

Pressure Dependence of Structural and Electronic Properties of Liquid ZnCl_2

— *An Ab initio Molecular-Dynamics Study* —

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The structural and bonding properties of liquid ZnCl_2 under pressure are investigated from first-principles molecular-dynamics simulations in the isobaric-isothermal ensemble. The pressure range covers from 0 to 80 GPa. It is shown that the ZnCl_4^{2-} tetrahedra are considerably deformed under pressure with keeping the nearest-neighbor distance between Zn and Cl atoms almost constant. The average coordination number of Cl atoms around Zn atoms changes from 4 at 0 GPa to about 5 at about 10 GPa, and increases monotonically with pressure. The Zn-Zn distance is nearly unchanged up to 10 GPa, and begins to decrease under further compression. On the other hand, the Cl-Cl distance decreases with increasing pressure from ambient conditions.

§1. Introduction

There are many experimental studies for liquid or glass ZnCl_4^{2-} to clarify the structure in the medium or long range scale.^{1)–4)} Liquid ZnCl_2 is a viscous liquid composed of linked ZnCl_4^{2-} tetrahedra, and one of typical network-glass-forming systems. It is intriguing to pay attention to the change in arrangement of ZnCl_4^{2-} tetrahedra under various external conditions.

The aim of this study is to evaluate the structural and bonding properties of liquid ZnCl_2 under pressure from first principles. Molecular-dynamics (MD) simulations in the isobaric-isothermal ensemble are carried out using interatomic forces calculated quantum mechanically in the framework of the density-functional theory. The pressure range covers from 0 to 80 GPa. We elucidate the compression mechanism of liquid ZnCl_2 under pressure.

§2. Method of calculation

The electronic states in liquid ZnCl_2 are calculated by projector-augmented-wave (PAW) method^{5),6)} within the framework of the density-functional theory in which the generalized gradient approximation⁷⁾ is used for the exchange-correlation energy. The plane wave cutoff energies are 19 and 120 Ry for the electronic pseudo-wave functions and the pseudo-charge density, respectively. The energy functional is minimized using an iterative scheme.^{8),9)} The Γ point is used for Brillouin-zone sampling. Projector functions of the s , p and d types are generated for the $3s$, $3p$, and $4d$ states of Cl, and the $4s$, $4p$, and $4d$ 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. In the construction of the PAW data sets, two reference energies are used except for the $4d$ states of Cl and Zn. 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.

Table I. Temperature T (K) and number density ρ (\AA^{-3}) used in MD simulations. The volume ratio V/V_0 , where V_0 is the volume at ambient pressure, and the calculated pressure P (GPa) are also listed.

T (K)	ρ (\AA^{-3})	V/V_0	P (GPa)
903	0.0331	1.000	0.0
903	0.0410	0.806	1.9
1200	0.0444	0.745	3.8
1650	0.0517	0.639	10.6
2000	0.0579	0.571	19.6
2500	0.0670	0.493	39.2
3000	0.0799	0.414	79.8

Our MD simulations are carried out at pressures from 0 to 80 GPa and temperatures from 903 to 3000 K, which are listed in Table I. Atomic number densities used in our simulations are obtained from the isobaric-isothermal ensemble simulations for 1000 or 1500 steps at each pressure. We use a 108-atom system, 36 atoms of Zn and 72 atoms of Cl, in a cubic supercell with periodic boundary conditions. Using Nosé-Hoover thermostat technique,^{10),11)} the equations of motion are solved via an explicit reversible integrator¹²⁾ with a time step of $\Delta t = 2.42$ fs. The quantities of interest are obtained by averaging over 16.96 ps (at 0 GPa) or 29.04 ps (other pressures) after an initial equilibration taking at least 1.2 ps.

§3. Results and discussion

Figure 1 shows the pressure dependence of X-ray structure factor $S(k)$ obtained from the partial structure factors $S_{\alpha\beta}(k)$ using the X-ray form factors. The calculated $S(k)$ at 4 GPa is in reasonable agreement with the experiments.⁴⁾ With increasing pressure, the heights of the peaks at about $k = 1.0$ and 3.8 \AA^{-1} decrease, and a peak grows up at about $k = 3.0 \text{ \AA}^{-1}$. The peak at about $k = 1.0 \text{ \AA}^{-1}$ is mainly contributed by the Zn-Zn correlation, which means that the disappearance of this peak results from the significant deformation or destruction of linked ZnCl_4^{2-} tetrahedra. Furthermore, the partial structure factors $S_{\text{Zn-Cl}}(k)$ and $S_{\text{Cl-Cl}}(k)$ participate the growth of the new peak at about $k = 3.0 \text{ \AA}^{-1}$.

Figure 2 shows the pressure dependence of the pair distribution functions $g_{\alpha\beta}(r)$. The nearest-neighbor distance $r_{\text{Zn-Cl}}$ between Zn and Cl atoms, which is estimated from the first-peak position of $g_{\text{Zn-Cl}}(r)$, has only weak pressure dependence. A characteristic feature is that the changes of $r_{\text{Cl-Cl}}$ and $r_{\text{Zn-Zn}}$ are very different. When the pressure is increased from 0 to 10 GPa, $r_{\text{Zn-Zn}}$ keeps almost the same value, while $r_{\text{Cl-Cl}}$ changes from 3.7 to 3.2 \AA . Upon further compression, $r_{\text{Zn-Zn}}$ decreases its value. In contrast to the nearest-neighbor distance, the average Zn-Cl coordina-

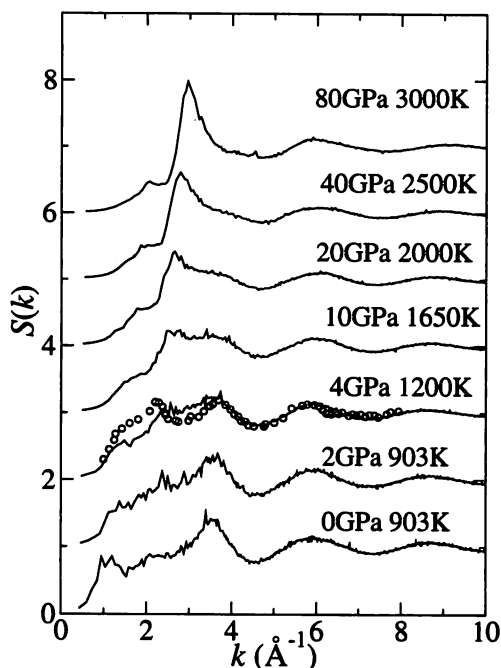


Fig. 1. Pressure dependence of X-ray structure factor $S(k)$ obtained from the partial structure factors using the X-ray form factors. The circles indicate the experimental results at 3.8 GPa.⁴⁾

tion number $n_{\text{Zn-Cl}}$ increases largely from 4 at 0 GPa to 7 at 80 GPa, which means that the ZnCl_4^{2-} tetrahedra are considerably deformed or destroyed under pressure. At 10 GPa, at which $r_{\text{Zn-Zn}}$ begins to decrease, $n_{\text{Zn-Cl}}$ becomes about 5, and the characteristic behavior of $r_{\text{Zn-Zn}}$ is expected to be related to the remarkable reduction of Zn atoms which are fourfold-coordinated to Cl atoms. Population analysis shows that covalent-like interactions between Zn and Cl atoms become weak with decreasing the number of ZnCl_4^{2-} tetrahedra.

Figure 3 shows the pressure dependence of the distribution of the coordination number of Cl atoms around Zn. The cutoff distance is $r = 2.8 \text{ \AA}$, which is the first-minimum position of $g_{\text{Zn-Cl}}(r)$ at 0 GPa. The results show that almost all atoms form ZnCl_4^{2-} tetrahedra at 0 GPa. When the pressure is relatively lower, the local structure with Zn atoms threefold- or fivefold-coordinated to Cl atoms is not stable, and it only appears accompanying atomic diffusion. With increasing pressure, Zn atoms fourfold-coordinated to Cl atoms decrease, and then the fivefold- and sixfold-coordinated Zn atoms increase. Under 10 GPa, the number of threefold-coordinated Zn atoms is almost unchanged with increasing pressure, then it disappears over 20 GPa. These results correspond to the decrease and increase of Cl atoms, which are twofold- and threefold-coordinated to Zn, respectively. As a result, the average of the coordination number of Cl atoms around Zn atoms rises to 7 at 80 GPa from 4 at ambient conditions.

Figure 4 shows the distribution of bond-overlap population between Zn and Cl atoms. At 0 GPa, there is a large peak at $\bar{O} = 0.4$, which reflects the covalent bonding

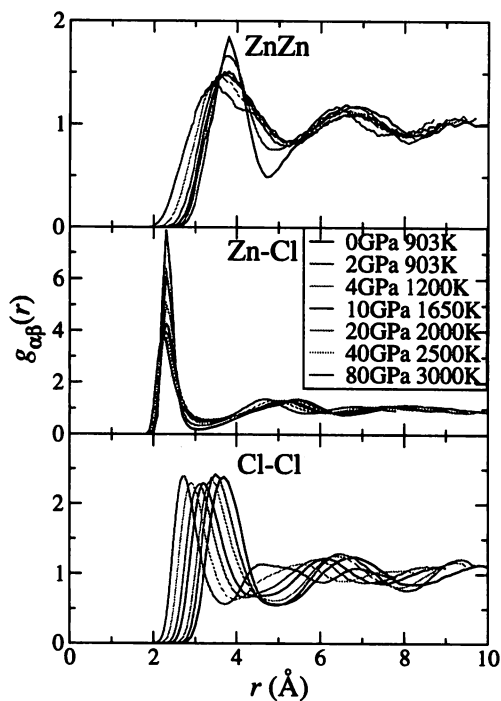


Fig. 2. Pressure dependence of the pair distribution functions $g_{\alpha\beta}(r)$

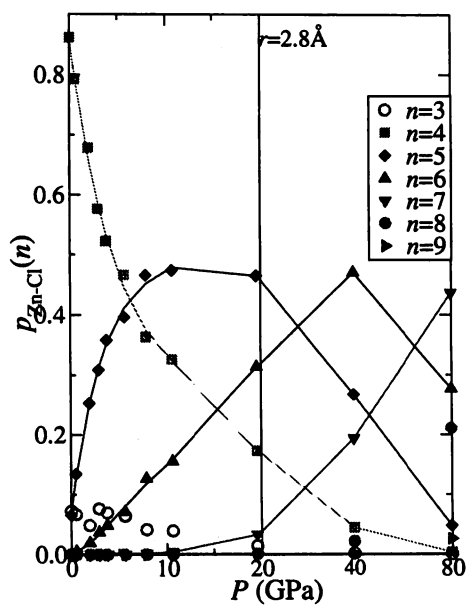


Fig. 3. Distribution $p_{\text{Zn-Cl}}(n)$ of the coordination number of Cl atoms around Zn atoms. The cutoff distance is $r = 2.8 \text{ \AA}$. In the left and right panels, the scales of the x axis are linear and logarithmic, respectively. The lines are drawn as a guide for the eyes.

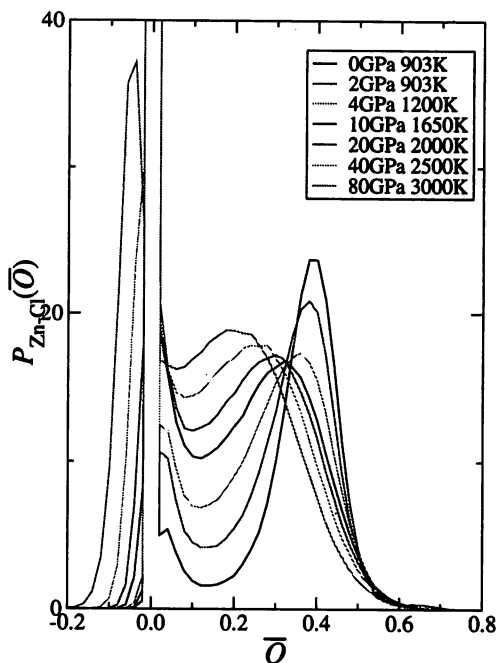


Fig. 4. Distribution $P_{\text{Zn-Cl}}(\bar{O})$ of bond-overlap population between Zn and Cl atoms.

between these atoms. As the pressure increases, the height of the peak decreases below 10 GPa, and increases over 10 GPa. The peak position shifts toward smaller \bar{O} with increasing pressure, which means that the covalency weakens due to the increase of the coordination number.

§4. Summary

The pressure dependence of the structural and electronic properties of liquid ZnCl_2 has been investigated by *ab initio* molecular-dynamics simulations. The local structure changes without changing the Zn-Cl and Zn-Zn bond distances with increasing pressure up to 10 GPa, while they become smaller above 10 GPa. On the other hand, the Cl-Cl distance decreases when the pressure is increased from ambient pressure. The average coordination number of Cl around Zn increases from 4 at 0 GPa to 7 at 80 GPa. There appear Zn atoms at 80 GPa, which are eightfold coordinated to Cl atoms. The bonding properties between Zn and Cl atoms are not purely ionic but is partially covalent. However, the covalent nature weakens as the pressure increases in particular over 10 GPa due to the increase of the average coordination number under pressure.

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