the actual melting temperature, 1373 K [4, 6]. During the first 2 ps after melting, the values of density decrease from those in the crystalline state at 1400 K, 3.66 g/cm^3, to a lower and almost constant value of 3.58 g/cm^3. However, such quasi-equilibrium states continue not so long, and the density values start increasing after few picoseconds. At 40 ps after the melting, the liquid density reached 3.69 g/cm^3 which is close to but slightly larger than the experimental value [18], 3.62 g/cm^3.

As for the short range order concerning to the nearest neighbors, structural relaxation after melting is completed within a short time of the picosecond order. Figure 1 shows the six pair correlation functions of BaB_2O_4 liquid calculated at 3 and 40 ps after melting from the β phase crystal. The pair correlation function of B-O pairs, which is divided into two peaks in the crystalline state, indicates only a single

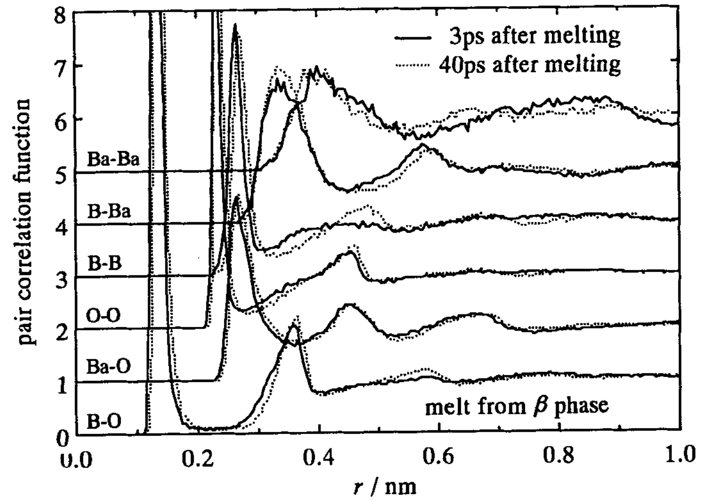

Figure 1 Pair correlation functions of each pair in BaB_2O_4 liquid at 1400 K obtained from β phase crystal.

peak at 0.135 nm in the liquid state. The value of the nearest neighbor distance of B-O pair is slightly smaller than those in Na_2O-B_2O_3 system [15] and Na_2O-B_2O_3-SiO_2 system [19]. The correlation function of Ba-O is also characterized by one broad peak at about 0.28 nm. The nearest neighbor distances for each

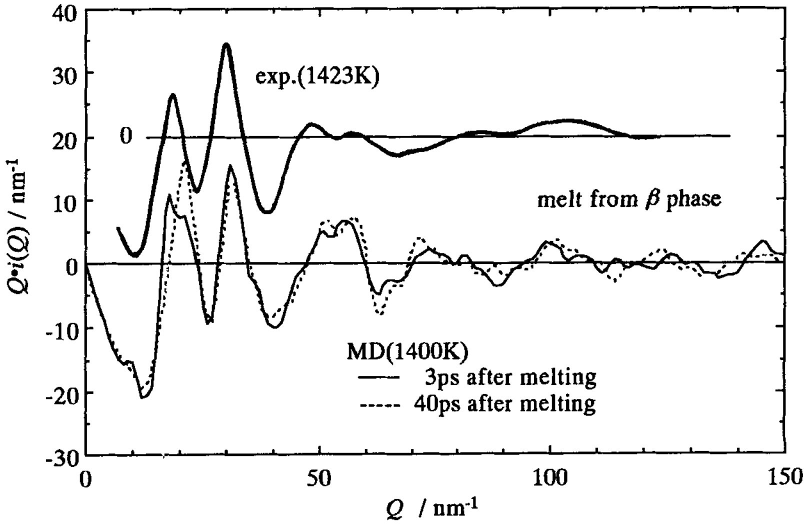

Figure 2 Simulated interference function of BaB_2O_4 liquid at 1400 K calculated by the pair correlation functions given in Figure 1, together with wthe experimental data of X-rays [20].

pair increases by 0.001 ~ 0.002 nm during 40 ps after melting. The so-called interference function of X-rays was calculated from these pair correlation functions as shown in Figure 2. The general profile of the function is quite resemble to the result of the recent X-ray diffraction measurement of which details will be published elsewhere [20]. It may be worth pointing out that the experimental result is more close to the simulated one at 3 ps after melting than that at 40 ps. We consider this contradiction is caused by the small discrepancy between the simulated and actual densities of the liquids.

Structural Relaxation of BaB_2O_4 Liquid During 40 ps After Melting

In the time scale of MD simulation, the liquid more or less keeps the memory of its original crystal structure just after melting, and show some relaxation phenomena toward the equilibrium state. For example, time variations in the medium range order in the simulated BaB_2O_4 liquid are noticeable especially for the cation-cation pairs as shown in Figure 1. The height of the correlation peak at the second neighbor distance of B-B pair increases, and those of B-Ba and Ba-Ba pairs decrease during from 3 to 40 ps after melting. Such variations are considered to be caused by the structural relaxation from a crystal-like structure to a liquid-like structure. The feature of the crystal-like structure in the liquid is easily detected as the periodicity in the basic cell by using the structure factor defined by,

$$S(k) = \frac{1}{N}\langle \rho \mathbf{k} \rho - \mathbf{k} \rangle, \qquad (2a)$$

$$\rho_{\mathbf{k}} = \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}, \qquad (2b)$$

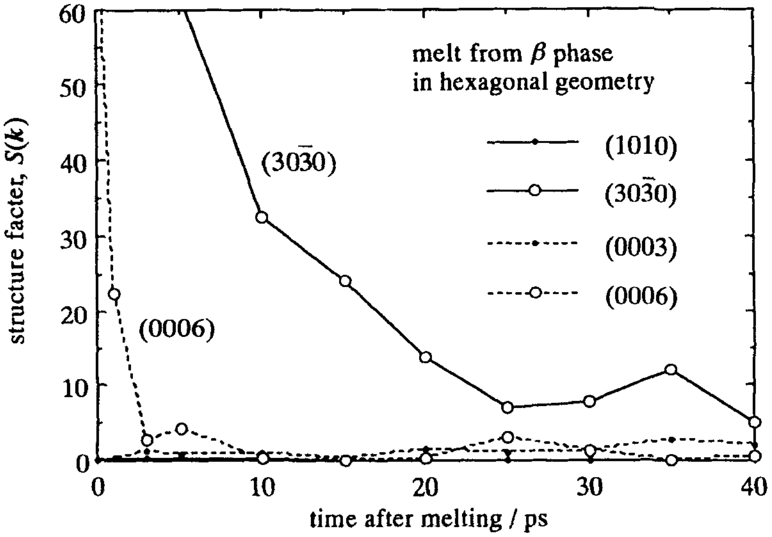

Figure 3 Time variations of the structure factors of oxygen in BaB_2O_4 liquid toward several k vectors.

where $\boldsymbol{k}$ is a vector in the reciprocal space, and r_i is the position of i-th atom. In Figure 3 are shown the structure factors of oxygen as an example toward several $\boldsymbol{k}$ vectors. As shown in the figure, most of the structure factors are almost unity in the liquid state, however the periodicity of $(30\bar{3}0)$ remained even at 40 ps after melting This fact means the BaB_2O_4 liquid is likely to maintain the memory of the periodicity on the *ab* plane in hexagonal geometry for a while after melting, and also suggests a possibility for the β phase-like, metastable state in the liquid proposed by Sasaki and Asoh [7].

Characterization of the liquid structure just after melting was also carried out by analyzing the ring structure. Here we define the ring as the closed bonding loop in the network structure composed by boron and oxygen, $(\text{-B-O-})_n$, including all loops sharing the same bondings in part. The boroxol ring is counted as one ring of $n = 3$ by this definition. The MD simulation indicates that the boroxol ring almost disappears after melting, whereas the rings with $n \geq 4$ are certainly formed. For convenience, in Figure 4 are shown the time variation of the number of rings in the liquid. As shown in this figure, the number of short rings of $n \leq 6$ is almost saturated at 10 ps after melting, however, the numbers of large rings of $n \geq 8$, which are composed by the atoms originally belonged to more than three boroxol rings, are still increasing even at 40 ps.

The variation of the liquid structure in the medium range order possibly affects the dynamic property such as shear viscosity. In order to estimate the shear viscosity and its time variation after melting, we calculated the stress autocorrelation function, $\langle P^{\alpha\beta}(0) \cdot P^{\alpha\beta}(t) \rangle$, where $P^{\alpha\beta}(t)$ is the off-diagonal element of the microscopic stress tensor calculated by,

$$P^{\alpha\beta}(t) = \frac{1}{V}\left\{\sum_i m_i r_i^{\alpha} r_i^{\beta} - \sum_{i<}\sum_j \frac{r_{ij}^{\alpha} r_{ij}^{\beta}}{r_{ij}} \cdot \frac{d\phi(r_{ij})}{dr_{ij}}\right\}, \tag{3}$$

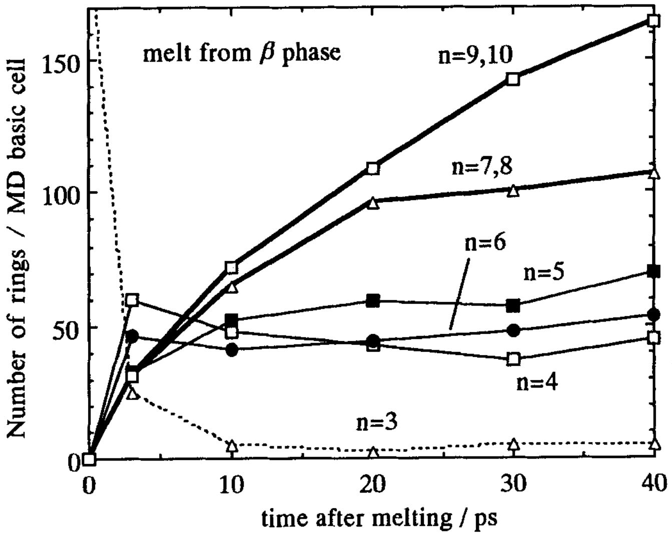

Figure 4 Time variation of the number of rings in BaB_2O_4 liquid after melting.

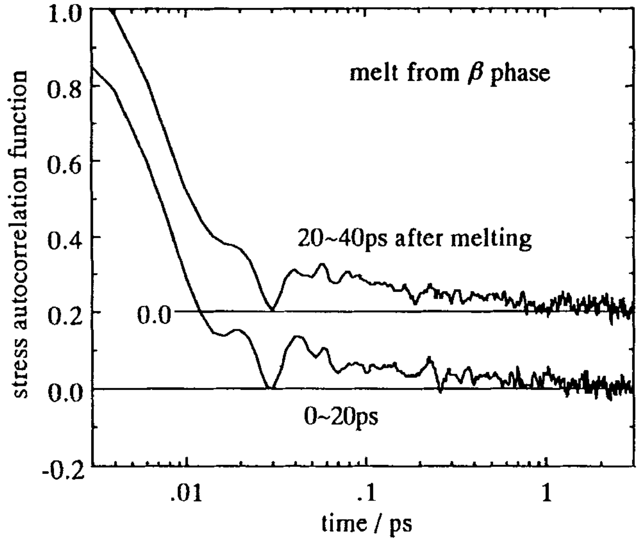

Figure 5 Normalized stress autocorrelation function of BaB_2O_4 liquid at 3 and 40 ps after melting.

for $\alpha\beta = xy$, yz, and zx. The resultant autocorrelation functions observed in the periods of 0 ~ 20 and 20 ~ 40 ps after melting are shown in Figure 5. It should be noted that the time in this figure is plotted in the logarithmic scales for better explaining the longer time variation. On the contrary to our expectation from the ring structure analysis, the autocorrelation functions in both periods are almost the same. From these autocorrelation functions, the shear viscosity of the liquid is estimated by,

$$\eta = \frac{V}{k_B T}\int_0^\infty \langle P^{\alpha\beta}(0)\cdot P^{\alpha\beta}(t)\rangle \mathrm{d}t. \tag{4}$$

The resultant value is about 0.01 Pa·s which is about ten times lower than the experimental one [18], hence the present simulation failed to reproduce the absolute value of shear viscosity. The authors consider the disagreement is not so surprising because the present work does not count the time correlation longer than 10 ps order which has a significant meaning for viscous liquids such as silicate or borate. On the contrary to the success for the low-viscosity liquids such as Lennard-Jones liquid [21] or molten alkali halides [22], it is still a difficult task to evaluate shear viscosity of a viscous liquid by MD and NEMD simulation [23], and a study in much larger scales is expected for that purpose.

4 DISCUSSION AND CONCLUSIONS

Although the present MD simulation is considered to provide reasonable results which are generally consistent with the experimental data, the following three important points should be suggested. The first one is the reliability of the interatomic potentials. The potential parameters for BaB_2O_4 were determined in this work by the try and error basis, and could explain the essential structural features of BaB_2O_4 crystals and liquid as shown in Tables 2, 3 and Figure 2. It should be, however, remembered that these interatomic potential parameters can be fully confirmed when reproducing the dynamic properties of BaB_2O_4 liquid, although their experimental data are quite limited at the present time.

The second point is the size of the basic cell. It is quite natural to consider that the simulated liquid structures is affected by the periodic boundary conditions. However, the cell dimensions in the present study is approximately $(4\,\mathrm{nm})^3$ in the liquid state which is considerably larger than those adopted in most of the conventional MD studies. All of the pair correlation function in the simulated liquids almost converge to unity at the half the cell dimension, ~2 nm. Hence we conclude the size of the basic cell in the present study is large enough for simulating the liquid structure at least for the short range orders.

The third point is the difference in the time scales. The representative time scale in the present study is 10^{-11} s, and it should be kept in mind a large gap exists between the simulation and experiments. Nevertheless, there is a possibility for the direct application of the simulation in picosecond order to the phenomena in the laboratory scale because the degree of freedom for the atomic configuration in the simulation is limited compared with the actual liquid, and hence the speed of structural relaxation is considered to be higher than the real nature. For example, in the simulation, the time variation of the liquid density is driven by the pressure variation in the basic cell. When the local atomic configuration at somewhere in the basic cell changes, the surrounding atoms in all replica cells will response to it, and the influence of the local variation spreads to the infinite distance immediately. The density variation in actual liquids, on the other hand, is considered to occur more slowly because the local pressure variation is dissolved by the cooperative motion of the atoms in the surrounding area of which time scale is restricted by the bulk properties such as viscosity.

From these arguments, the present authors maintain the view that the results of this work provide one possible answer for explaining the anomalous behaviors found in BaB_2O_4 liquid after melting. It would be interesting to do some further investigation of BaB_4O_4 liquid, so that the usefulness of the present MD simulation results may be tested on a wider base.

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