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The Determination of Empirical Pair-Potential Functions for $CaCl_2$ Crystal and Melt by Molecular Dynamics Calculation†

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KEY WORDS: (Molecular Dynamics) ($CaCl_2$) (Structure) (Crystal) (Melt)

In recent years, a **molecular dynamics (MD)** method is increasingly being used to study physical properties of computer-simulated solids and liquids. Unfortunately, most of the calculated systems have been simple ionic liquids such as molten alkali chlorides[1]. However, complex ionic liquids such as molten alkaline-earth chlorides are of interest from many points of view. The most remarkable difference in physical properties between alkali chlorides and alkaline-earth chlorides is the volume expansion $\Delta V_m/V_m^s$ (%) on melting. It is well known that alkali chlorides have rather large $\Delta V_m/V_m^s$ values, i.e., LiCl (26.2%), NaCl (25.0%) and KCl (17.3%), whereas alkaline-earth chlorides have much smaller than values, i.e., $CaCl_2$ (0.9%), $SrCl_2$ (4.2%) and $BaCl_2$ (3.5%), as listed in **Table 1**[2]. This property of alkaline-earth chlorides may be attributed to the small change of coordination numbers and the minimal structural disordering on melting. However, the structures of molten alkaline-earth chlorides and the mixed systems of them have hardly been studied[3-6] and are not yet clear.

The purpose of this note is, therefore, to present the following suitable pair potential functions of $CaCl_2$ crystal and melt for the MD calculation:

$$u_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i+b_j)\exp\left[\frac{(a_i+a_j-r_{ji})}{(b_i+b_j)}\right] \quad (1)$$

where z_i is the formal charge number of ion i (e.g., +2 for Ca^{2+} ion), e the unit charge, r_{ij} the distance between ion i and j, f_0 a force constant arbitrarily taken here to be 1 kcal·mol^{-1}·Å^{-1}, and a_i and b_i are the crystal constant and compressibility of ion i, respectively. The simple expression used for the lattice energy of $CaCl_2$ crystal and melt described above, Busing form potential[7], consists of the terms in the Coulomb energy and repulsive energy. For any successful MD calculation, the proper choice of potential parameters is of prime importance. As the potential parameters for Ca^{2+} and Cl^- have not been reported yet, we have empirically determined these values by performing MD runs. In order to check the validity of the parameters for Ca^{2+} and Cl^-, we have performed a MD simulation of $CaCl_2$ crystal.

Table 1 Volume change $\Delta V_m/V_m^s$ (%) of alkali and alkaline earth chlorides of melting[2].

Salt	r_c/r_a	m.p. temp. (K)	$\Delta V_m/V_m^s$ (%)
LiCl	0.33	887	26.2
NaCl	0.53	1092	25.0
KCl	0.79	1063	17.3
RbCl	0.82	999	14.3
CsCl	0.91	919	10.5
$CaCl_2$	0.55	1045	0.5
$SrCl_2$	0.64	1147	2.3
$BaCl_2$	0.75	1234	2.3

r_c/r_a: ratio of ionic radii of cation and anion

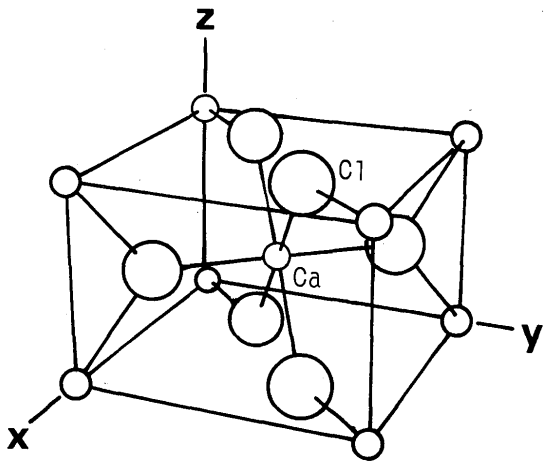

Fig. 1 The orthorhombic unit cell of calcium chloride. The small spheres represent calcium ions and the large ones chloride ions. This is a distorted rutile structure.

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The structure of $CaCl_2$ crystal (Space group: P_{nnm}[7]; Distorted rutile structure) is shown in **Figure 1**[8]. The symmetry is orthorhombic with calcium ions at 0, 0, 0, and 1/2, 1/2, 1/2. All chloride ions are equivalent and lie in mirror planes at x, y, 0; $\bar{x}$, $\bar{y}$, 0; $\bar{x}$, y, 1/2; and x, $\bar{y}$, 1/2. Thus each calcium ion is coordinated to six chloride ions in an almost perfect octahedral arrangement, and each chloride ion adjoins three calcium ions in nearly planar triangular coordination. This observed calcium chloride structure is a slight distortion of the tetragonal rutile arrangement in which the lattice parameters a and b are equal as are the anion parameters x and y.

The potential parameters used in MD calculation of $CaCl_2$ crystal at room temperature are given in **Table 2**. The MD calculation assumed an orthorhombic cell as a basic cell. The number of particles within the basic cell was 216 (Ca: 72; Cl: 144). In evaluating the potential energy and force, the Coulombic term was calculated at each time step by the application of the Ewald technique[1] given by

$$\Phi_i = \Phi_{1i} + \Phi_{2i} - \Phi_{3i} \tag{2}$$

$$\Phi_1 = q_i \sum_j q_j \frac{\mathrm{erf}(\alpha |\boldsymbol{r}_{ij}|)}{|\boldsymbol{r}_{ij}|} \tag{3}$$

$$\Phi_2 = \frac{q_i}{\pi V} \sum_{\boldsymbol{n}} \left\{ \exp\left(\frac{-\pi^2 |\boldsymbol{n}'|^2}{\alpha^2}\right) \cdot \frac{1}{|\boldsymbol{n}'|^2} \cdot \left[\cos(2\pi \boldsymbol{n}\cdot\boldsymbol{r}_i') \sum_j q_j \cos(2\pi \boldsymbol{n}\cdot\boldsymbol{r}_j') - \sin(2\pi \boldsymbol{n}\cdot\boldsymbol{r}_i') \sum_j q_j \sin(2\pi \boldsymbol{n}\cdot\boldsymbol{r}_j')\right]\right\} \tag{4}$$

$$\Phi_{3i} = \frac{q_i^2 \alpha}{\sqrt{\pi}} \tag{5}$$

where erf is the usual error function defined by $\mathrm{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-u^2) du$, and $\boldsymbol{n}$ denotes the reciprocal

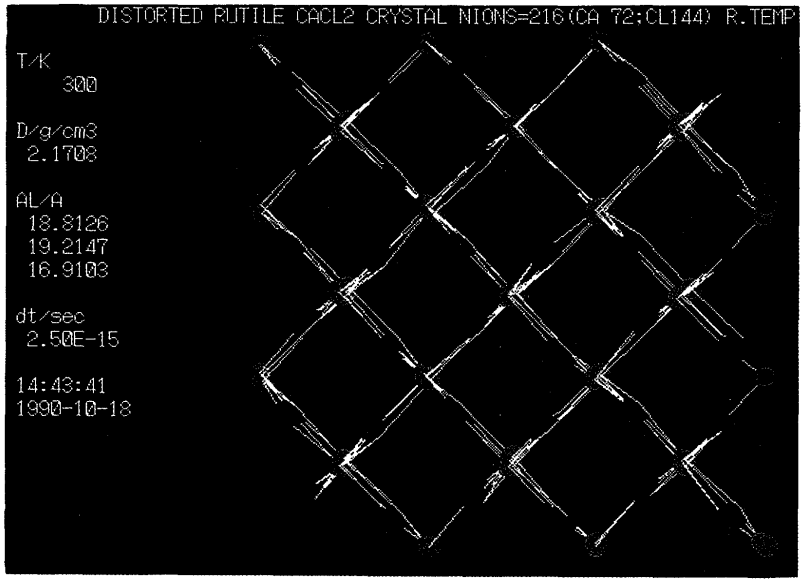

Fig. 2 The structural view of a typical instantaneous configuration of the MD-simulated $CaCl_2$ crystal at 300 K.

Table 2 Values for the potential parameters considered in this work.

	W	z	a	b
Ca	40.08	+2	1.414	0.080
Cl	35.453	−1	1.920	0.085

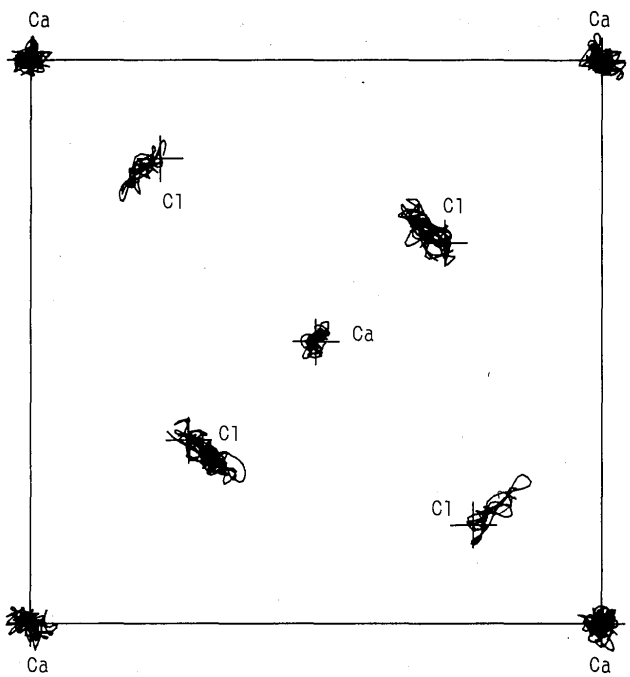

Fig. 3 The X-Y plane of the trajectories of Ca^{2+} and Cl^- in the MD-simulated $CaCl_2$ crystal at 300 K.

lattice position vectors corresponding to the real cell vectors $\boldsymbol{h}$. The force on each ion is obtained by differentiating the computed interatomic potential energy for every ion:

$$F_i = -(d\Phi_{ij}/dr_{ij})(dr_{ij}/du_i) \quad (6)$$

where F_i is the force on ion i in the u direction ($u=x, y, z$), Φ_{ij} potential energy between ions i and j, r_{ij} the distance between ions i and j, and du the x, y, or z component of ion i. Once the instantaneous force on each ion has been determined, its position and velocity are calculated for the next time step by using the algorithm of Verlet[1]:

$$\boldsymbol{r}_i(t+\Delta t) = 2\boldsymbol{r}_i(t)-\boldsymbol{r}_i(t-\Delta t)+(\Delta t)^2\boldsymbol{F}_i(t)/m_i \quad (7)$$

Table 3 Comparison of observed and calculated quantities for calcium chloride crystal.

Parameter	Observation	Calculation	
		M.D.	Lattice Energy[7]
a_0 (Å)	6.24[8]	6.26	6.310
b_0 (Å)	6.43[8]	6.46	6.310
c_0 (Å)	4.20[8]	4.26	4.261
u Cl	0.275[8]	0.273	0.304
v	0.325[8]	0.357	0.304
Distance Ca-Cl (Å)	2.70[8]	2.76	2.72
	2.76[8]	2.76	2.76
Density (g/cm³)	2.40[7]	2.14	
Energy	−538.2[7]	−575.2	−537.3

$$\Delta\boldsymbol{r}_i(t) = \Delta_i\boldsymbol{r}(t-\Delta t)+(\Delta t)^2\boldsymbol{F}_i(t)/m_i \quad (8)$$

$$\boldsymbol{r}_i(t+\Delta t) = \boldsymbol{r}_i\mathbf{r}(t)+\Delta\boldsymbol{r}_i(t) \quad (6)$$

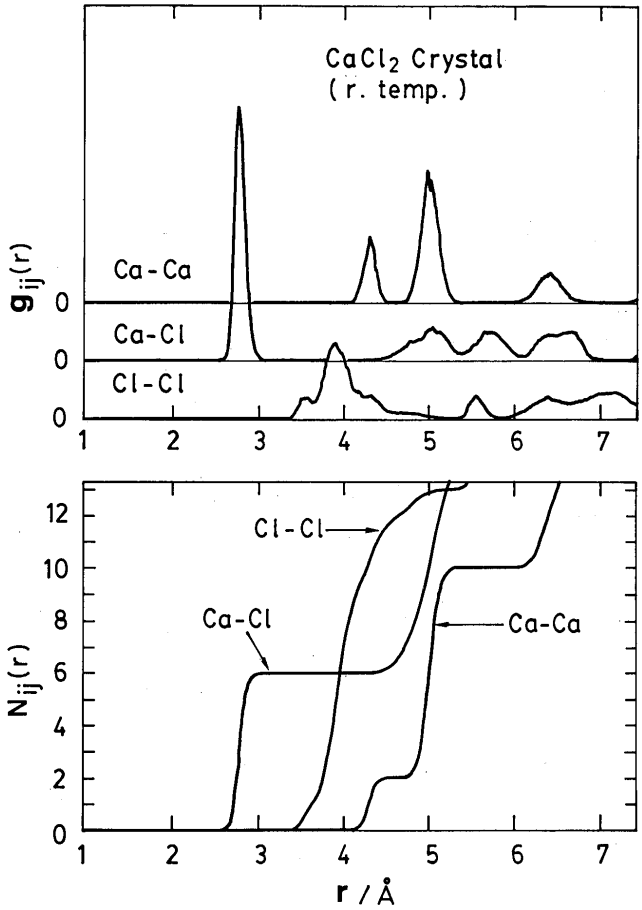

Fig. 4 The pair correlation functions $g_{ij}(r)$ and the distribution of coordination numbers $N_{ij}(r)$ of ionic pairs Cl-Cl, Ca-Cl and Ca-Ca in MD-simulated $CaCl_2$ crystal at 300 K.

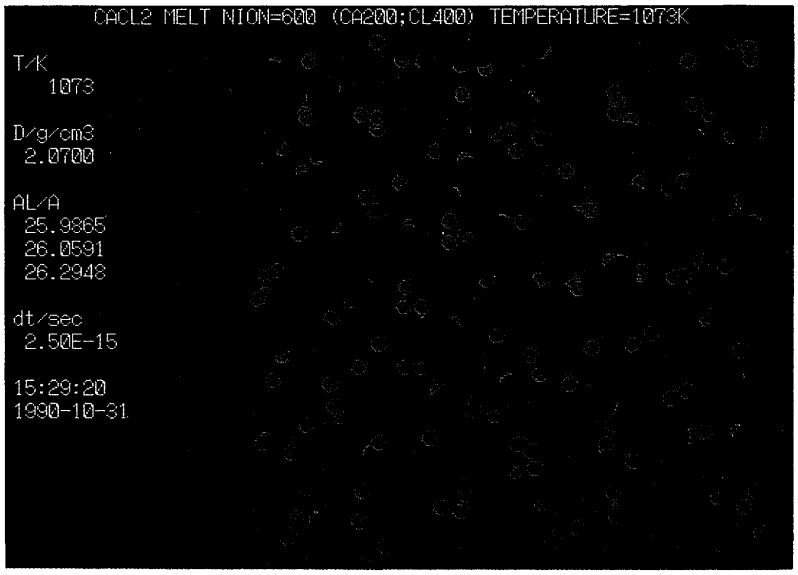

Fig. 5 The structural view of a typical instantaneous configuration of MD-simulated $CaCl_2$ melt at 1073 K.

where $r(t)$ is the position of an ion at time t. The value of Δt in our MD run was 2.5×10^{-15} sec at room temperature. As shown in **Figures 2** and **3** and **Table 3**, the distorted rutile structure of $CaCl_2$ crystal was reproduced by our MD calculation. The pair correlation functions $g_{ij}(r)$ and the distribution of the coordination numbers $N_{ij}(r)$ of the ionic pairs Cl-Cl, Ca-Cl and Ca-Ca in $CaCl_2$ crystal at room temperature are illustrated in **Figure 4**. The lattice parameters a and b change by less than one percent to become equal, and the cation/anion coordinates become equal in a similar way. The calculated nearest-neighbor distances differ by at most 0.04Å from those observed[8]. Our MD runs were made on a personal computer systems—NEC PC-9801RA (CPU80386/16MHz+WTK3167) and PC-9801RA21 (CPU80386/20MHz+IIT2C87). For 216 particles, interacting a Coulombic potential, a single time step could be done in about 6~8 seconds.

Figure 5 shows the structural view of a typical instantaneous configuration of molten $CaCl_2$ at 1073K.

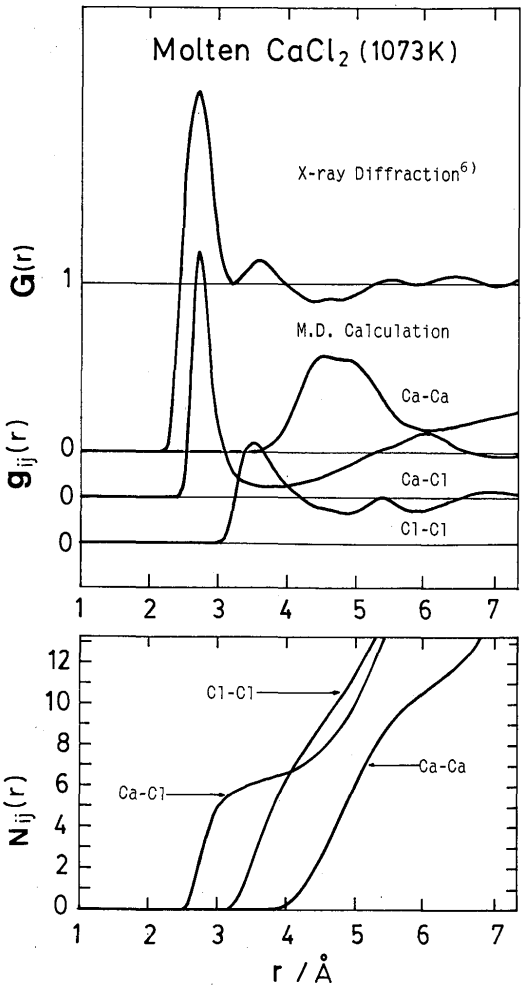

Fig. 6 A comparison of the pair correlation functions g_{ij} (r) and the distribution of coordination numbers N_{ij} (r) obtained from our MD simulation with the total X-ray correlation function G (r)[6] for molten $CaCl_2$ at 1073 K.

The MD calculation assumed a cube as a basic cell. The edge length of the basic cell was calculated from the observed value of density of the molten $CaCl_2$ at 1073K (ρ=2.07 g/cm^3)[9]. The number of particles within the basic cell were 360 (Ca: 120; Cl: 240) and 600 (Ca: 200, Cl: 400), respectively. The pair correlation functions $g_{ij}(r)$ and the distribution of the coordination numbers $N_{ij}(r)$ of the ionic pairs Cl-Cl, Ca-Cl and Ca-Ca in molten $CaCl_2$ at 1073K are illustrated in **Figure 6** in comparison with the corresponding total correlation function $G(r)$ obtained from our X-ray structural analysis[6]. The calculated coordination number $N_{Ca/Cl}$=5.6 is closed to the $N_{Ca/Cl}$=5.8 estimated from volume expansion given by

$$\frac{\Delta V_m}{V_m^s}=\frac{(r^s_{Ca-Cl})^3}{(r^l_{Ca-Cl})^3}\times\frac{N^l_{Ca-Cl}}{N^s_{Ca-Cl}} \tag{10}$$

where subscripts s and l mean solid and liquid sates at the melting point, respectively. The distances calculated, r_{Ca-Cl} and r_{Cl-Cl}, and the coordination numbers, $N_{Ca/Cl}$ and $N_{Cl/Cl}$, of the nearest-neighbor pairs Ca-Cl and Cl-Cl are close to those found in the crystalline form[8], which are consistent with the extraordinary small value of $\Delta V_m/V_m^s$ on melting. Since $CaCl_2$ has a rutile structure, Ca^{2+} cations are centered at slightly distorted $CaCl_6$ clusters composed of six Cl^- ions with Ca-Cl distance of 2.7~2.76Å. It is, therefore, believed that the distances and the coordination numbers of the nearest-neighbor ionic pairs scarcely change on melting. **Figure 7** shows a comparison between the calculated and observed[6] interference function curves $S\cdot i(S)$ in the reciprocal lattice

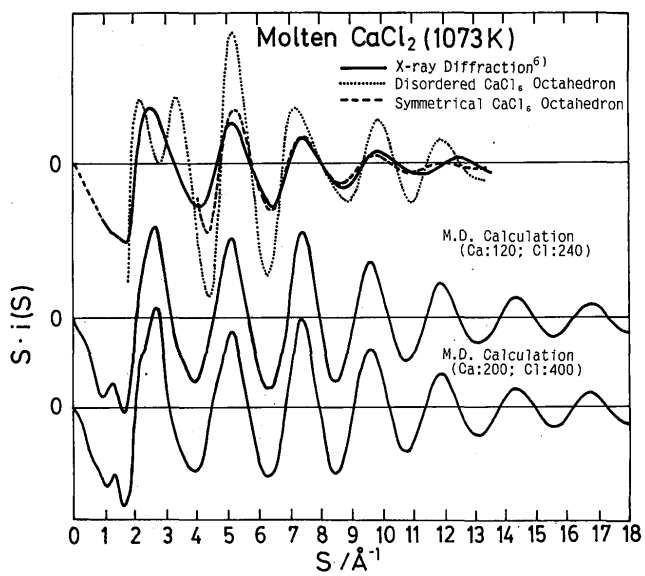

Fig. 7 The X-ray total interference functions $S\cdot i(S)$ of molten $CaCl_2$ at 1073 K for our MD simulation compared to X-ray experiment[6].

space. Unfortunately, it is considered that calculated $S \cdot i(S)$ may contain some calculation errors, such as Fourier transformation error caused by small size of the basic cell used, whereas observed $S \cdot i(S)$ may contain some experimental errors, so that no quantitative discussion is possible. However, our MD simulation reveals that the $S \cdot i(S)$ curves calculated are in good agreement with that from X-ray diffraction[6], as shown in Figure 7.

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