Supplementary Information

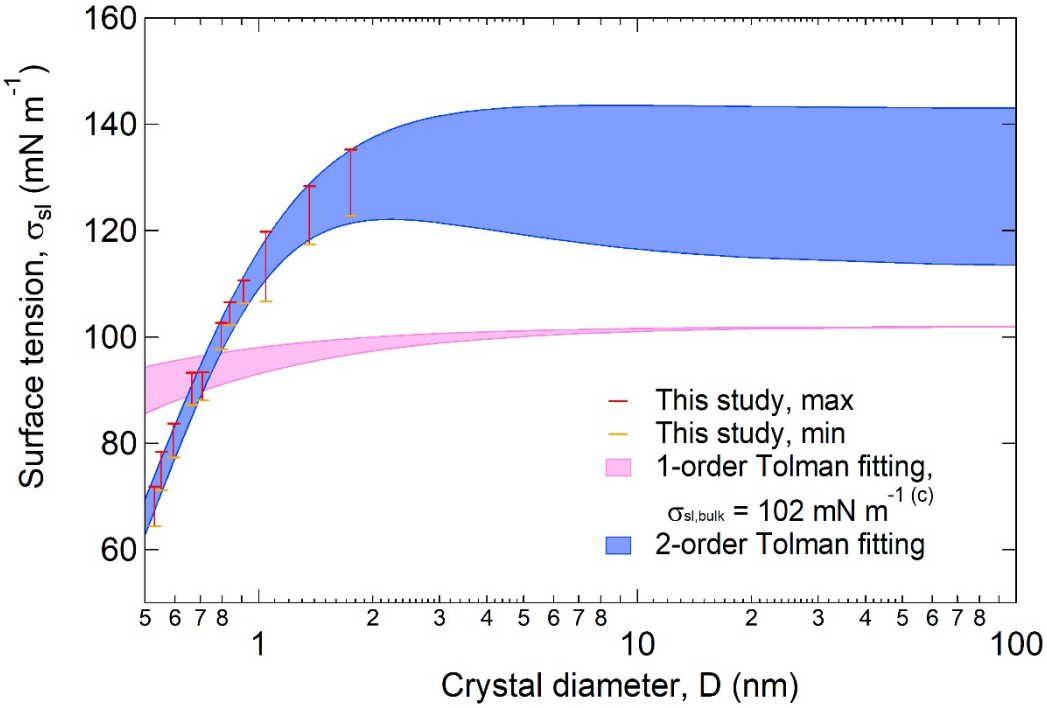


Figure S1. Size-dependent solid-liquid surface tension of NaCl nanoparticles at 300 K. The solid-liquid surface tension of NaCl nanoparticles is obtained from the MD simulated solubility data sets by the combination of the Ostwald-Freundlich equation with the Gibbs-Duhem equation (red and orange bars). The blue shaded curves are derived from the 2nd Tolman equation. (c)The light pink shaded curves are derived from the 1st order Tolman equation with the bulk solid-liquid surface tension from Bahadur and Russell[17].

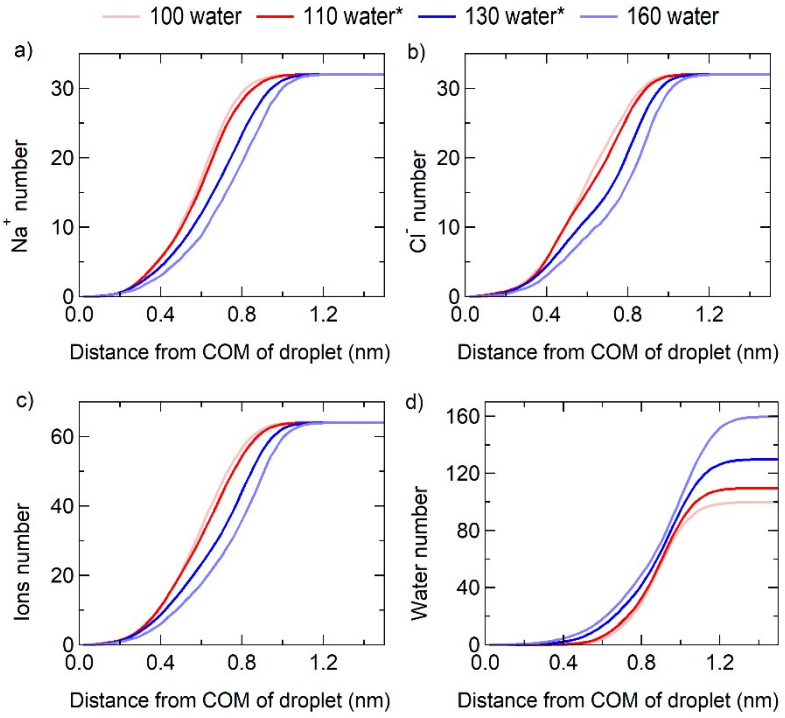


Figure S2. Cumulative number profiles of ions and water molecules in the particles composed of 1 nm NaCl (32 pairs) and different numbers of water molecules. (a) for Na^+ ions, (b) for Cl^- ions, (c) for ions, and (d) for water molecules. Particles with less than 110 water molecules are in the incompletely dissolved state (light red lines). Particles with 110-130 water molecules are in the critically dissolved state (red and blue lines). And particles with more than 130 water molecules are saturated NaCl aqueous nanodroplets (light blue lines).

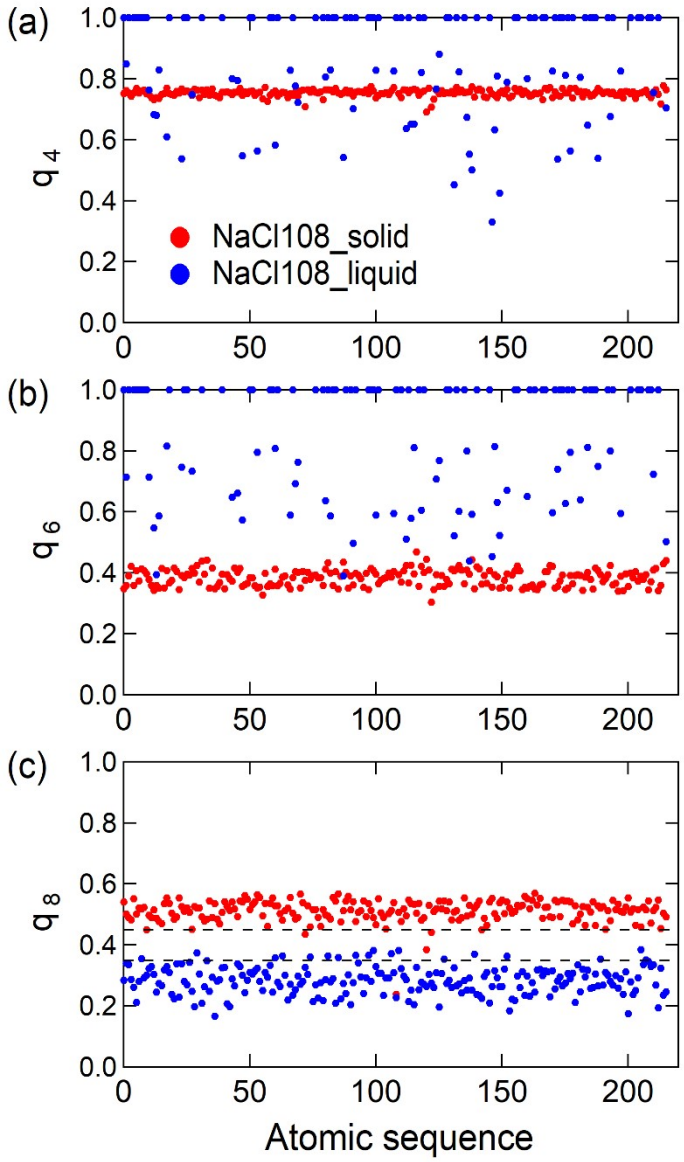


Figure S3. **q_4, q_6, q_8 atomic distributions for the cubic nanocrystal with 108 pairs of NaCl in the solid phase and a dissolved state as representative of the liquid phase at 300 K.** This figure indicates that q_8 provides the best separation between liquid and solid phase distributions compared to q_4 and q_6. The vertical dash line in (c) indicates the selected threshold ($q_8 = 0.35$).

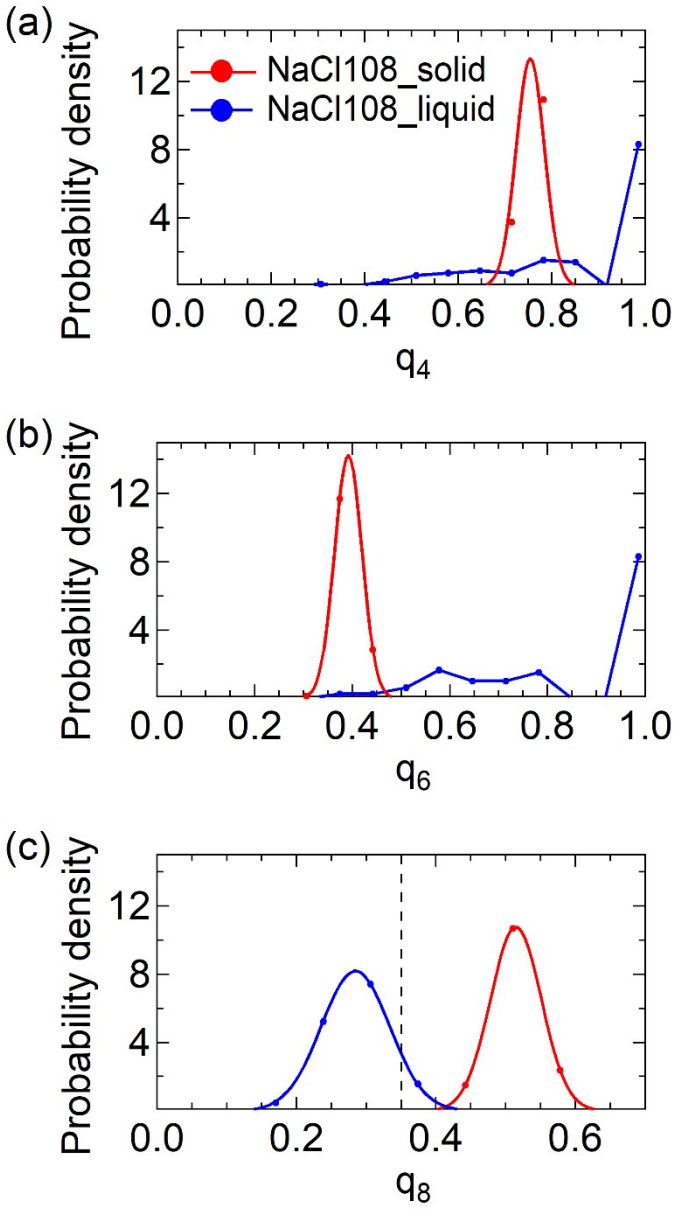


Figure S4. **q_4, q_6, q_8 probability density distributions for the cubic nanocrystal with 108 pairs of NaCl in the solid phase and a dissolved state as representative of the liquid phase at 300 K.** This figure indicates that q_8 provides the best separation between liquid and solid phase distributions compared to q_4 and q_6. The vertical dash line in (c) indicates the selected threshold ($q_8 = 0.35$).

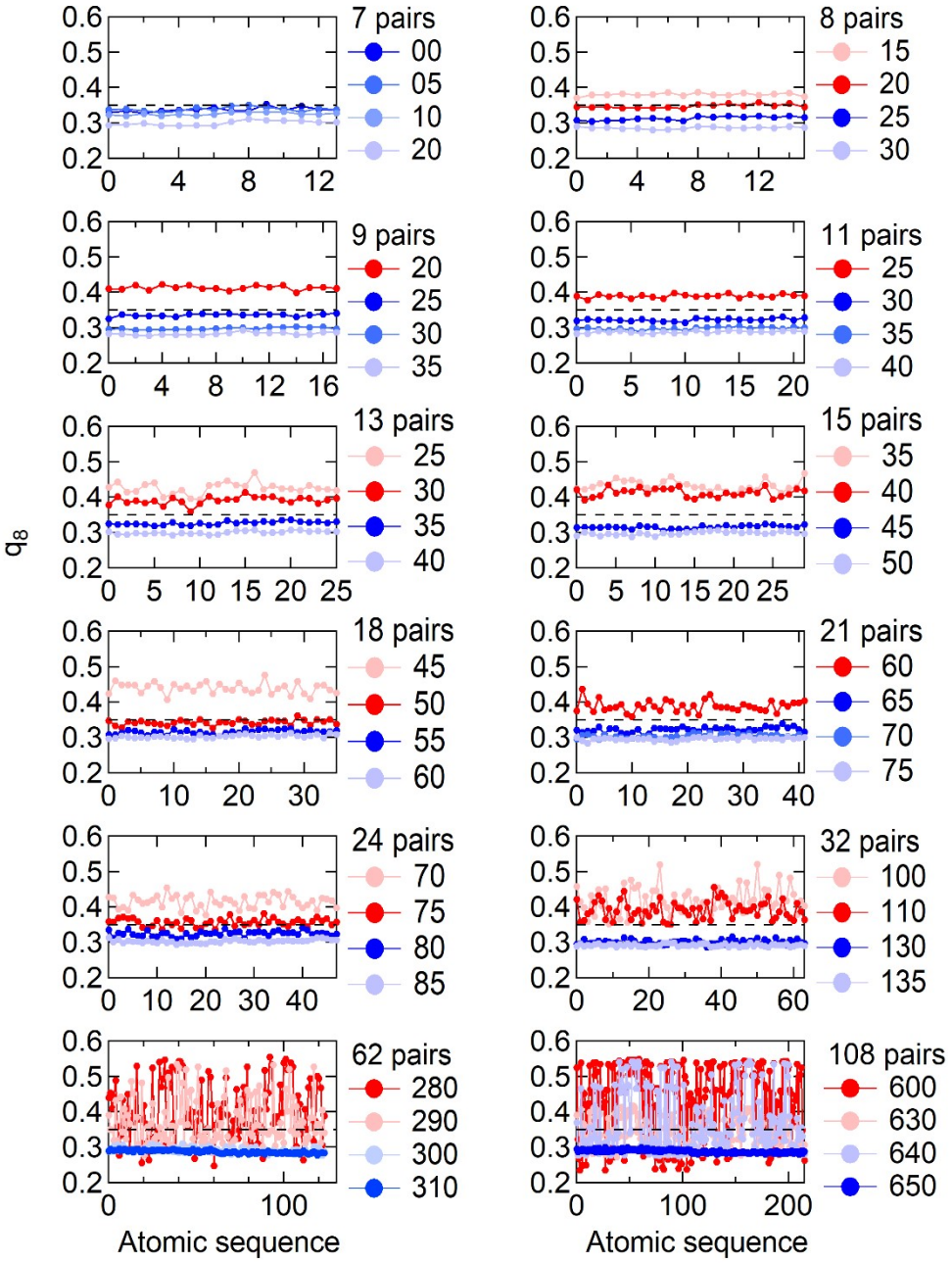
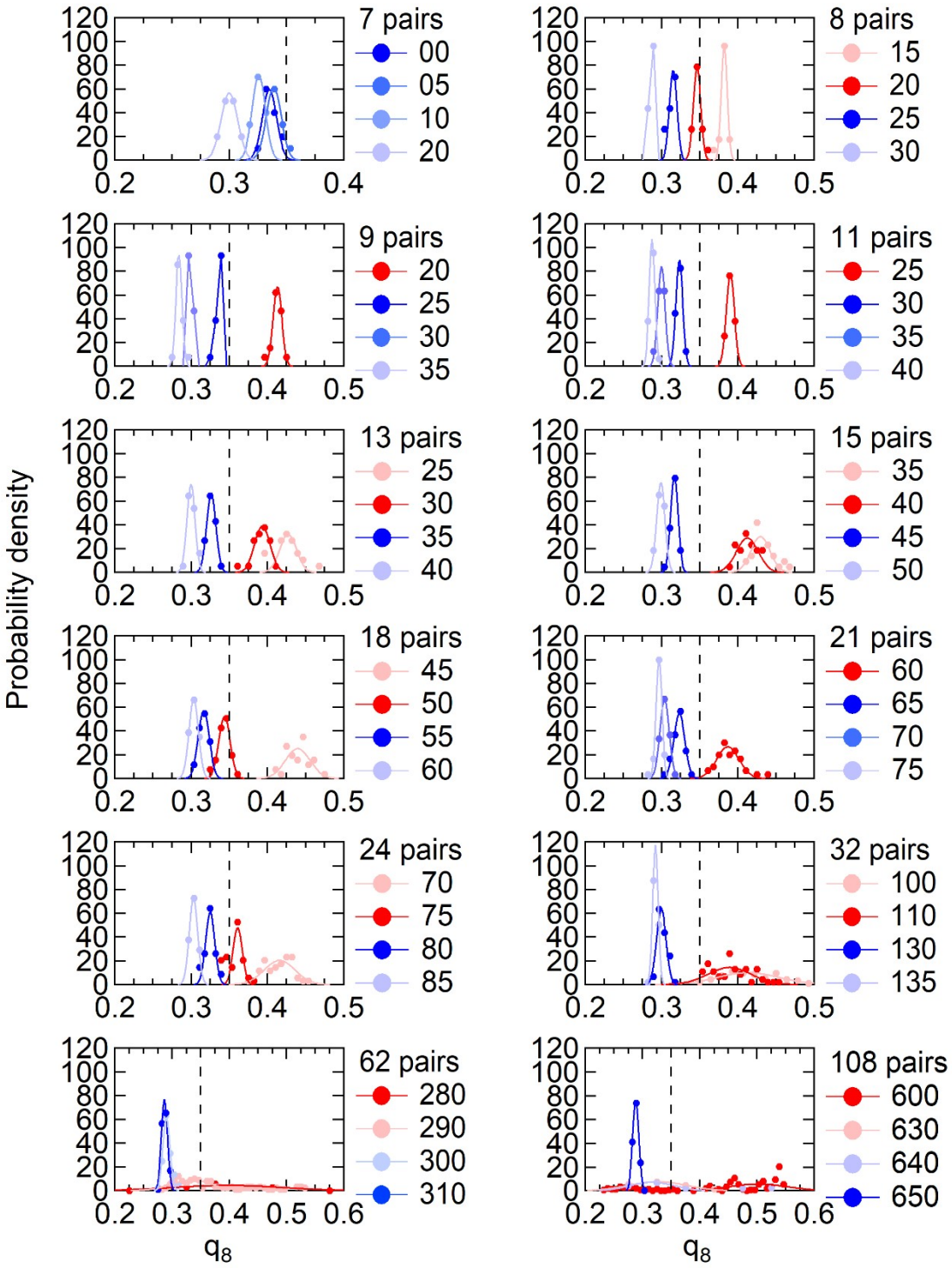


Figure S5. q_8 atomic distributions for ions in NaCl aqueous nanoparticles with different sizes in solid and liquid phase. This figure indicates that $q_8 = 0.35$ (dash lines) is a good choice for the threshold to distinguish solid-like and liquid-like structures of NaCl nanoparticles.


Probability density
7 pairs
00
05
10
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8 pairs
15
20
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9 pairs
20
25
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11 pairs
25
30
35
40
13 pairs
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15 pairs
35
40
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18 pairs
45
50
55
60
21 pairs
60
65
70
75
24 pairs
70
75
80
85
32 pairs
100
110
130
135
62 pairs
280
290
300
310
108 pairs
600
630
640
650
q8
q8

38

Figure S6. q_8 probability density distributions for ions in NaCl aqueous nanoparticles with different sizes in solid and liquid phase. This figure indicates that $q_8 = 0.35$ (dash lines) is a good choice for the threshold to distinguish solid-like and liquid-like structures of NaCl nanoparticles.

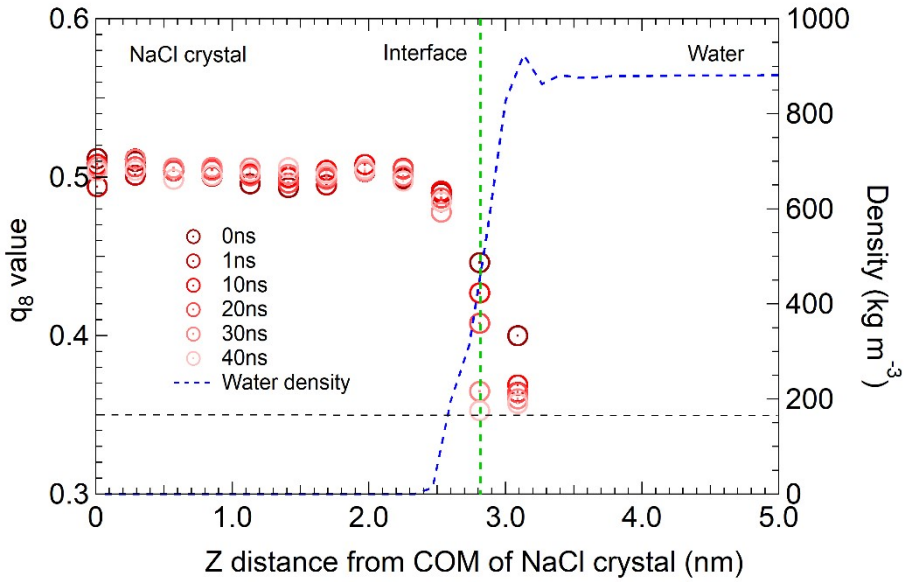


Figure S7. Variation of q_8 distributions with simulation time for different layers of NaCl planar slab interface with water. This figure indicates that $q_8 = 0.35$ (grey horizontal dash line) is a good choice for the threshold to distinguish solid-like and liquid-like structures in different layers of NaCl planar slab. The dissolution starts from the interface with water where q_8 is decreasing to be less than 0.35 (around 3 nm in Z distance from COM of NaCl crystal). q_8 is larger than 0.35 within the undissolved layers of the NaCl planar slab. The interface (green dash line) is determined based on half of the water density profile.

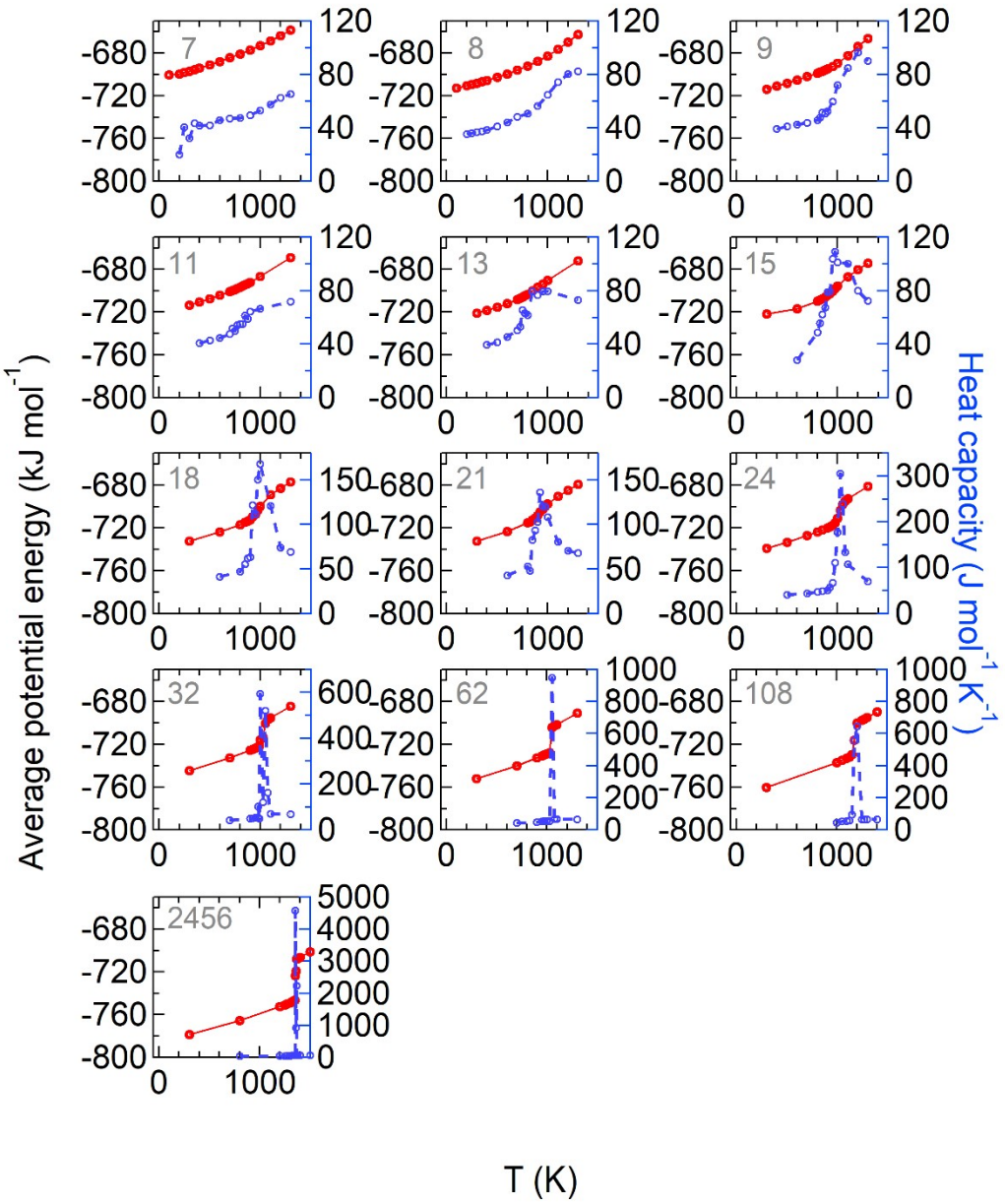


Figure S8. The average potential energy (left axis) and heat capacity (right axis) as a function of temperature T for NaCl crystals with different sizes. The heat capacity (blue circles and dash lines) is evaluated according to Eq. S1 with the average potential energy data (red circles). The melting point is the temperature with the maximum apparent heat capacity. No clear maximum heat capacity is found for 7, 8, 9, 11, 13 pairs of NaCl nanoparticles.

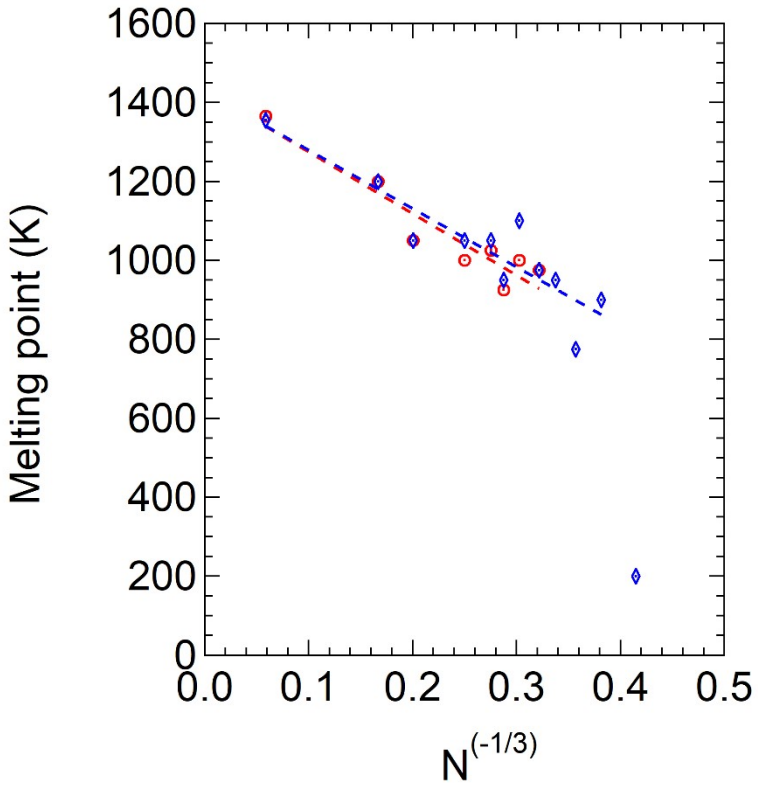


Figure S9. Melting points for NaCl crystals as a function of $N^{(-1/3)}$. The labels above the data are the numbers of the pairs of NaCl ions. N is the number of ions. The red circles are the melting points of NaCl nanocrystals at the maximum heat capacity derived from Eq. S1. The blue diamonds are the melting points of NaCl nanocrystals when q_8 of NaCl nanocrystals is less than 0.35. The red dashed line shows the linear fitting of the melting point respect to $N^{(-1/3)}$ based on the red circles. The blue dashed line shows the linear fitting of the melting point respect to $N^{(-1/3)}$ based on the blue diamonds except for the diamond at 7 pairs of NaCl.

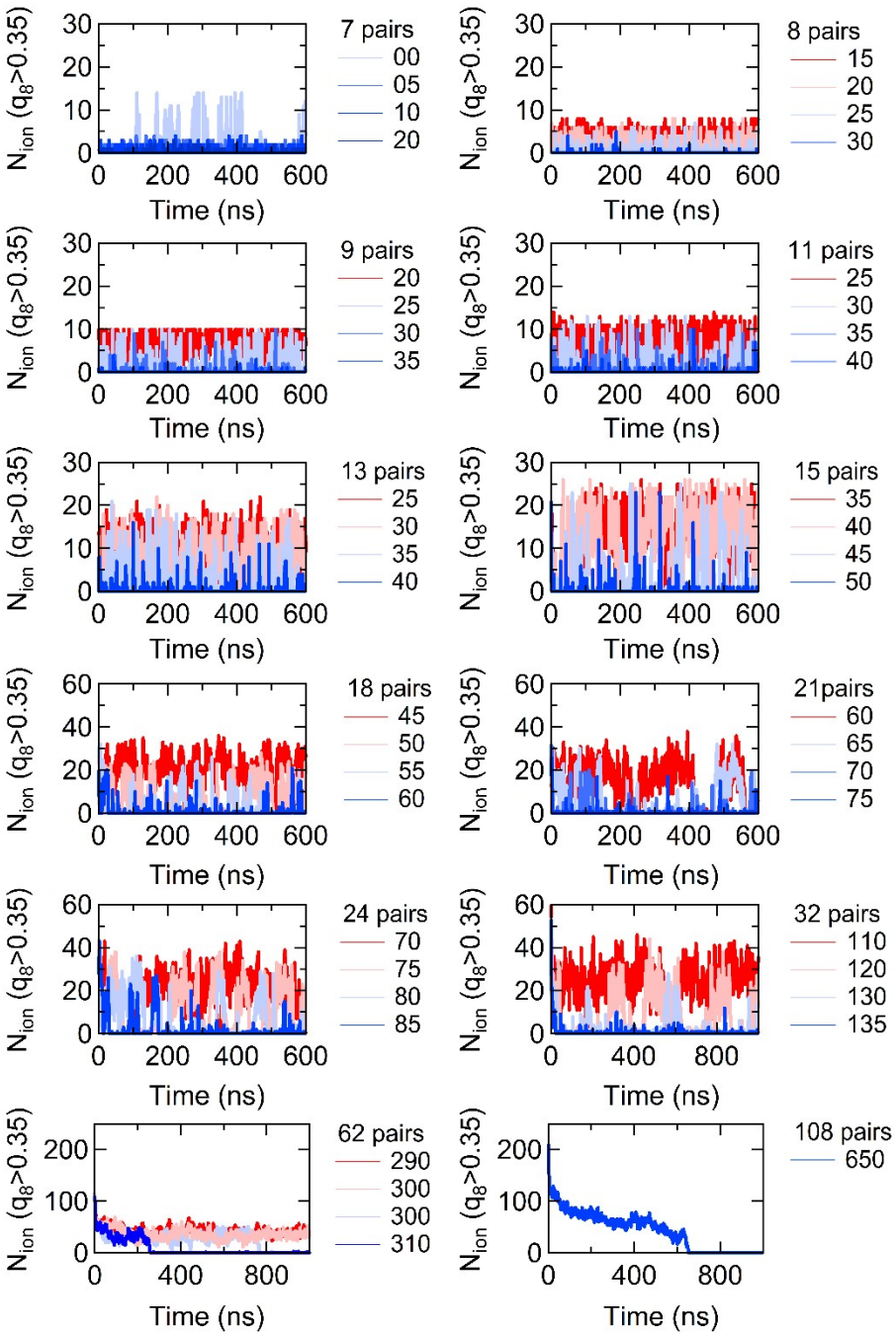


Figure S10. The time required for the dissolution of NaCl nanoparticles of different sizes. The red line represents the state when the whole particle is completely dissolved by the excess water molecules. The pink line represents the state when the particle is dissolved by the upper limit of the critical number of water molecules. The light blue line represents the state when the particle is not dissolved by the lower limit of the critical number of water molecules. The blue line represents the state when the particle is not dissolved by enough water molecules.

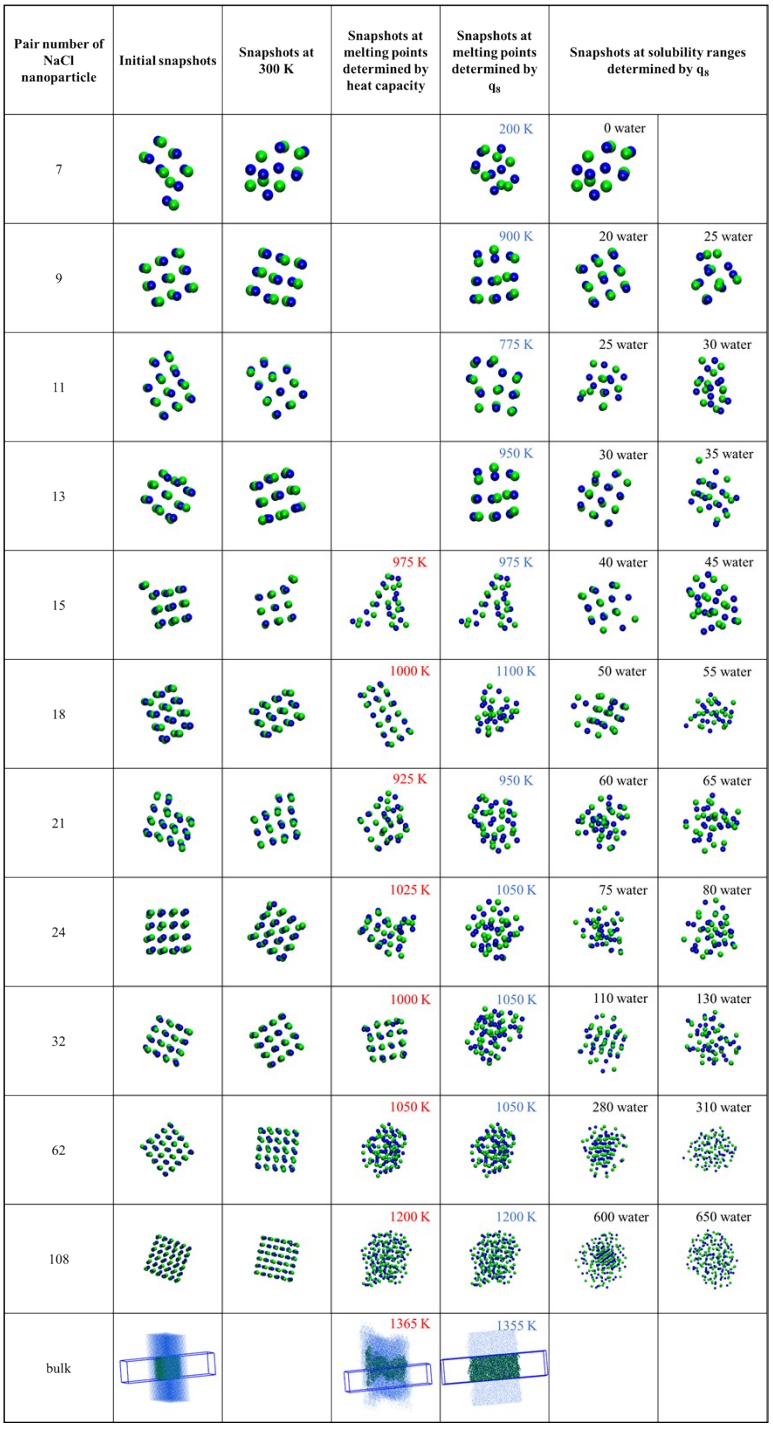


Figure S11. Snapshots of NaCl nanoparticles during the melting and dissolution processes.

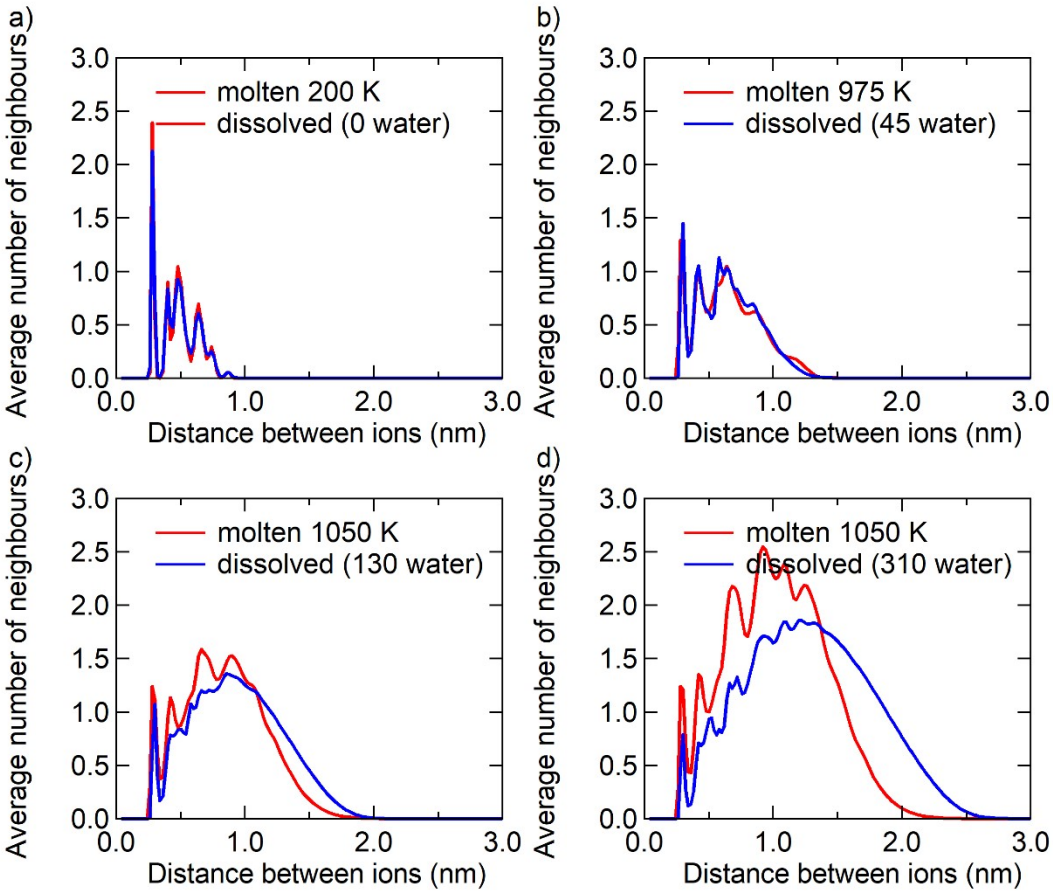


Figure S12. $RDF_{ions\text{-}ions}$ of the molten NaCl and dissolved NaCl in saturated solution nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm).

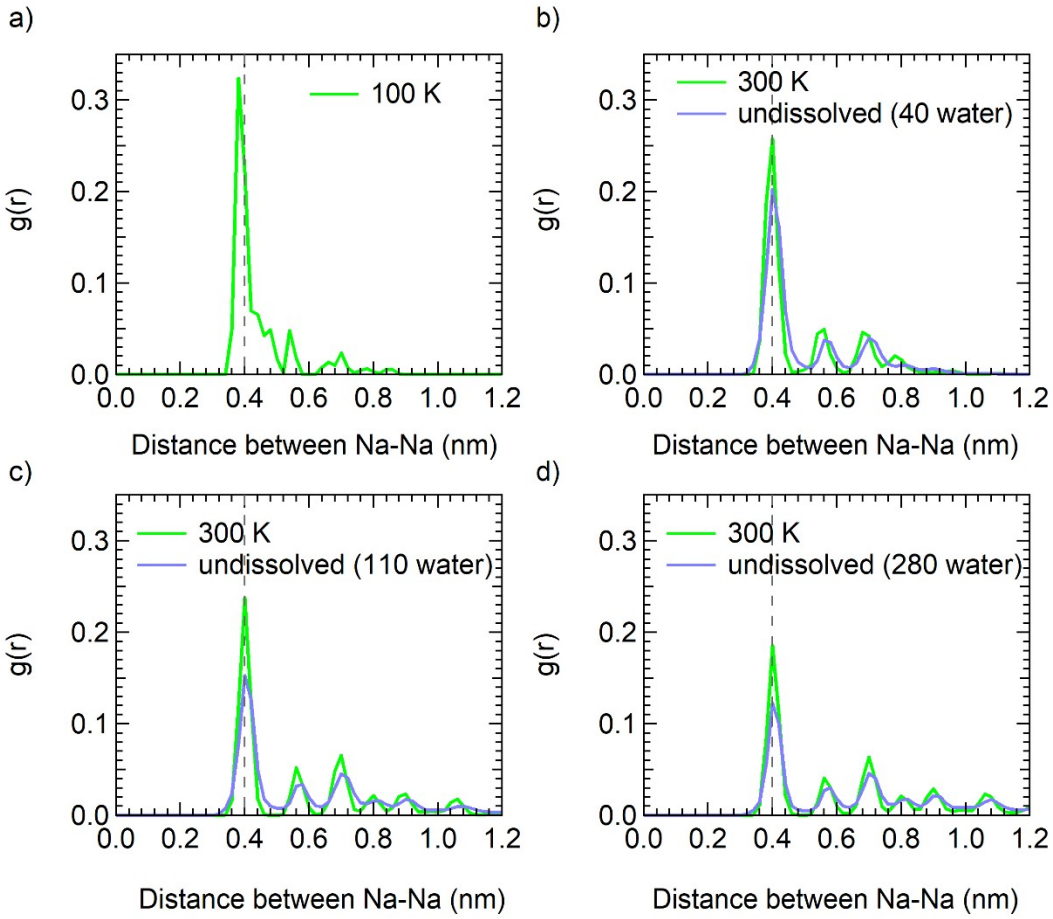


Figure S13. $RDF_{Na\text{-}Na}$ of the unmelted NaCl nanocrystal and undissolved NaCl in nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.4 nm between Na^+ and Na^+ ions nearest neighbors.

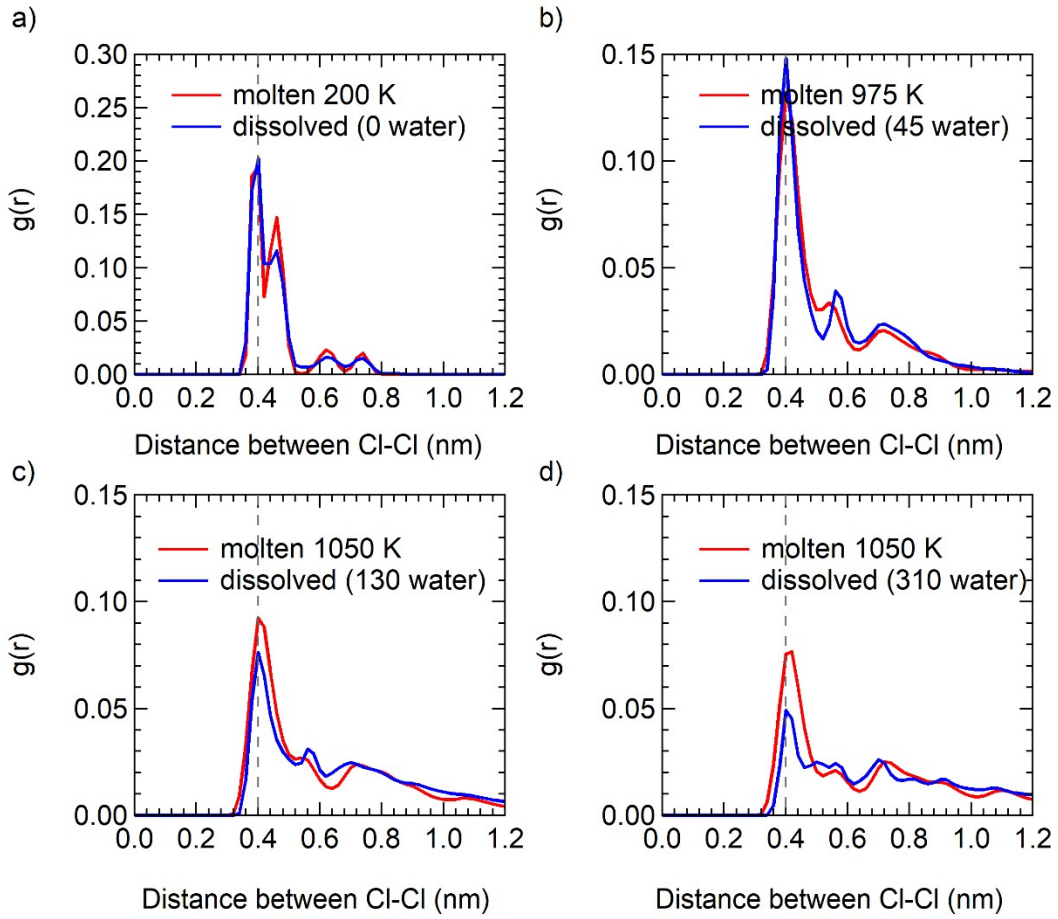


Figure S14. $RDF_{Cl\text{-}Cl}$ of the molten NaCl and dissolved NaCl in saturated solution nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.4 nm between Cl^- and Cl^- ions nearest neighbors.

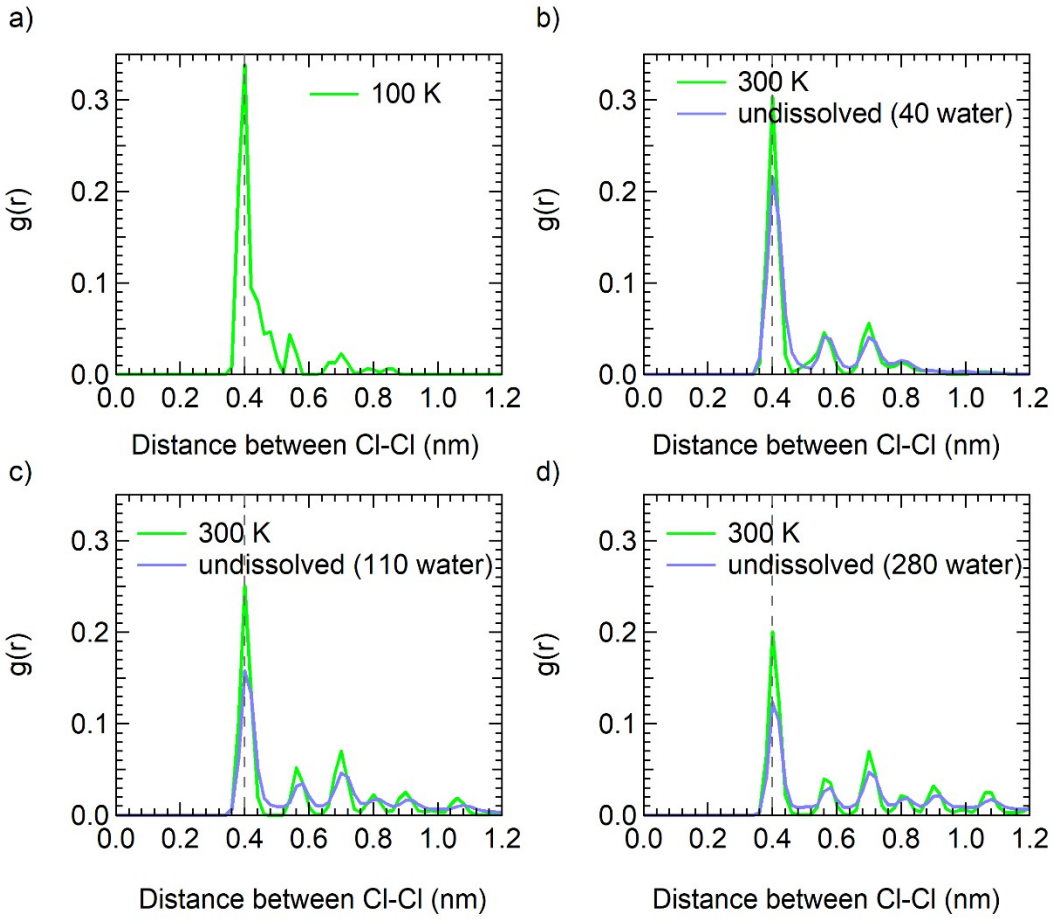
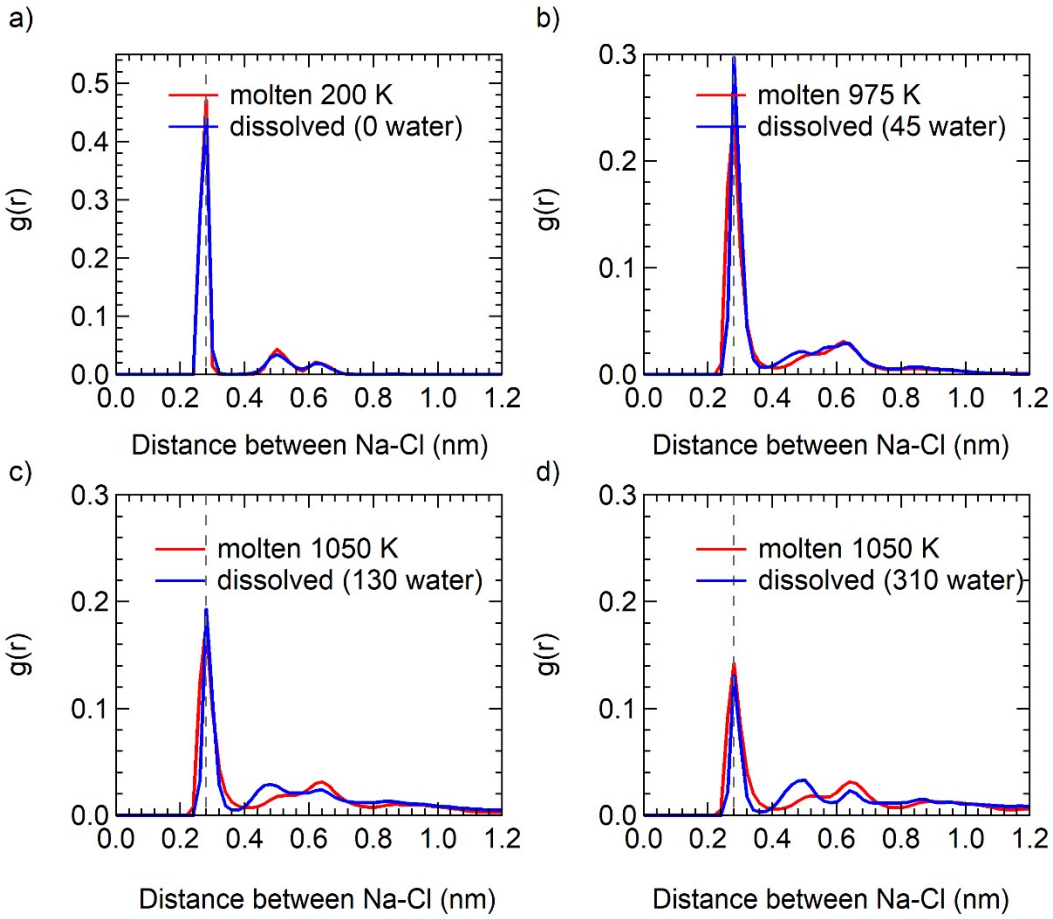


Figure S15. $RDF_{Cl\text{-}Cl}$ of the unmelted NaCl nanocrystal and undissolved NaCl in nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.4 nm between Cl^- and Cl^- ions nearest neighbors.



111

112 **Figure S16. $RDF_{Na\text{-}Cl}$ of the molten NaCl and dissolved NaCl in saturated solution**
113 **nanodroplets.** (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of
114 NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter =
115 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates
116 the theoretical position where peak should occur according to the ideal NaCl crystal structure with
117 the distance of ~0.28 nm between Na^+ and Cl^- ions nearest neighbors.

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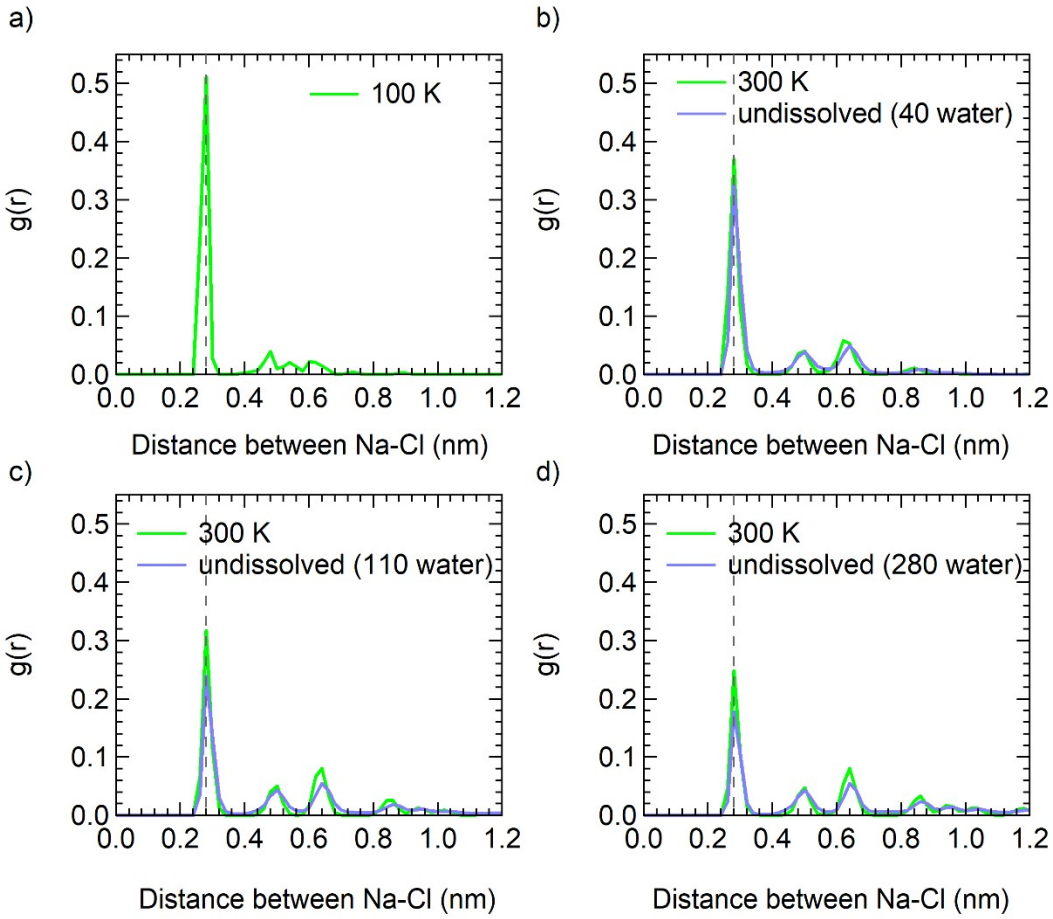


Figure S17. $RDF_{Na\text{-}Cl}$ of the unmelted NaCl nanocrystal and undissolved NaCl in nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.28 nm between Na^+ and Cl^- ions nearest neighbors.

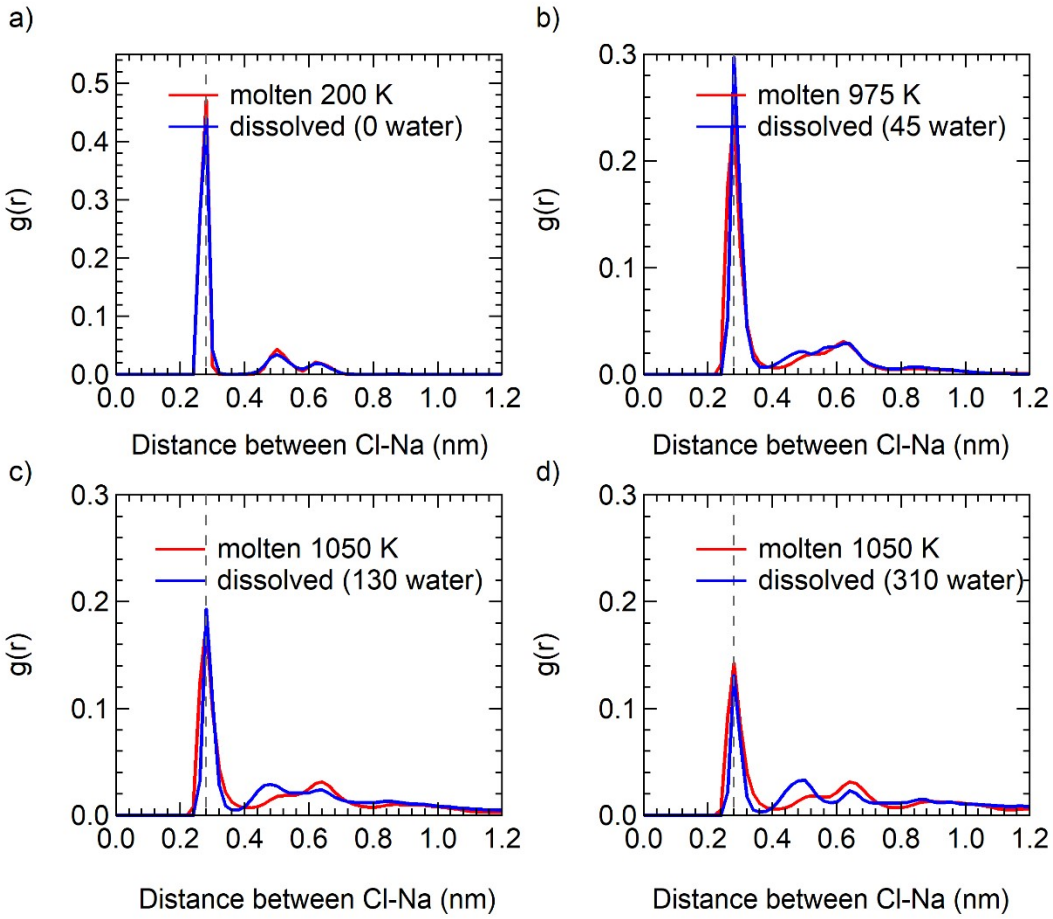


Figure S18. $RDF_{Cl\text{-}Na}$ of the molten NaCl and dissolved NaCl in saturated solution nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.28 nm between Cl^- and Na^+ ions nearest neighbors.

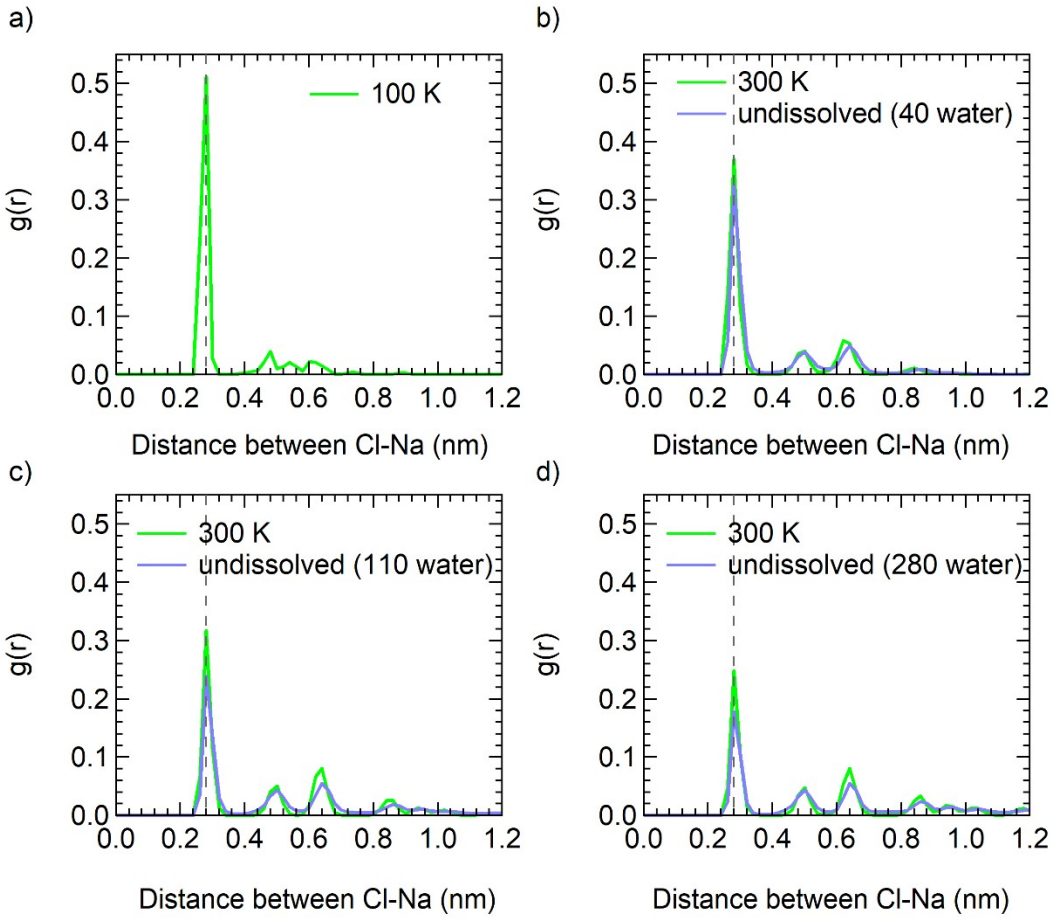
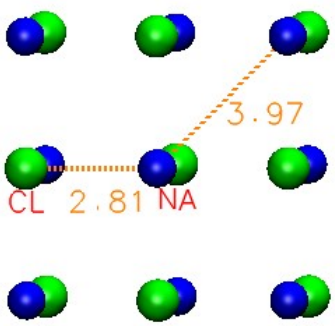


Figure S19. $RDF_{Cl\text{-}Na}$ of the unmelted NaCl nanocrystal and undissolved NaCl in nanodroplets. (a) For 7 pairs of NaCl ions particles (diameter = 0.507 nm). (b) For 15 pairs of NaCl ions particles (diameter = 0.709 nm). (c) For 32 pairs of NaCl ions particles (diameter = 1.042 nm). (d) For 62 pairs of NaCl ions particles (diameter = 1.358 nm). The dash line indicates the theoretical position where peak should occur according to the ideal NaCl crystal structure with the distance of ~0.28 nm between Cl^- and Na^+ ions nearest neighbors.



142

143 **Figure S20. The snapshot of initial 9 pairs of NaCl nanocrystal.** The nearest neighbor distance
144 of Na^+ and Cl^- is ~0.281 nm, and the nearest neighbor distance of Na^+ and Na^+ (Cl^- and Cl^-) is
145 ~0.397 nm.

Supplementary Tables

Table S1. Summary of the number of ion pairs, equivalent volume diameter, lower limit of the critical number of H2O that dissolve entire particle, upper limit of the critical number of H_2O that dissolve entire particle, saturated mass fraction range, average potential energy of NaCl in dissolved state, at 300 K, and in melting point, and melting point. [a]Bulk saturated mass fraction is determined from MD simulations in [9]. The potential energy of molten NaCl is near -698.39 kJ/mol for all size.

Pair number of NaCl ions in the particle	Diameter (nm)	Lower limit of the critical number of H_2O that dissolve entire particle	Upper limit of the critical number of H_2O that dissolve entire particle	Saturated mass fraction max (x_s^* max)	Saturated mass fraction min (x_s^* min)	Simulation time for solubility (ns)	Average potential Energy of NaCl in dissolution (kJ mol^{-1})	error	Average potential Energy of NaCl crystal at 300 K (kJ mol-1)	error	Average potential Energy of NaCl in melting point (kJ mol^{-1})	error	Melting Point (K) determined by the heat capacity	Melting Point (K) determined by the q_8 method
7	0.507	-	-	1.000	1.000	600	-697.223	0.000	-697.237	0.420				200
8	0.530	20	25	0.565	0.510	600	-663.653	11.663	-708.286	0.018				
9	0.551	20	25	0.594	0.539	600	-683.027	14.850	-713.802	0.023				900

11	0.594	25	30	0.588	0.543	600	-676.178	11.882	-713.430	0.031				775
13	0.665	30	35	0.585	0.547	600	-676.890	12.270	-721.005	0.030				950
15	0.709	40	45	0.549	0.520	600	-668.226	12.680	-721.740	0.054	-698.007	1.7	975	975
18	0.795	50	55	0.539	0.515	600	-657.628	12.228	-732.450	0.050	-699.750	5.5	1000	1100
21	0.837	60	65	0.532	0.512	600	-657.900	5.762	-732.257	0.026	-705.110	3.3	925	950
24	0.910	75	80	0.510	0.493	600	-644.977	12.635	-739.004	0.032	-703.529	1.2	1025	1050
32	1.042	110	130	0.486	0.444	1000	-624.098	35.152	-744.722	0.028	-716.009	5.6	1000	1050
62	1.358	280	310	0.418	0.394	1000	-566.344	37.290	-752.285	0.068	-704.305	1.3	1050	1050
108	1.745	600	650	0.369	0.350	1000	-521.377	41.787	-760.184	0.045	-700.252	1.9	1200	1200

2456	cubic (4.5 nm^3)	37000	37000	0.178 [a]	0.178 [a]	-	-358.350	20.950	-778.709	0.32	-708.070	3.7	1365	1355

Supplementary Note 1: simulation of the melting process

The NaCl nanoparticles with different diameters were simulated at different temperatures with a ΔT (= 50 to 100 K). Following the approach of Qi et al. [19], the melting point is the temperature with the maximum apparent heat capacity. The heat capacity was evaluated according to the following equation:

$$C_p(T) = \frac{\partial U}{\partial T} + \frac{3}{2}R_{gas} \#(S1)$$

where U is the average potential energy and R_{gas} the universal gas constant. The melting process simulation for NaCl nanocrystals with different diameters in this study is summarized in Supplementary Table S1. By fitting the potential energy to a linear function of T in the solid and liquid phase (above and below the transition temperature), the melting point of NaCl crystal can be obtained (Fig. S8). The simulation demonstrates that the melting point of the NaCl nanocrystal is size-dependent, and this phenomenon also occurs in other substances. The nanocrystal with 7 pairs of NaCl ions is in liquid-like (molten) state at 300 K in the simulation.

Supplementary Note 2: a_w determination

Water activity (a_w) of NaCl is determined by the modified TM model [3, 38]. It is expressed as a segmentation function of the solute mass fraction (x_s):

$$a_w = \begin{cases} 1 + \sum C_l (100 \cdot x_s)^l & (x_s \le 0.45) \\ \dfrac{a_1 \cdot x_s^2 + a_2 \cdot x_s + a_3}{x_s^2 + a_4 \cdot x_s + a_5} & (x_s > 0.45) \end{cases} \quad \text{(S2)}$$

where the respective coefficients for NaCl $(x_s \le 0.45)$ are C_1 = -6.366 × 10^{-3}, C_2 = 8.624 × 10^{-5}, C_3 = -1.158 × 10^{-5}, and C_4 = 1.518 × 10^{-7}, and the respective coefficients for NaCl $(x_s > 0.45)$ are a_1= 0.1703, a_2= -0.6018, a_3= 0.4315, a_4= -0.4594, a_5= 0.4343.

Supplementary Note 3: Estimation of size-dependent solid-liquid surface tension

The solid-liquid surface tension of the NaCl nanoparticle (σ_{sl}) is determined by the MD solubility data based on the combination of the Ostwald-Freundlich [6, 7] and Gibbs-Duhem equations [34-36] as

$$\sigma_{sl} = \frac{RTD}{4\nu}\ln\left(\frac{a_s^*}{a_{s,bulk}^*}\right) = -\frac{RTD}{4\nu}\int_{x_{s,bulk}^*}^{x_s^*} M\frac{1-x_s}{x_s}dlna_w \#\ (S3)$$

where R is the universal gas constant, T is the temperature, D is the volume equivalent diameter of NaCl crystal at the saturation dissolution point, which equals to the diameter of the equilibrium droplet of equivalent volume, ν is the molar volume of NaCl solid phase (atomic volume) given as 2.7×10^{-5} m^3 mol^{-1}, and M is the molar weight of solute. $x_{s,bulk}^*$ is the mass fraction of solute in a saturated bulk solution, and $a_{s,bulk}^*$ is the solute activity at $x_{s,bulk}^*$. x_s^* is the mass fraction of solute in a saturated droplet, and a_s^* is the solute activity at x_s^*. a_w is the water activity retrieved from modified TM model (Supplementary Note 2).

The calculated solid-liquid surface tension of NaCl is fitted by the first-order Tolman equation and second-order Tolman equation, respectively [39]:

$$\sigma_{sl} = \frac{\sigma_{sl,bulk}}{\left(1+\frac{4\delta}{D}\right)} \#\ (S4)$$

$$\sigma_{sl} = \frac{\sigma_{sl,bulk}}{\left(1+\frac{4\delta}{D}+8\left(\frac{l}{D}\right)^2\right)} \#\ (S5)$$

where $\sigma_{sl,bulk}$ is the bulk solid-liquid surface tension, D is the volume equivalent diameter of NaCl crystal at the saturation dissolution point, which equals to the diameter of the equilibrium droplet of equivalent volume. δ is the Tolman length, and l is a parameter that has the dimension of length.

The calculated σ_{sl} shows a significant size dependence with particle diameter larger than 0.530 nm (8 pairs of NaCl ions) (red and orange bars in Fig. S1). σ_{sl} decreases as the size of NaCl nanocrystals decreases. This size dependence is well explained by the second-order Tolman equation (Eq. S5), corresponding to the derived bulk solid-liquid surface tension ($\sigma_{sl,bulk}$ = (113.16, 142.95] mN m^{-1}) and a negative Tolman length (δ = (-0.082, -0.018] nm) (blue shaded curves in Fig. S1), while the first-order Tolman equation fit with fixed $\sigma_{sl,bulk}$ = 102 mN m^{-1} calculated by MD[17] (light pink shaded curves in Fig. S1) performs poorly.

According to the blue shaded curves in Fig. S1, σ_{sl} has a critical decrease when the particle diameter is less than ~2 nm. This indicates that the bulk solid-liquid surface tension is applicable, but this may not be the case for the particles less than ~2 nm. Besides, it is still on debate if there is agreement between the interfacial energy at the solid-liquid interface σ_{sl} and at the solute embryo γ_{sl} [3, 40]. We estimate $\sigma'_{sl,7}$ = (63.88, 70.57] mN m^{-1} based on the second-order Tolman equation, which is close to the interfacial energy of solute embryo γ_{sl} range from 41 to 63 mN m^{-1} [41]. This indicates that σ_{sl} and γ_{sl} may be uniform when the particle is small enough. Note that, since the particle with 7 pairs of NaCl ions is in the molten state at 300 K, the directly calculated $\sigma_{sl,7}$ = 100.82 mN m^{-1}, which is close to the solid-vapor surface tension $\sigma'_{sl,7}$ = 101.85 mN m^{-1} [42], may not represent the interfacial energy at the solid-liquid interface.

Supplementary Note 4: q_8 validation

We confirm that q_8 is a good indicator for determining whether sodium chloride is solid or liquid. Firstly, we demonstrate that q_8 provides the best separation between liquid and solid phase distributions compared to q_4 and q_6. Based on Eq. 1 and Eq. 2, we choose $l =$ 4, 6, and 8 and calculate $q_l(i)$ for each ion in the NaCl solid and liquid particle with 108 pairs of ions, respectively. As shown in Fig. S3 and S4, q_8 atomic and probability distributions of ions can well distinguish NaCl solid and liquid phase. When q_8 <~0.35, ions are supposed to be liquid. Lanaro and Patey's study [32] yielded a similar result. They chose $l =$ 2, 4, 6, 8 and 10 and investigated $q_l(i)$ for the NaCl spherical crystal with ~2000 ions as the solid phase and a supersaturated solution with NaCl mole fraction equal 0.20 as the liquid phase at 300 K. And q_8 was proved to be the best choice for NaCl solid and liquid phase separation, which is similar to the results in this study. Secondly, it is demonstrated that q_8 = 0.35 is a good choice for the threshold to distinguish solid-like and liquid-like structures of NaCl nanoparticles. We investigated $q_l(i)$ for the NaCl solid and liquid nanoparticles with different pairs of NaCl ions, respectively. As shown in Fig. S5 and S6, q_8 atomic and probability distributions of ions is less than 0.35 (grey dash line) in each NaCl liquid nanoparticle. Thus, q_8=0.35 can well separate the solid and liquid phase NaCl nanoparticles. Thirdly, we demonstrate that q_8=0.35 is a good choice for the threshold to distinguish solid-like and liquid-like structures in different layers of a NaCl planar slab. We conduct the study of the NaCl crystal planar slab (4.5 nm^3, 5.6 nm

volume equivalent diameter) dissolved in 37000 water molecules for 100 ns in the MD simulation. The q_8 distribution of dissolved ions at the interface tends to be less than 0.35, while the q_8 distribution of undissolved ions inside the crystal remains larger than 0.35 (Fig. S7). This implies that q_8 = 0.35 is still effective for separating solid and liquid phase ions in the dissolution process of the NaCl planar slab system. Overall, q_8 can be examined as a universal standard for separating liquid and solid phase NaCl ions, not only for nanoparticles but also for planar plate systems.