Dissolution of an NaCl crystal with the (1 1 1) and
(−1−1−1) faces

Hitoshi Ohtaki*, Nobuhiro Fukushima
Department of Electronic Chemistry, Tokyo Institute of Technology
at Nagatsuta, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 Japan

Abstract— The dissolution process of an NaCl crystal with the (1 1 1) and
(−1−1−1) faces, the former consisting of only chloride ions and the latter
only sodium ions, as well as the {1 0 0} faces, in water has been demonstrated
by means of molecular dynamics simulation. Ion-ion, ion-water and water-
water interactions are assumed to be described in terms of the Tosi-Fumi,
Popkie-Kistenmacher-Clementi and Matsuoka-Clementi-Yoshimine potentials,
respectively. Twenty-eight sodium ions, twenty-eight chloride ions and 189
water molecules were placed in a box having the side-length of 2000 pm. Col-
lision of water molecules with the walls of the box was assumed to be com-
pletely elastic. The temperature of the system was kept at 298 K during the
simulation procedure, which was carried out for 7 ps (the time step $\Delta t = 1.0 \times 10^{-15}$ s, the total steps performed were 7000) after starting dissolution of the
NaCl crystal. The first, second and third ions dissolved are chloride ions at the
corners of the crystal, as have been found in the previous work (ref. 1). The
fourth one liberated was also a chloride ion on the (1 1 1) face. As we have
seen in the previous simulation using another NaCl crystal with the {1 0 0}
faces (ref. 1), no sodium ion was removed within 7 ps even from the
(−1−1−1) face which was exposed to the bulk water phase. Repulsive forces
arising between the chloride ions and water molecules which tend to hydrate
sodium ions around the chloride ions are the force for separating the chloride
ions from the crystal.

INTRODUCTION

The dissolution process of a sodium chloride crystal having {1 0 0} faces in water has been
demonstrated by using molecular dynamics simulations, and we found that chloride ions were dis-
solved but no sodium ions were removed from the crystal within 7 ps (ref. 1). Thus, questions
arose why chloride ions are first liberated from the crystal surfaces, what is the driving force for
separating chloride ions from sodium ions, and what ions will be dissolved when other sodium
chloride crystals with different faces are immersed in water. The first two questions are rather
general for the dissolution process of ionic crystals, and the third question requests us to demon-
strate the molecular dynamics simulation procedure for another type of a sodium chloride crystal.
In the present study we applied the molecular dynamics simulation to a sodium chloride crystal
with the (1 1 1) and (−1−1−1) faces, the former consisting of only chloride ions and the latter
only sodium ions and compared the result with that obtained for a cubic crystal in the previous
paper (ref. 1).

THE SYSTEM USED AND POTENTIAL FUNCTIONS EMPLOYED

The sodium chloride crystal has 28 Na$^+$ and 28 Cl$^-$ ions, and 189 water molecules were
employed as solvent molecules. The ratio of the number of ions to that of the solvent molecules
was approximately the same as that in the previous case. The side-length of the box as the con-
tainer of the system was 2000 pm. Collision between water molecules and the walls of the box

* Present address: Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji-cho,
Okazaki, 444 Japan. To whom correspondence should be addressed.
was assumed to be completely elastic at the center of gravity of water molecule. The layers of 
the crystal were named as shown in Fig. 1. The temperature was kept at 298 K during the simu-
lation process. The step $\Delta t$ was set to be $1.0 \times 10^{-15}$ s and the simulation was performed over 
the period of 7 ps (7000 steps).

Pair potentials for ion-ion, ion-water and water-water intermolecular interactions were those pro-
posed by Tosi-Fumi (ref. 2), Popkie-Kistenmacher-Clementi (ref. 3) and Matsuoka-Clementi-
Yoshimine (ref. 4), respectively. Details of the pair-potentials have been described in ref. 1.

![Fig. 1. Definition of the layers of 
the sodium chloride crystal 
having (1 1 1) and (−1 −1 −1) 
faces.](image)

**RESULTS AND DISCUSSION**

Shots of the dissolution process of the sodium chloride crystal at different layers are shown in 
Fig. 2, which have been taken every 1 ps (the process is visualized on a video tape, as we have 
done so in the previous work, ref. 1). It is seen from the pictures that the chloride ion at the 
corner of the layer b first removed from the crystal surface, as we have seen in the case of a 
cubic crystal of sodium chloride (ref. 1). The second and third ions separating from the crystal 
were also chloride ions at the corners of layer b'. These ions are all those situating at the rect-
angular corners of the crystal. The fourth ions started to remove from the crystal after about 6 
ps is a chloride ion on the (1 1 1) face, as seen in Fig. 2 (layer a, 4 ps, the chloride ion is depicted in 
the shots of layer b after 4 ps because of its positional shifts). No sodium ion has been dis-
solved in this case, too, within 7 ps even the crystal has a face consisting of only sodium ions 
which is exposed to the water phase.

Displacements of ions from the center of the system with time are shown in Fig. 3. It is obvious 
from the figure that sodium ions are oscillating around the lattice coordinates of the original posi-
tions, while four chloride ions are going out from the original places.

![Fig. 3. Displacements R of sodium (a) and chloride (b) ions from the center of the 
box with time.](image)

Forces working to each ion in the system were calculated on the basis of potential functions of all 
atom-pairs in the system. Forces acting toward a sodium ion at a corner of the crystal was 
slightly negative (directing to the center) and thus the sodium ion cannot go out from the crystal.
Fig. 2. Shots of the dissolution process of the sodium chloride crystal in water with times. Large circle: Cl⁻, small circle: Na⁺, ⊙: H₂O.
Fig. 2. (contd.)

2 ps

3 ps
layer

b

a

a'

b'

4 ps

5 ps

Fig. 2. (contd.)
Fig. 2. (contd.)
On the other hand, a chloride ion at another corner of the crystal tends to go out from the crystal owing to the repulsive forces due to interactions with water molecules. It is seen from Fig. 4, in which forces acting to the sodium and chloride ions are plotted against time. In this case the forces are those summed up all forces working to the ions and over the time. The summed force for the chloride ion is mostly positive, which means that the force is acting toward outside the crystal. On the other hand, the force acting to the sodium ion is always negative.

Fig. 4.
Sums of variation of forces among an ion and all the other particles.

From these results, we concluded that repulsive forces arising between chloride ions and water molecules which are strongly attracted to sodium ions around the chloride ions push chloride ions out from the crystal surface and thus chloride ions, which have a smaller hydration energy than sodium ions, leave the crystal surface (Fig. 5).

As we can see in Fig. 2, the crystal largely deforms due to thermal vibrations and ion-water interactions at 298 K, and after some chloride ions have left the crystal some other ions can construct new corners. Although we did not see the process beyond 7 ps in this study, we can predict that even more chloride ions may leave the crystal and then finally the rest of the crystal which is highly positively charged will be decomposed to each ion.

Fig. 5. Scheme of liberation of a chloride ion at a corner of a sodium chloride crystal in water.

REFERENCES
1. H. Ohtaki, N. Fukushima, E. Hayakawa and I. Okada, Pure & Appl. Chem., in press. The dissolution process is graphically displayed on a video tape under the cooperation project of us and Fujitsu®. The tape can be rent, but not commercially available.