

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

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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. Collision of water molecules with the walls of the box was assumed to be completely 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 *dissolved* 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 demonstrate 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 container of the system was 2000 pm. Collision between water molecules and the walls of the box

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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 simulation process. The step Δt was set to be 1.0×10^{-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 proposed 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.

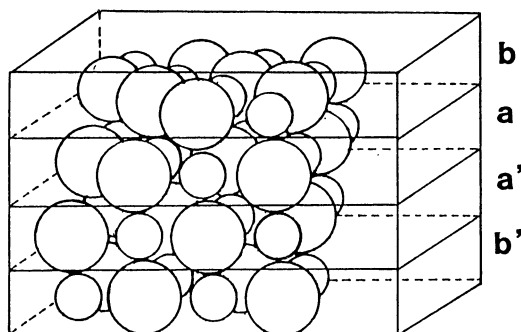


Fig. 1. Definition of the layers of the sodium chloride crystal having (1 1 1) and $(-1-1-1)$ faces.

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 rectangular 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 dissolved 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 positions, while four chloride ions are going out from the original places.

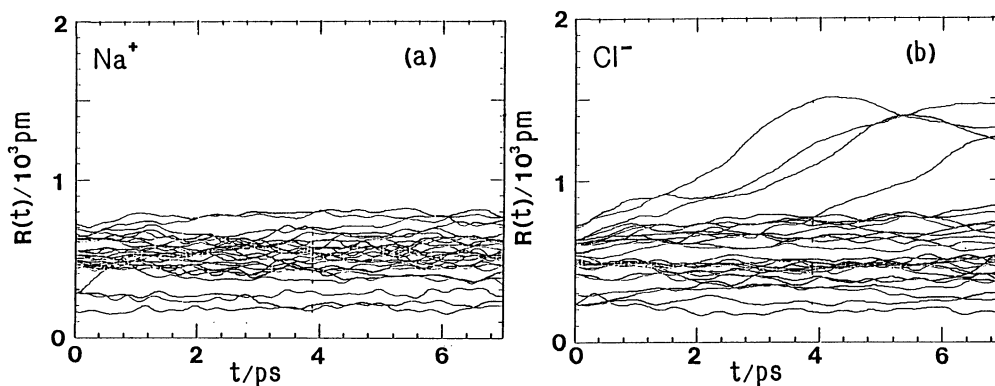
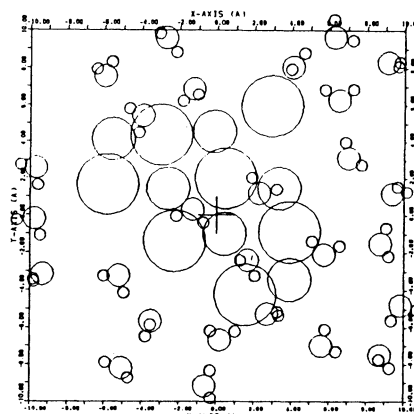
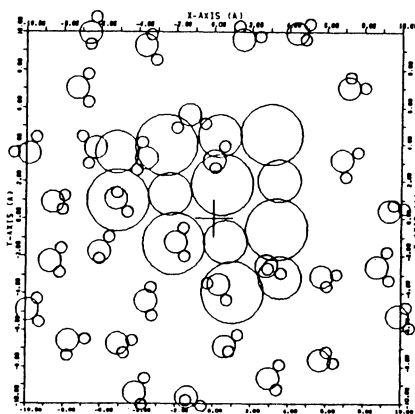


Fig. 3. Displacements R of sodium (a) and chloride (b) ions from the center of the box with time.

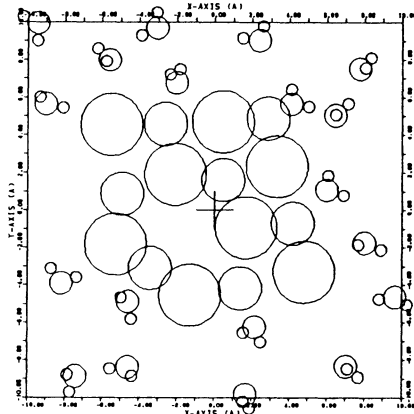
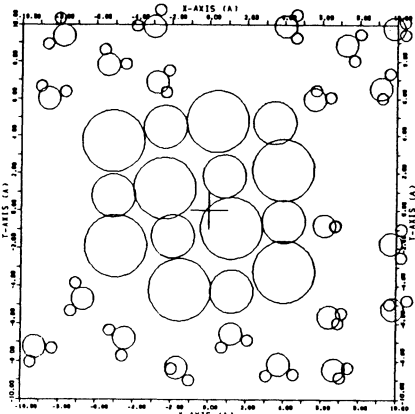
Forces working to each ion in the system were calculated on the basis of potential functions of all atom-pairs in the system. Forces acting toward a sodium ion at a corner of the crystal was slightly negative (directing to the center) and thus the sodium ion cannot go out from the crystal.

layer

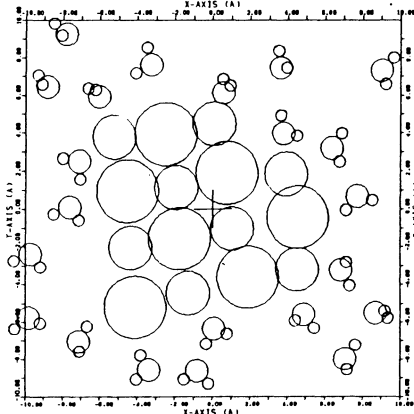
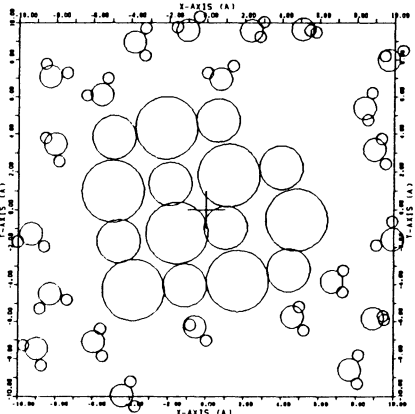
b



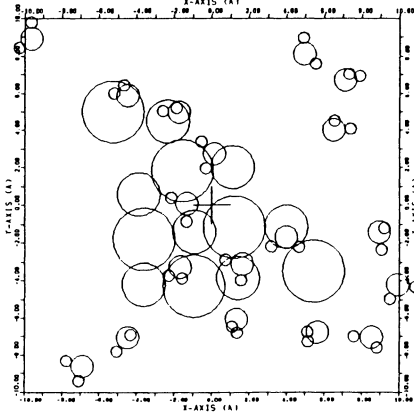
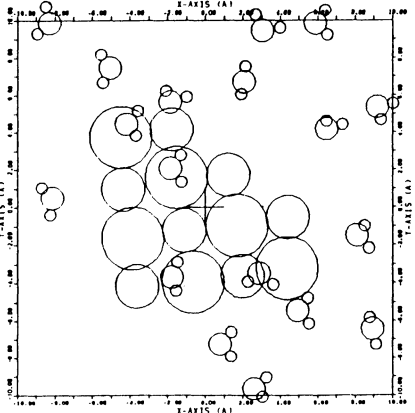
a



a'



b'



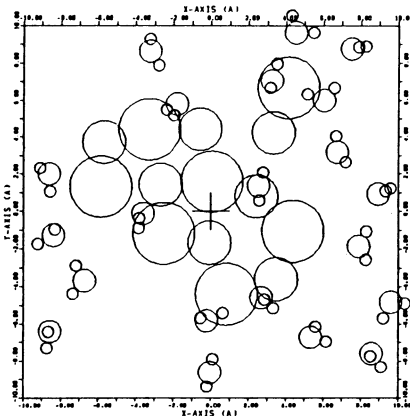
0 ps

1 ps

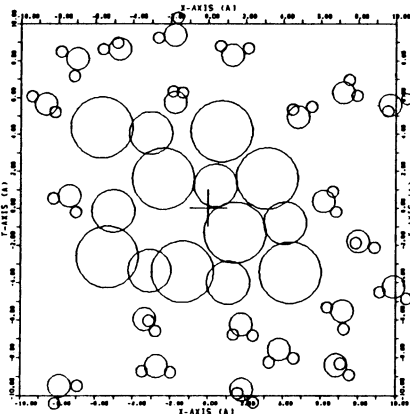
Fig. 2. Shots of the dissolution process of the sodium chloride crystal in water with times. Large circle: Cl^- , small circle: Na^+ , H_2O .

layer

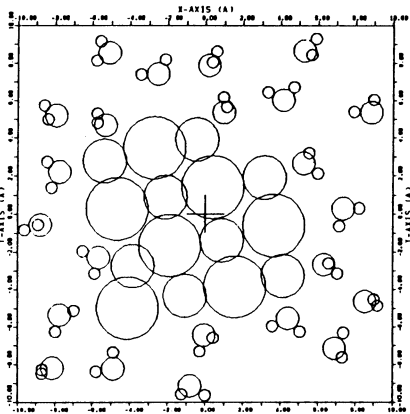
b



a



a'



b'

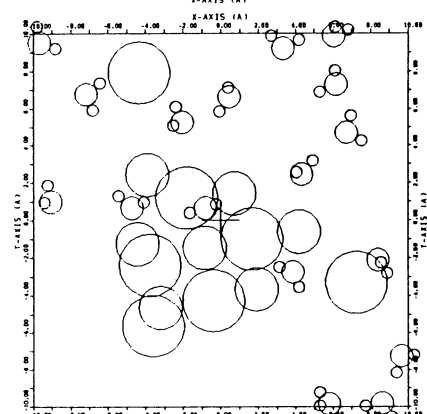
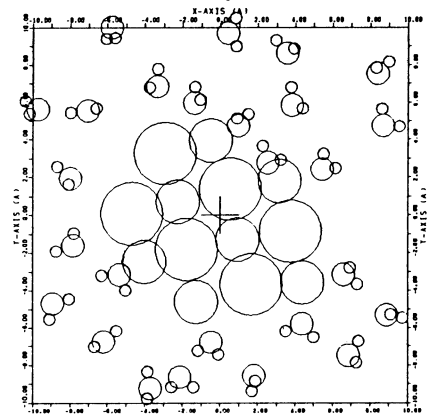
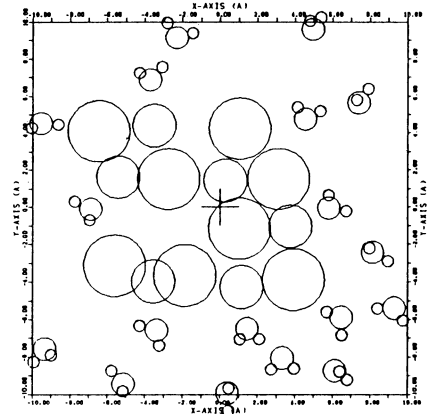
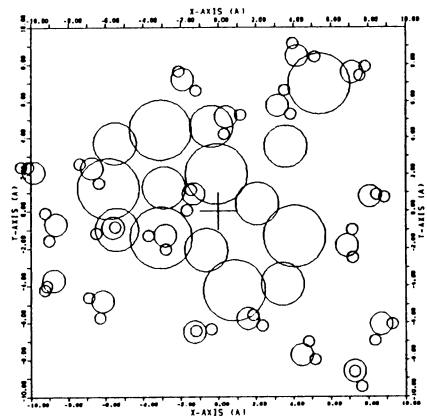
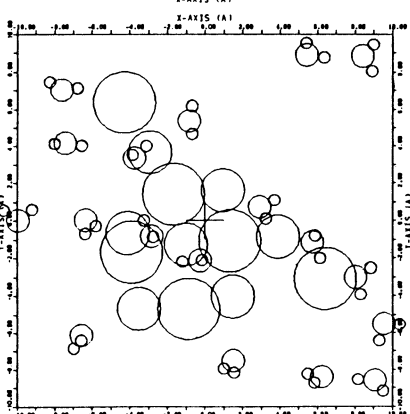


Fig. 2. (contd.)

2 ps

3 ps

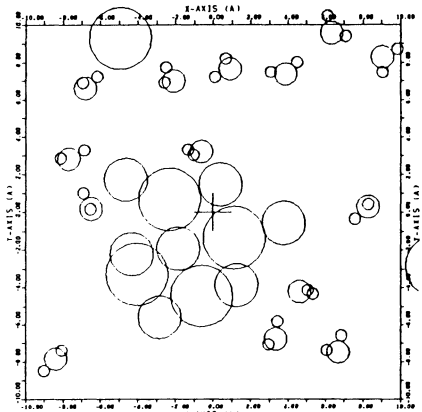
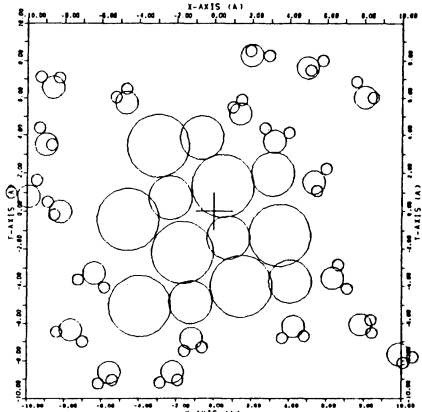
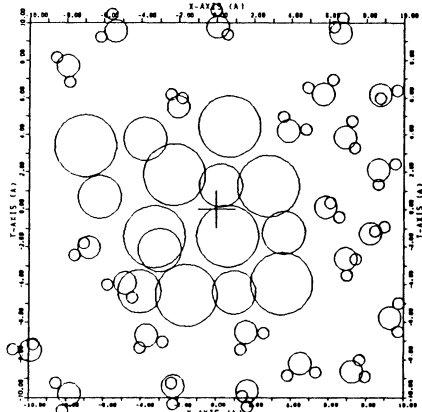
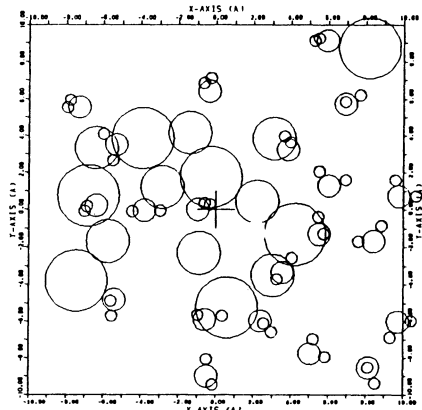
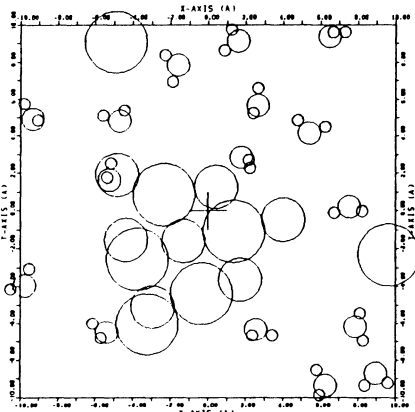
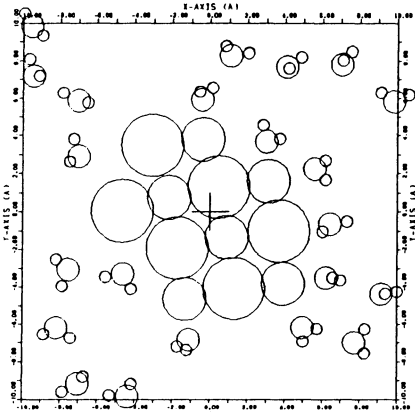
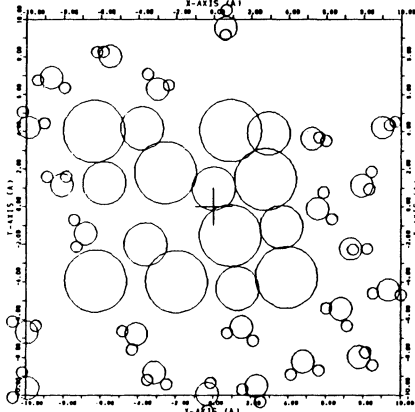
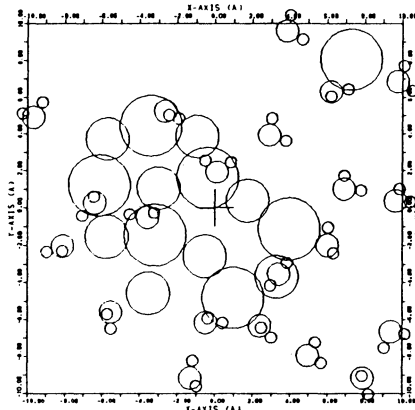
layer

b

a

a'

b'



4 ps

5 ps

Fig. 2. (contd.)

layer

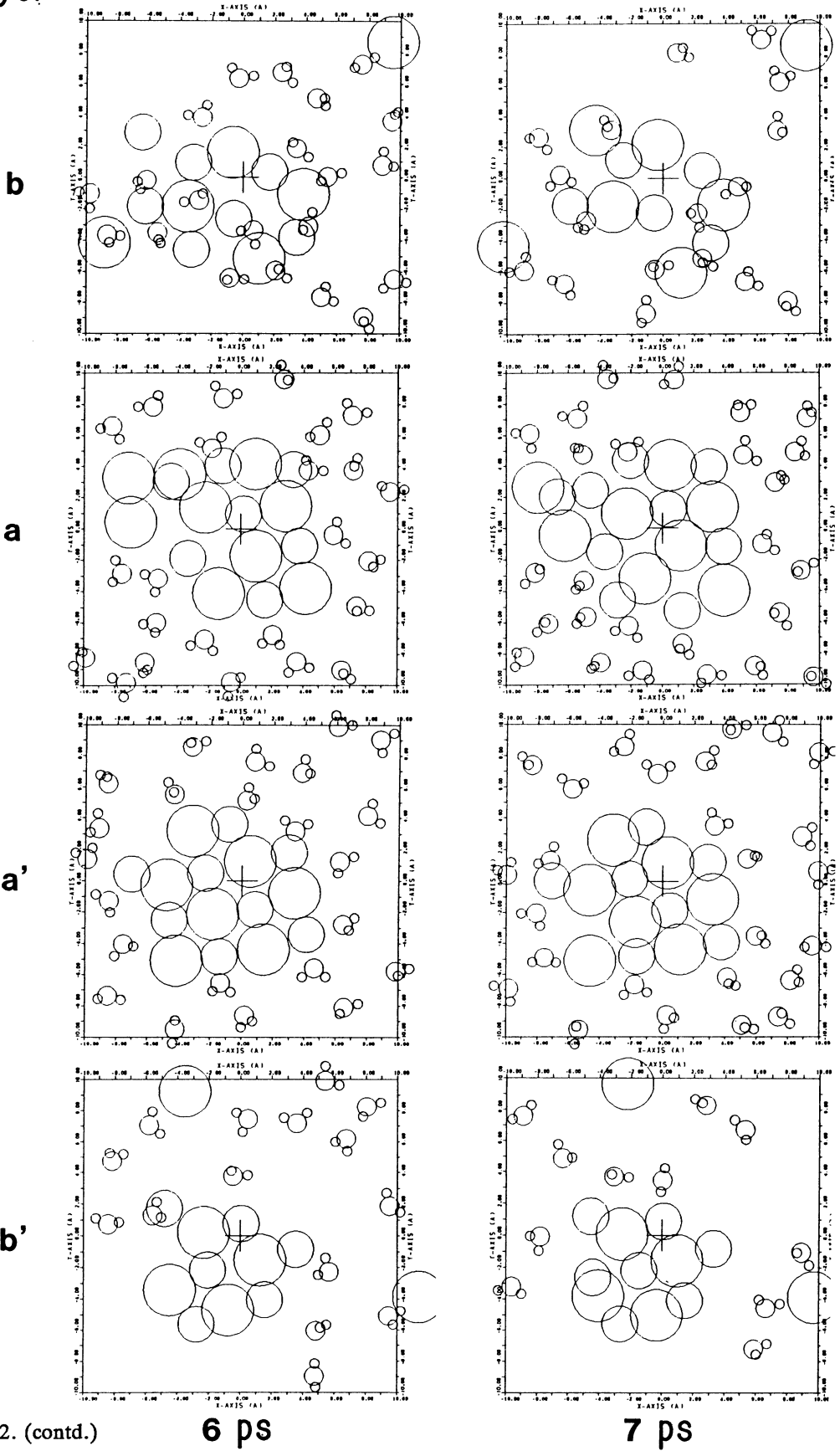


Fig. 2. (contd.)

6 ps

7 ps

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.

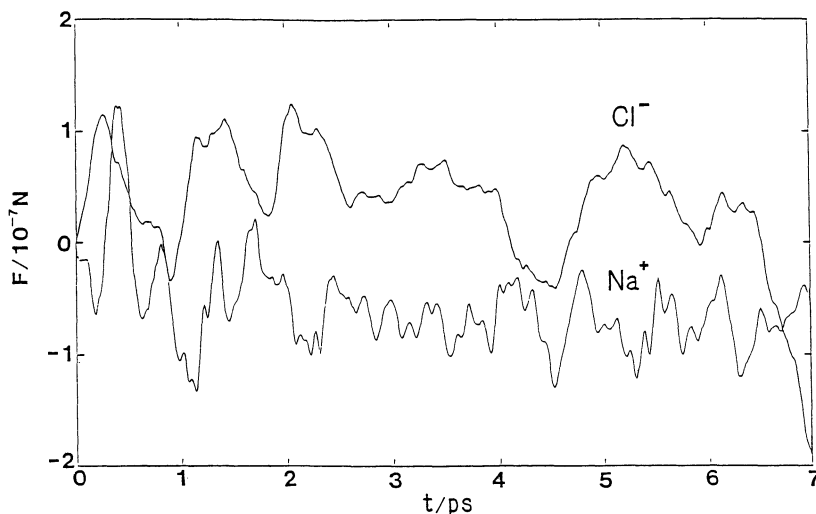


Fig. 4. Sums of variation of forces among an ion and all the other particles.

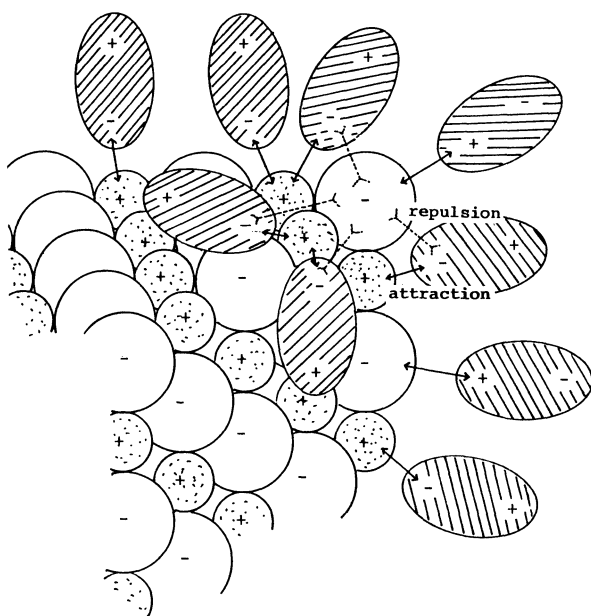


Fig. 5. Scheme of liberation of a chloride ion at a corner of a sodium chloride crystal in water.

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.

REFERENCES

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