

Nucleation processes of NaCl and CsF crystals from aqueous solutions studied by molecular dynamics simulations

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Abstract - Nucleation processes of NaCl and CsF crystals from supersaturated aqueous solutions of (a) 9.25, and (b) 15.42 mol (kg H₂O)⁻¹ NaCl and (c) 36.34 mol (kg H₂O)⁻¹ CsF have been studied by molecular dynamics simulations. The periodically bound condition with the Ewald summation has been employed in the course of the simulation calculations. Numbers of cations (M⁺), anions (X⁻) and water (W) molecules in the systems (M⁺ : X⁻ : W) are (a) 56:56:336, (b) 80:80:288, and (c) 127:127:194. All ions and water molecules have been first randomly distributed in the cells and, except for (a), water molecules have been allowed to move until the thermal equilibrium attains between the water molecules and the ions which have been fixed at the given lattice points. Then, the simulation for the nucleation has been started. In (a) all water molecules and ions have been allowed to move freely in the pre-equilibrium step. Temperature has been kept constant at 298 K. Potential functions used in the simulations are the Fumi-Tosi, Kistenmacher-Popkie-Clementi, and Matsuoka-Clementi-Yoshimine potentials for ion-ion, ion-water, and water-water interactions, respectively. The simulation procedure has been continued for 18 ps with the time step $\Delta t = 1.0$ fs. Formation of ion clusters in the systems was slow down after about 12 ps.

INTRODUCTION

In a series of molecular dynamics simulations of dissolution and nucleation of crystals, we have examined the dissolution of sodium chloride crystals with different shapes (refs. 1, 2) and other alkali halide crystals with the rock-salt type (ref. 3). In the present study the first attempt has been made to observe the nucleation of crystals in water.

No word may be necessary to explain the importance of the knowledge of nucleation of crystals, but no information has practically been given for this phenomenon in spite of a large accumulation of knowledge for crystal growth from the morphological view point. Molecular dynamics simulations may be a good tool to study such reactions at the molecular level, although the system employable may be rather restricted. In this study we examined molecular dynamics simulations to elucidate an initial stage of the nucleation process of NaCl and CsF crystals from supersaturated aqueous solutions.

THE SYSTEMS EMPLOYED AND POTENTIAL FUNCTIONS USED

The systems employed in this study are NaCl and CsF aqueous solutions. Sodium chloride can be dissolved in water up to 26.43 % w/w (6.15 mol (kg H₂O)⁻¹ or NaCl:H₂O molar ratio = 1:9.09) at 298 K. The concentration of the saturated CsF aqueous solution at 298 K under an atmospheric pressure is 78.6 % w/w (24.13 mol (kg H₂O)⁻¹ or CsF:H₂O = 1:2.30). Supersaturated NaCl and CsF solutions artificially prepared were used in the course of the simulations. The systems examined in the study are summarized in Table 1. The Fumi-Tosi (ref. 4), Kistenmacher-Popkie-Clementi (ref. 5), and Matsuoka-Clementi-Yoshimine (ref. 6) potentials were used for describing ion-ion, ion-water and water-water interactions, respectively. The pair potential for the Cs⁺-H₂O interaction was derived from the ST2 water molecule and the charged Lennard-Jones Cs⁺ ion (ref. 7) as described in a previous work (ref. 3). The side lengths of the unit cells have been estimated from the sizes of the NaCl and CsF crystals containing the same numbers of ions examined here and volumes of water included in the systems.

The simulation has been carried out in the following ways: All ions were randomly placed at the 448 (= 7 × 8 × 8) lattice points in the basic cell. Water molecules were allowed to move freely in the cell until the thermal equilibrium was attained among the water molecules and the fixed ions. Then, we allowed the ions to move freely to start the simulation. In system (a) both water molecules and ions could move

until the thermal equilibrium was attained among them. In this case potentials for ion-ion attractive interactions were weakened in order to avoid ionic association during the pre-equilibrium treatment. Temperature of the systems was monitored from the velocities of the species and kept at 298 K. The step Δt was 1.0 fs. The time examined for the nucleation process was 18 ps. The Ewald summation (ref. 8) was employed for correcting long range Coulombic interactions.

TABLE 1. Conditions of the molecular dynamics simulations for the nucleation of NaCl and CsF Crystals.

	NaCl (a)	NaCl (b)	CsF (c)
Number of cations	56	80	127
Number of anions	56	80	127
Number of water molecules	336	288	194
Concentration/mol·(kg H ₂ O) ⁻¹	9.25	15.42	36.34
Length of cell/pm	2327	2304	2336
Step/fs	1.0	1.0	1.0

Concentrations of Saturated NaCl and CsF aqueous solutions are 6.16 and 24.13 mol (kg H₂O)⁻¹, respectively, at 298 K and at 1.01325×10^5 Pa. Temperature was kept at 298 K and the time examined was for 18 ps.

RESULTS AND DISCUSSION

The results of the simulations are graphically displayed in Figs. 1a through 1c. From the pictures we see that nuclei or ion clusters are formed in the systems. Small size clusters containing a few cations and anions already present at the beginning of the simulation calculations grew up to large clusters with time. The shape of the clusters was irregular.

Since the process is a non-equilibrium one, it is difficult to extract some statistics from the result as we usually do in calculations of molecular dynamic data in the equilibrium state. Nevertheless, we tried to estimate some statistical quantities such as pair correlation functions $g_{ij}(r)$ and the running coordination numbers n_{ij} around the cation and anions in the solutions at each moment. The pair correlation function is defined in the usual form as follows:

$$g_{ij}(r) = \frac{1}{4\pi\rho_i r^2 \Delta r} \frac{N_{ij}(r)}{N_i} \quad (1)$$

where $N_{ij}(r)$ denotes the number of particles of species j between the distances r and $r + \Delta r$ around the particle i , N_i the number of particles in the volume V , ρ_i the number density. The time dependence of the pair correlation functions for cation-anion, cation-cation and anion-anion are shown in Figs. 2 through 4. Since the probability of the existence of ions around a given ion at a given time is shown in the figures, the pair correlation functions are represented as the collection of bars which converge at unity at the infinite r value. The figures at 0 ps indicate the randomly distributed positions of ions at the initial stage of the calculations.

Since $g_{ij}(r)$ was expressed as a discrete function, the running coordination number of i surrounded by particles j is given as

$$n_{ij} = 4\pi\rho_j \sum_0^r r^2 g_{ij}(r) \Delta r \quad (2)$$

and the results are summarized in Table 2. At the calculation of the running coordination number, the upper limit r of the summation in eq. (2) is taken as follows:

(1) r_1 is defined as the range of the first coordination sphere so as to be a half of the lattice constant (564.5 pm for NaCl and 602.5 pm for CsF) of the crystals for ions with different charges and $1/\sqrt{2}$ times the lattice constant for ions with the same charge.

(2) The running coordination number up to the *second coordination sphere* has also been calculated. In this case, the range of the second coordination sphere is defined so as to be given as $r_2 = \sqrt{3}/2$ time the lattice constant of the crystals for the ions with different charges and the lattice constant for the ions with the same charges.

System (a) (see Table 2, Figs 1a and 2) In this case ions as well as water molecules had been allowed to move until thermal equilibrium had been attained among them, and thus the correlation functions for all ion pairs at 0 ps give patterns of much random distributions of ions compared with other cases. The

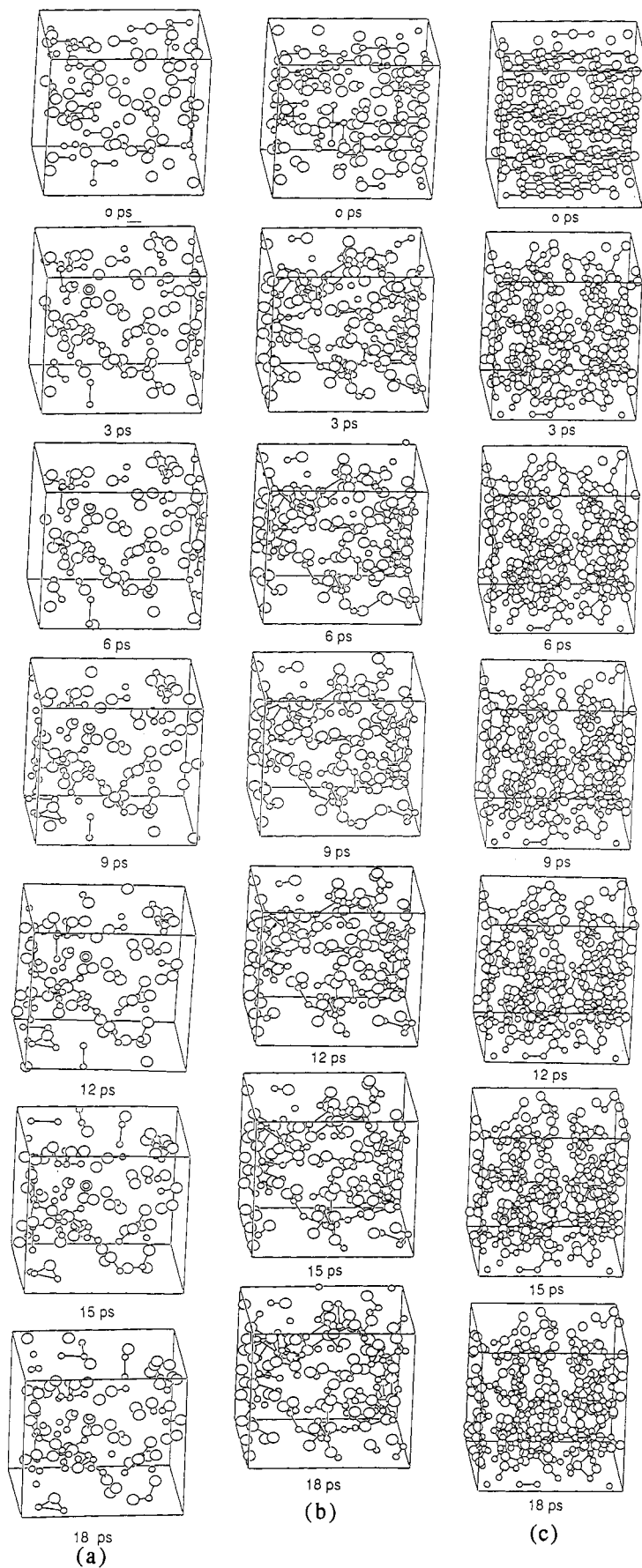


Fig. 1. ORTEP pictures of oversaturated NaCl and CsF aqueous solutions with time. Water molecules are omitted in the pictures.

(a) 9.25, (b) 15.42 mol (kg H₂O)⁻¹ NaCl (small circles: Na⁺, large circles: Cl⁻), and (c) 36.34 mol (kg H₂O)⁻¹ CsF (large circles: Cs⁺, small circles: F⁻).

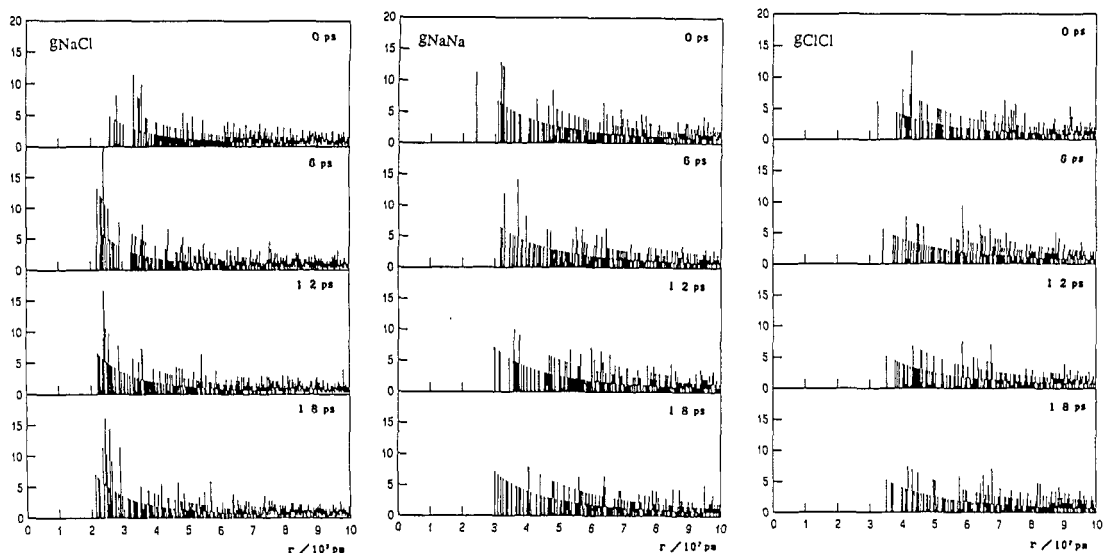


Fig. 2. Pair correlation functions $g_{ij}(r)$ for (a) NaCl with time.

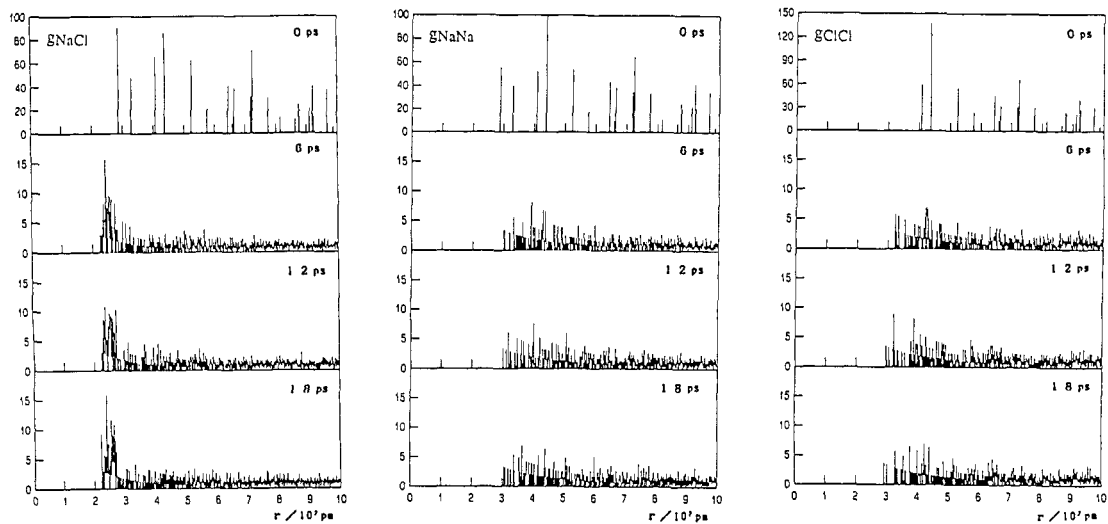


Fig. 3. Pair correlation functions $g_{ij}(r)$ for (b) NaCl with time.

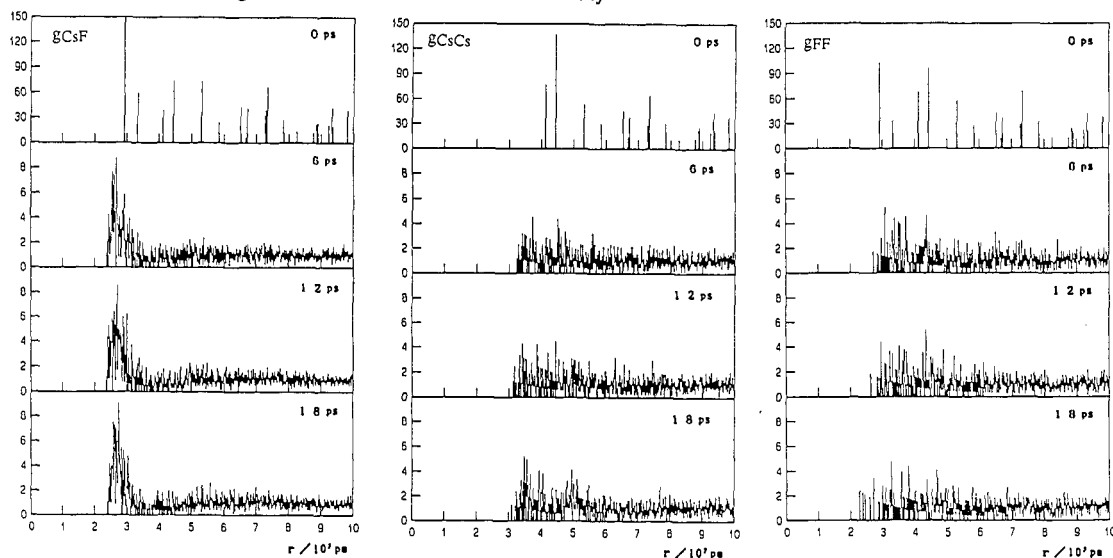


Fig. 4. Pair correlation functions $g_{ij}(r)$ for (c) CsF with time.

TABLE 2. The time dependence of the coordination numbers within the first and second coordination spheres.

	Coordination Number n_{ij}	r/pm	Time/ps			
			0	6	12	18
(a)NaCl 9.25m*	n_{NaCl}	282.5	0.13	0.64	0.55	0.55
	n_{NaNa}	489.3	1.98	2.36	2.38	2.43
	n_{ClCl}	399.5	0.95	0.69	0.69	0.58
		564.5	3.75	3.02	3.02	2.84
		399.5	0.15	0.18	0.18	0.18
		564.5	2.51	2.15	2.15	2.25
(b)NaCl 15.42m*	n_{NaCl}	282.5	0.00	1.25	1.25	1.24
	n_{NaNa}	489.3	3.53	3.55	3.65	3.76
	n_{ClCl}	399.5	0.94	0.96	0.94	0.99
		564.5	4.43	4.41	4.43	4.66
		399.5	0.00	0.71	0.81	0.78
		564.5	4.20	4.15	4.18	4.25
(c)CsF 36.34m*	n_{CsF}	301.5	1.66	1.79	2.01	1.90
	n_{CsCs}	522.1	5.15	6.06	6.01	5.85
	n_{FF}	426.3	1.65	2.24	2.29	2.27
		602.5	8.17	8.78	9.00	9.30
		426.3	3.00	2.37	2.37	2.38
		602.5	8.54	8.33	8.54	8.76

*m: mol (kg H₂O)⁻¹.

g_{NaCl} function shows a distinct bar at about 250 pm. At 6 ps some significant bars appear in the shorter r range than 250 pm, but they decreased their lengths at 12 ps. The g_{NaCl} function in the range 260 - 300 pm increases at 18 ps.

Long bars in both of g_{NaNa} and g_{ClCl} diminish their lengths and the functions seem to become flat as a whole with time. From Fig. 1a we see coagulation of ions in the solution. In this system no remarkable cluster formation has been seen and various small aggregates of ions as well as free ions exist.

The running coordination number $n_{\text{NaCl}}(r_1)$ increased up to 6 ps and then slightly decreased, and the value became practically constant after 12 ps. $n_{\text{NaCl}}(r_2)$ increased from 1.98 to 2.36 with time from 0 to 6 ps, and the value remained almost unchanged. Similar trends could be seen in $n_{\text{NaNa}}(r_1)$, $n_{\text{NaNa}}(r_2)$, $n_{\text{ClCl}}(r_1)$ and $n_{\text{ClCl}}(r_2)$. From these results it is suspected that the cluster formation may reach an almost equilibrated state.

System (b) (see Table 2, Figs 1b and 3) Results in this case are similar to those in system (a). The values of $n_{\text{NaCl}}(r_1)$ and $n_{\text{NaNa}}(r_1)$ were almost double the values in system (a) at 18 ps, and the value of $n_{\text{ClCl}}(r_1)$ became four times larger than the corresponding value in system (a). Therefore, in this system much larger clusters may be formed. Since the degree of supersaturation of system (b) is much larger than system (a), this conclusion seems to be reasonable. As we see from Fig. 3, the clusters formed in this system have more complicated shape than those in system (a).

System (c) (see Table 2, Figs 1c and 4) The bar at about 260 pm became longest at 6 ps and some long bars appeared in the long r range with time. Bars around 250 - 350 pm in g_{CsF} seem to construct a peak as we usually see in the $g(r)$ function. The peak became wider with time until 12 ps, but it sharpened at 18 ps. In g_{CsCs} at 18 ps peak-like shapes could be seen around 340 and 500 pm, which suggested that Cs⁺ ions were present in the second sphere of a central Cs⁺ ion. In the g_{FF} function bars appeared in the short r range where no bar existed in the initial stage of ionic distributions.

The running coordination numbers $n_{\text{CsF}}(r_1)$, $n_{\text{CsF}}(r_2)$ and $n_{\text{CsCs}}(r_1)$ gradually increased until 12 ps and they seemed to be slightly decreased at 18 ps. $n_{\text{FF}}(r_1)$ became practically constant after 6 ps. No remarkable change could not see in $n_{\text{FF}}(r_2)$ during the simulations. On the other hand, $n_{\text{CsCs}}(r_2)$ constantly increased with time and it became larger than $n_{\text{FF}}(r_2)$ at 18 ps. The trend that $n_{\text{MM}}(r_2)$ became larger than $g_{\text{XX}}(r_2)$ has been seen in all the case examined in this study and was independent of the size of ions. The results suggest that the clusters formed have a larger number of cations than anions and thus many of the clusters formed in NaCl and CsF solutions may be positively charged.

CONCLUSIONS

In the bulk systems examined with the periodically boundary condition and the Ewald summation, many small clusters containing a few cations and anions are formed. Many of the clusters formed in the NaCl and CsF solutions are positively charged due to a larger number of cations than anions in the clusters. The formation of the clusters does not significantly progress and seems to approach the equilibrium state after 12 - 18 ps, because no remarkable increase in the $n_{ij}(r)$ values has been observed. Solution X-ray diffraction experiments examined for supersaturated aqueous solutions of KF and CsF (ref. 9) gave similar results to those of the present simulation calculations that the supersaturated solutions contain ion clusters with the average coordination number in the first coordination shell of a cation or an anion was 2.29 and 3.33 for KF and CsF, respectively, which indicated the formation of clusters of higher order than 1:1 or 2:2 ion pairs. Moreover, the clusters contain different numbers of cations and anions because the coordination numbers of M-M and X-X pairs are different. On the other hand, slightly undersaturated aqueous solutions of NaCl and KCl contained only 1:1 ion pairs. Thus, the solution X-ray diffraction experiments carried out under an equilibrium condition support the simulation results.

The present simulations are still not enough to generalize the mechanism of the nucleation of crystals in supersaturated solutions because of the lack of statistics, but the results seem to be suggestive to understand the nucleation mechanism. In the real case, microclusters with irregular shapes may be formed at the very early stage of formation, and then some of the clusters may gather each other to form larger aggregates, and then, after the size of the aggregates will be beyond the limiting radius, the crystal growth which is observable under a macroscopic condition may begin.

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