

Pressure dependence of the diffusivity of liquid ZnCl_2 at high temperature by *ab initio* molecular-dynamics study

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We investigate the isothermal pressure dependence of the diffusion properties of liquid ZnCl_2 at 1650 K by means of *ab initio* molecular-dynamics simulations. With increasing pressure, the self-diffusion coefficient of Zn atoms, D_{Zn} , decreases slower than that of Cl atoms, D_{Cl} . As a result, the difference between D_{Zn} and D_{Cl} becomes larger with increasing pressure up to about 10 GPa. Under further compression, the difference becomes smaller. The microscopic origin of the dynamic asymmetry under pressure is discussed.

§1. Introduction

Many scientists believed crystalline ZnCl_2 has three structure phases at ambient pressure until recent years.^{1),2)} However, it is known that the complicated phases are caused by the hygroscopicity, i.e., the water in the air. In the desiccated state, crystallized ZnCl_2 is in an orthorhombic phase.^{3),4)} In recent studies, the desiccated ZnCl_2 is used for the experimental studies to clarify the static structure in crystalline, glassy, and liquid state.⁵⁾⁻⁷⁾ The all phases of them consist of ZnCl_4 tetrahedra, a centered Zn atom and four neighboring Cl atoms in common. The ZnCl_4 tetrahedra are connected by Cl atoms with corner-sharing to next ZnCl_4 unit.⁷⁾

ZnCl_4 tetrahedra remain in the liquid state also.^{5),6)} Unlike in the crystalline state, some of the tetrahedra are connected by the edge-sharing in the liquid state. In the static structure factor $S(k)$, there is a first sharp diffraction peak (FSDP) at about $k = 1 \text{ \AA}^{-1}$, which indicates intermediate range order. The FSDP is mainly constructed by the correlation of Zn-Zn atoms, $S_{\text{ZnZn}}(k)$, that is, the FSDP originates from the connection between the centered Zn atoms in ZnCl_4 tetrahedral units. Under compression, the decrease of the height of the FSDP and the break down of the short and middle range structures are suggested. While, the diffusion coefficients of Zn atoms, D_{Zn} , and that of Cl atoms, D_{Cl} , are almost similar from empirical molecular-dynamics (MD) simulation.^{8),9)} However, it is not clear about dynamic properties under pressure and the diffusion mechanism.

In this paper, we investigate the isothermal pressure dependence of the dynamic properties of liquid ZnCl_2 at high temperature from *ab initio* molecular-dynamics simulations, which in isobaric-isothermal ensemble are carried out using quantum mechanically in the framework of the density functional theory (DFT). The pressure covers from ambient to 79.1 GPa. The temperatures at all pressure ranges are at 1650 K.

§2. Method of calculation

The calculations were carried out by using *ab initio* molecular-dynamics simulations. The electronic states were calculated by projector-augmented-wave (PAW) method^{10),11)} within the framework of DFT in which the generalized gradient approximation (GGA)¹²⁾ was used. The energy functional was minimized using an iterative scheme.^{13),14)} The plane wave cutoff energies are 19 Ry and 120 Ry for the electronic pseudo-wave functions and for the pseudo-charge densities, respectively. We use the Γ point for Brillouin-zone sampling. Projector functions of the *s*, *p*, and *d* types are generated for the 3*s*, 3*p*, and 4*d* states of Cl, and the 4*s*, 4*p*, and 4*d* states of Zn. The cutoff radii r_{cl} , beyond which the pseudo-wave functions coincide with the all-electron wave functions, are chosen as $r_{\text{cl}} = 2.0$ and 2.6 a.u. for Cl and Zn, respectively. Two reference energies are used except for the 4*d* state of Cl and 4*d* state of Zn in the construction of the PAW data sets. By investigating the energy dependence of the logarithmic derivatives of the pseudo-wave functions, we verify that our data sets have good transferability, and do not possess any ghost states in the energy range considered.

Molecular-dynamics simulations were carried out at pressures P from 0.3 GPa to 79.1 GPa and the atomic number densities ρ , which were obtained from the isobaric-isothermal ensemble simulation for 1000 or 1500 steps at each pressure, were listed in table I. All of them were calculated at temperatures $T=1650$ K. We use 108 atoms, i.e., 36 Zn atoms and 72 Cl atoms, in a cubic supercell with periodic boundary conditions. Using Nosé-Hoover thermostat technique,^{15),16)} the equations of motion are solved via an explicit reversible integrator¹⁷⁾ with a time step of $\Delta t = 1.8$ fs for 0.3 and 4.5 GPa, and 2.4 fs for 10.6, 19.8, 39.4, and 79.1 GPa. The quantities of interest were obtained by averaging more over 6000 steps after an initial equilibration taking at least 500 steps.

Table I. Pressures P (GPa) and number densities ρ (\AA^{-3}) at 1650 K used in MD simulation.

P (GPa)	ρ (\AA^{-3})
0.3	0.0346
4.5	0.0439
10.6	0.0517
19.8	0.0589
39.4	0.0688
79.1	0.0817

§3. Results and discussion

Figure 1 shows the pressure dependence of the X-ray static structure factors using X-ray form factors. The bottom line and the symbol shows the result of our calculation and that of experiment at ambient,⁵⁾ respectively. In spite of the temperature difference between the theoretical result and the experimental result, they have similar positions of the FSDP at about 1.0 \AA^{-1} and that of main peak

at about 3.8 \AA^{-1} . With increasing pressure, the height of the FSDP decreases and the FSDP disappears at about 10 GPa. The disappearance of the FSDP indicates the break down of the intermediate range order, i.e., the tetrahedral corner-sharing network structure vanishes at about 10 GPa. At about 40 GPa or more, $S_X(k)$ have a spiky main peak at about 3 \AA^{-1} . In these pressure ranges, liquid ZnCl_2 becomes to solid state.

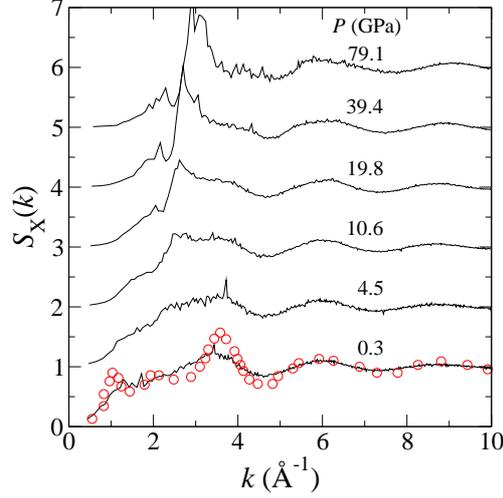


Fig. 1. The pressure dependence of X-ray static structure factors of liquid ZnCl_2 . The solid lines are our calculated results and the circles are experimental results.

Figure 2 shows the pressure dependence of the self-diffusion coefficients for Zn atoms, D_{Zn} , and Cl atoms, D_{Cl} , estimated by slope of the mean square displacements of Zn atoms and Cl atoms as follows:

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{6t} \frac{1}{N_\alpha} \sum_i \langle \mathbf{r}_i(t) - \mathbf{r}_i(0) \rangle \quad (3.1)$$

where the bracket means average of time evolution.

At ambient pressure, D_{Zn} and D_{Cl} are similar. With increasing pressure, D_{Cl} decreases monotonically from ambient to about 40 GPa. On the other hand, D_{Zn} decreases slower than D_{Cl} . As a result, D_{Zn} becomes two times larger than D_{Cl} between about 5 and about 10 GPa. The difference between D_{Zn} and D_{Cl} decreases to almost the same under further compression. Therefore the dynamic asymmetry occurs like covalent liquid B_2O_3 under pressure.¹⁸⁾ Under ultra high pressure, the phase transition from liquid state to solid state occurs in this temperature.

The origin of the difference between the diffusion coefficients is suggested by fig. 3, which is the pressure dependence of the distributions of the coordination numbers of α -type atoms connected to β -type atoms $f_{\alpha\beta}^{(n)}$ ($\alpha, \beta = \text{Zn, Cl}$). At ambient pressure, almost all Zn atoms have the fourfold-coordination to Cl atoms. With increasing pressure, the number of the fourfold-coordinated Zn atoms decreases and the fivefold- and sixfold-coordinated Zn atoms increase. At 5 GPa, the distributions

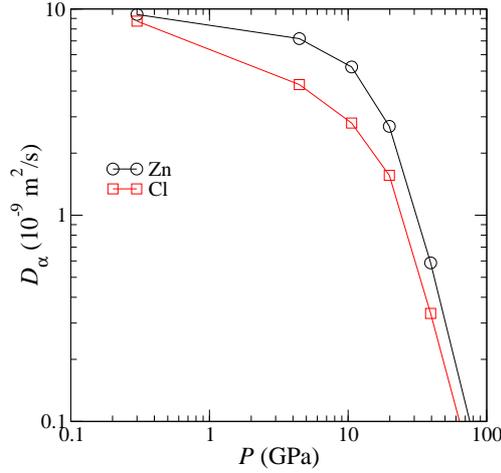


Fig. 2. The pressure dependence of the self-diffusion coefficients of Zn atoms and Cl atoms. The circle symbols and the square symbols indicate the self-diffusion coefficients of Zn atoms and Cl atoms, respectively.

$f_{\text{ZnCl}}^{(4)}$ and $f_{\text{ZnCl}}^{(5)}$ are almost the same, and at 10 GPa, there is almost no fourfold-coordinated Zn atoms but fivefold- and sixfold-coordinated. While, almost all Cl atoms have twofold-coordination to Zn atoms at ambient condition. As the pressure increases, however the number of threefold-coordination increases, the distribution of the number of twofold-coordinated Cl atoms, $f_{\text{ClZn}}^{(2)}$, decreases slower than $f_{\text{ZnCl}}^{(4)}$. As a result, twofold-coordinated Cl atoms remain below 20 GPa. Hence, fourfold-coordinated Zn atoms can move toward twofold-coordinated Cl atoms, i.e., diffusing α -type atoms need lower coordinated β -type atoms.

§4. Summary

We clarified the pressure dependence of the diffusion properties of molten ZnCl_2 at high temperature. At ambient pressure, the diffusion coefficient of Zn atoms D_{Zn} and that of Cl atoms D_{Cl} are almost the same. With increasing pressure, D_{Zn} becomes about two times larger than D_{Cl} between 5 and 10 GPa, the difference between D_{Zn} and D_{Cl} occurs. The difference decreases under further compression. The origin of the dynamic asymmetry was discussed.

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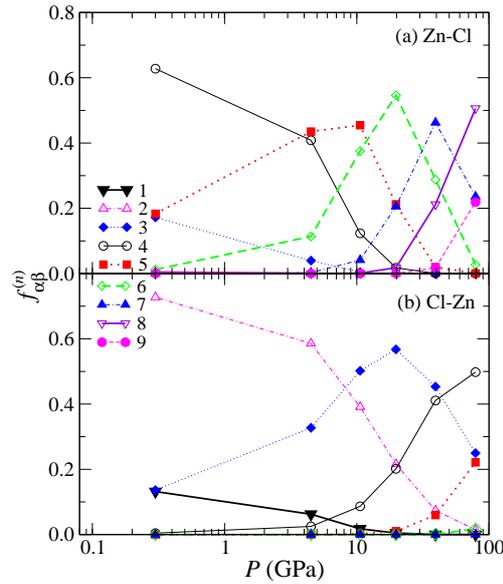


Fig. 3. The pressure dependence of the distributions of the coordination numbers between Zn atoms and Cl atoms. The upper figure shows the distribution of the number of Cl atoms surrounding Zn atoms, and the lower shows that of Zn atoms surrounding Cl atoms.

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