Supporting Information: Effect of Sodium Chloride Adsorption on the Surface Premelting of Ice

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1   Description of calculation of local Steinhardt q_6 order parameter

The local Steinhardt q_6 order parameter allows one to identify the orientational order of the local environment around a particle and to catalogue it as either liquid or solid-like. The algorithm makes use of the complex bond-order parameter $q_{6m}(i)$, $m = $ -6...6 which is defined in the following way:

We identify the neighbors of particle i as the particles j within a cutoff radius $r_q = 3.5$ Å which is the the first minimum of the radial distribution function of the liquid. Let $\mathbf{r}_i$, $\mathbf{r}_j$ be the position vectors of particle i and j, their distance is $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ with modulus $\mathbf{r}_{ij} = |r_{ij}|$ and orientation $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/ \, \mathrm{r}_{ij}$. If i and j are neighbors we define as bond-functions the set of spherical harmonics $Y_{lm}(\hat{\mathbf{r}}_{ij})$. The latter is a vector of $2l+1$ components. In this work, we chose $l = 6$. We denote with $N_b(i)$ the number of neighbors of particle i and with N_b the total number of bonds in the system. The relation $N_b = \sum_{i=1}^{N} N_b(\frac{i}{2})$ holds but note that N_b is not the number of pairs of particles because it is defined on neighbors only. For each particle i we construct the average of the bond-functions $Y_{lm}(\hat{\mathbf{r}}_{ij})$ on the neighboring bonds $j = 1 \ldots N_b(i)$, to get the vector:

$$\bar{q}_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{6m}(\hat{\mathbf{r}}_{ij})$$

Then for particle i we loop over the neighbors j and compute the normalized dot product:

$$q_6(i) = d_{ij} = \frac{\sum_{m=-6}^{6} \bar{q}_{6m}(i)\bar{q}_{6m}^{*}(j)}{(\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2)^{1/2}(\sum_{m=-6}^{6} |\bar{q}_{6m}(i)|^2)^{1/2}}$$

Where $d_{ij} = d^*_{\ ij} = d_{ji}$. Therefore since $d_{ij} = q_6(i)$, then $q_6(i) \in \mathbb{R}$ and moreover $-1 \leq q_6(i) \leq 1$.

We calculated the local Steinhardt q_6 order parameter for the oxygen atoms of the system. This calculation was extended to the whole system in three dimensions and not carried out layer by layer. The lines labeling the bilayers in Figure 5 are just representative of where the first four bilayers are located. The scatter plots show the z coordinate position and q_6 value for a given oxygen atom averaged over the 200 ns trajectory.
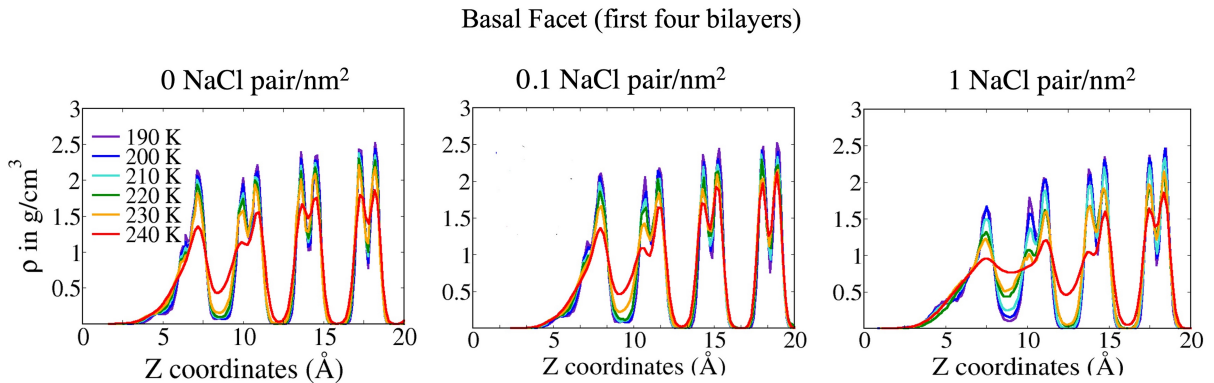
2   Extended data

Figure S1: Oxygen atoms density profile as a function of temperature for the basal facet for each sampled NaCl surface density, averaged over 200 ns production runs.
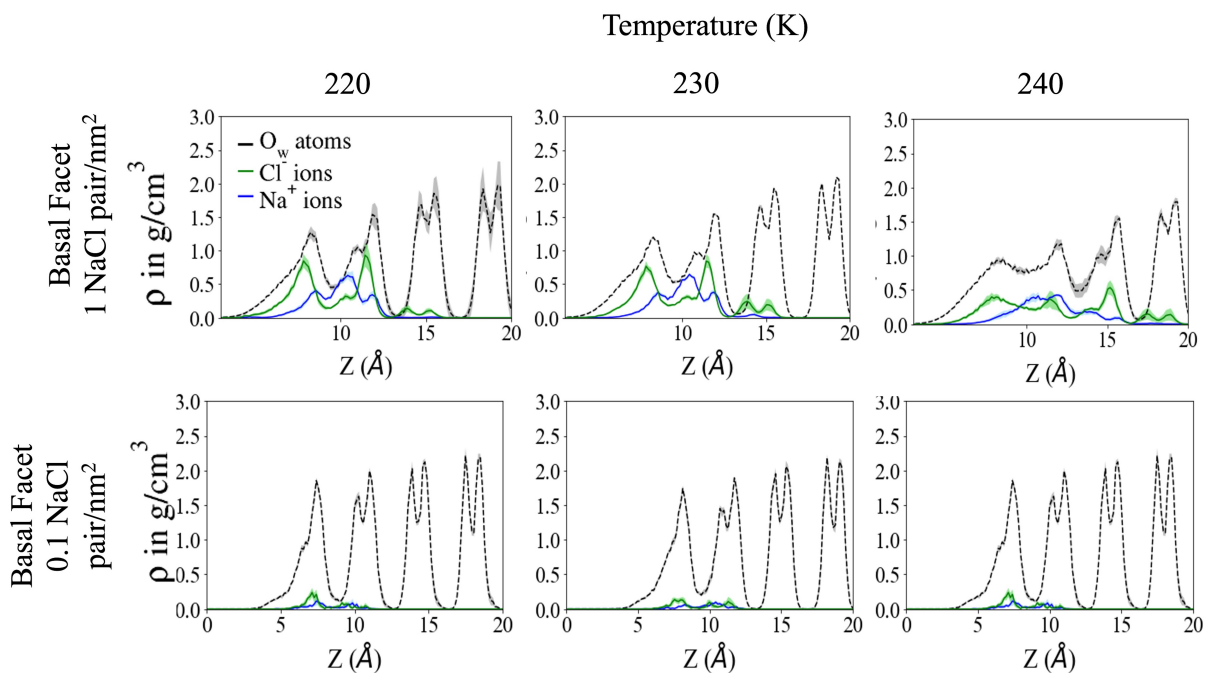
Figure S2: Cl^- and Na^+ density profiles for the three highest temperatures sampled for the basal facet at the NaCl surface density of 0.1 NaCl pair/nm^2. Respective oxygen atom density profiles are included to show where the density of the ions is in relation to the bilayers. Ion density is scaled by a factor of 5×. The density profiles were calculated over the 200 ns production run, using a block averaging over 8 blocks of 25 ns each. The shaded regions corresponds to the standard deviation in the density profiles.
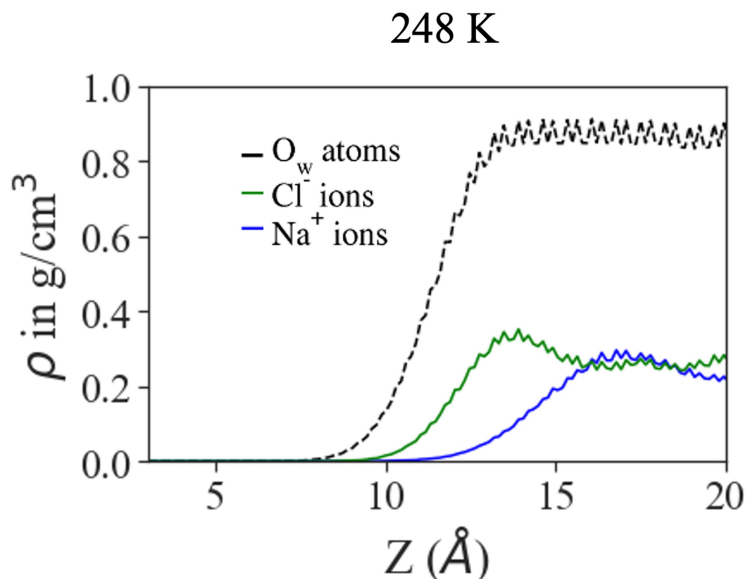

Figure S3: Cl^- and Na^+ density profiles for a run at 248 K for a liquid water system with a NaCl surface density of 1 NaCl pair/nm^2. Respective oxygen atom density profiles are included to show where the density of the ions is in relation to the interface. Ion density is scaled by a factor of 5×. The density profiles were calculated over the 200 ns production run.

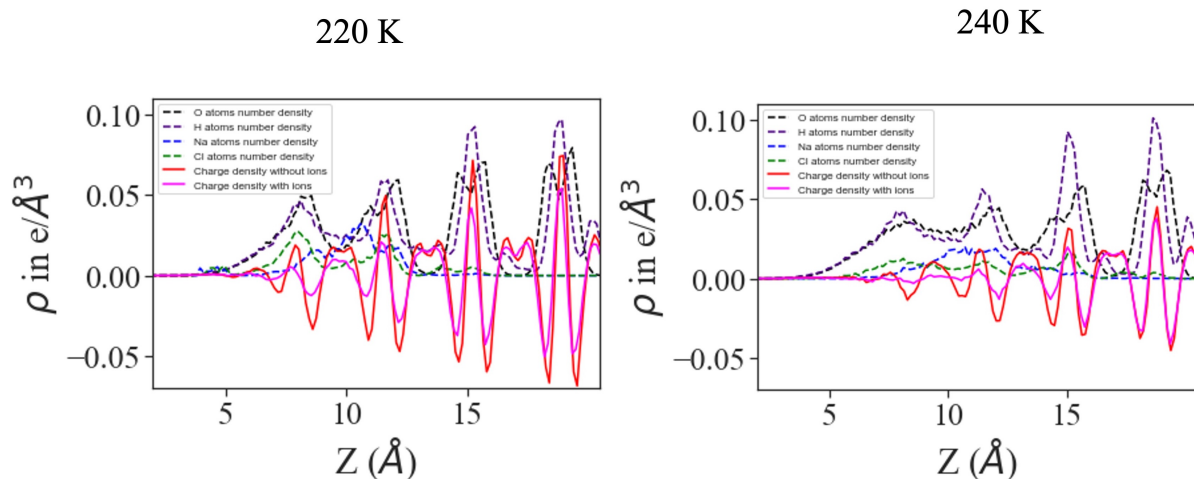220 K   240 K

Figure S4: Charge density profiles for a two sampled temperatures at the basal facet with and with out NaCl, plotted atop the number density of all four species in the system (O, H, Cl, Na). Ion density is scaled by a factor of 5×. The charge density profiles were calculated over the 200 ns production run.

Bilayer 2
Temperature (K)

210   220   230   240
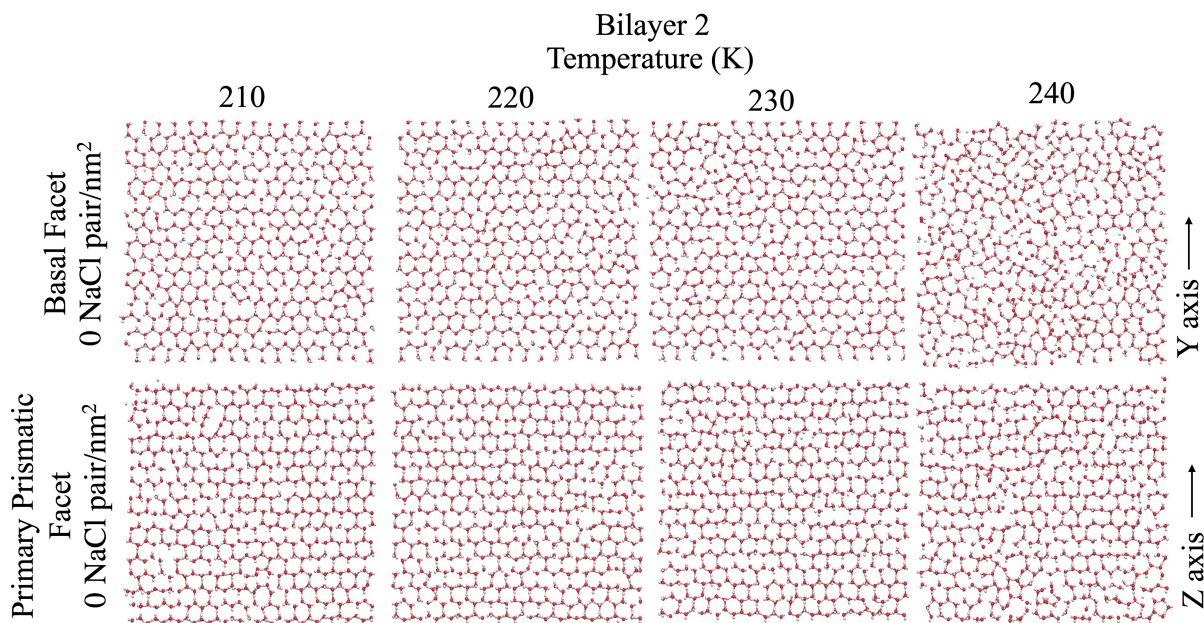

Figure S5: Snapshots from a top down view of the third bilayers of the basal and primary prismatic facet with a surface density of pristine ice of 0 NaCl pair/nm^2 as a function of temperature. Bonds shown are for a bond length cutoff 1.9 $\mathring{A}$ to display the crystalline structure (or lack there of) in each layer. Na$^+$ ions are represented by blue spheres and Cl$^-$ ions are represented by green spheres.
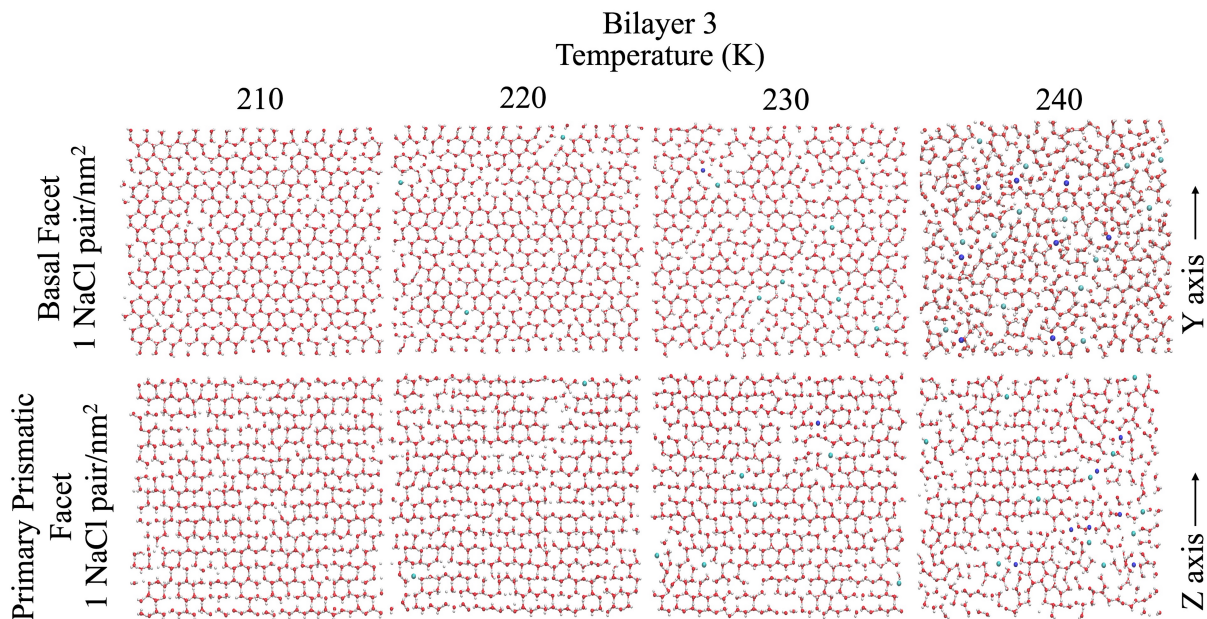
Figure S6: Snapshots from a top down view of the third bilayers of the basal and primary prismatic facet with the high surface density of 1 NaCl pair/nm^2 as a function of temperature. Bonds shown are for a bond length cutoff 1.9 Å to display the crystalline structure (or lack there of) in each layer. Na$^+$ ions are represented by blue spheres and Cl$^-$ ions are represented by green spheres.
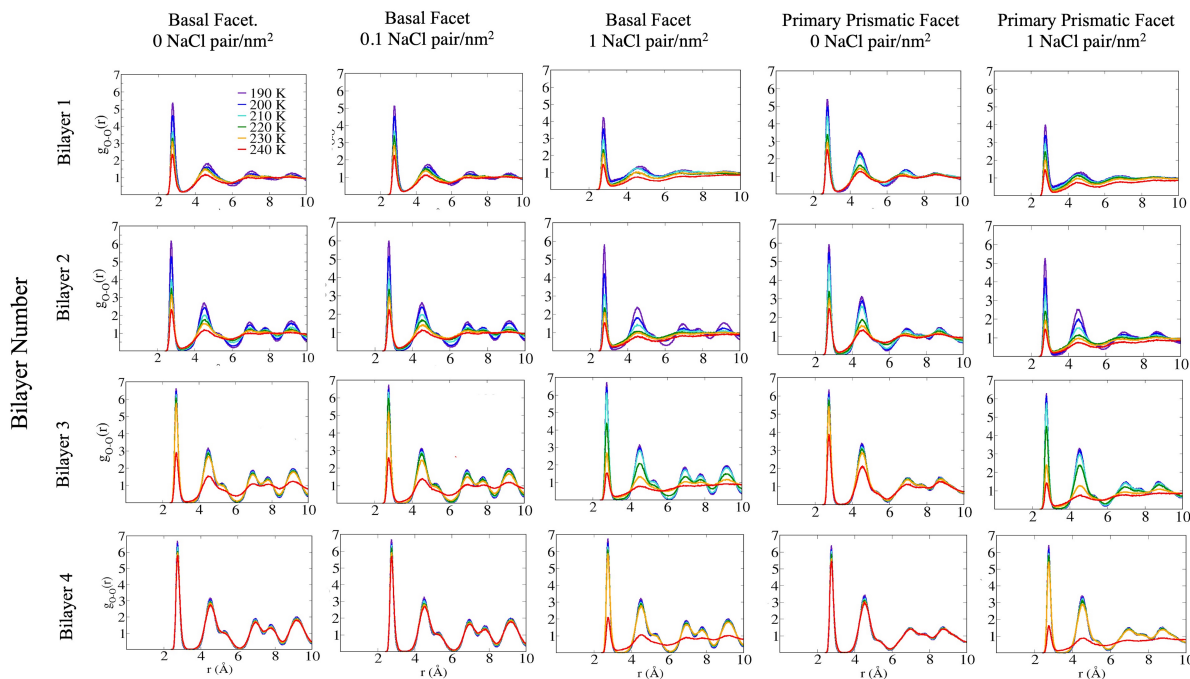

Figure S7: Oxygen-oxygen radial distribution functions of the first, second, and fourth bilayers as a function of temperature for the each ice facet orientation with NaCl surface densities of 0, 0.1, and 1 NaCl pair/nm^2, averaged over 200 ns production runs
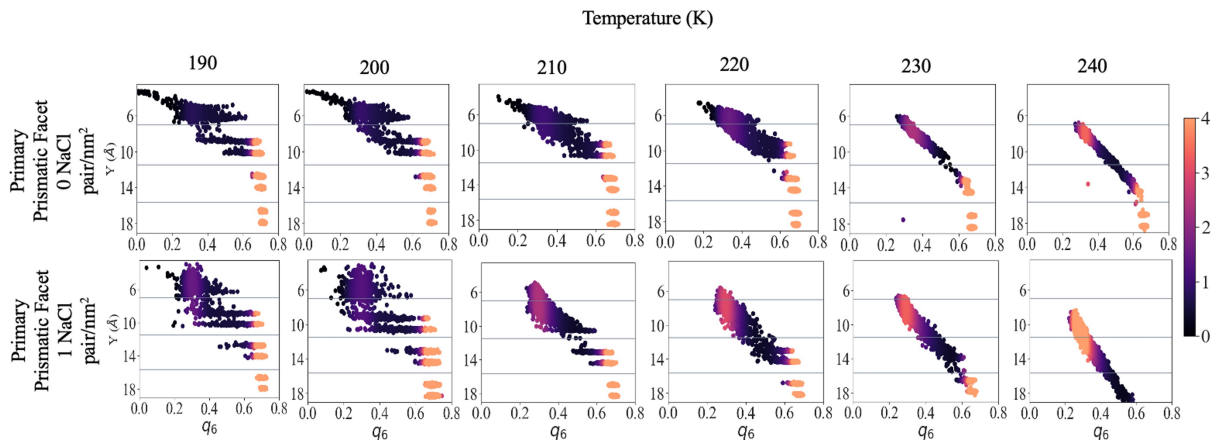
Figure S8: Local Steinhardt q_6 order parameter density map of the first four bilayers as a function of temperature, for the primary prismatic facet for both sampled surface densities, averaged over 200 ns production runs.
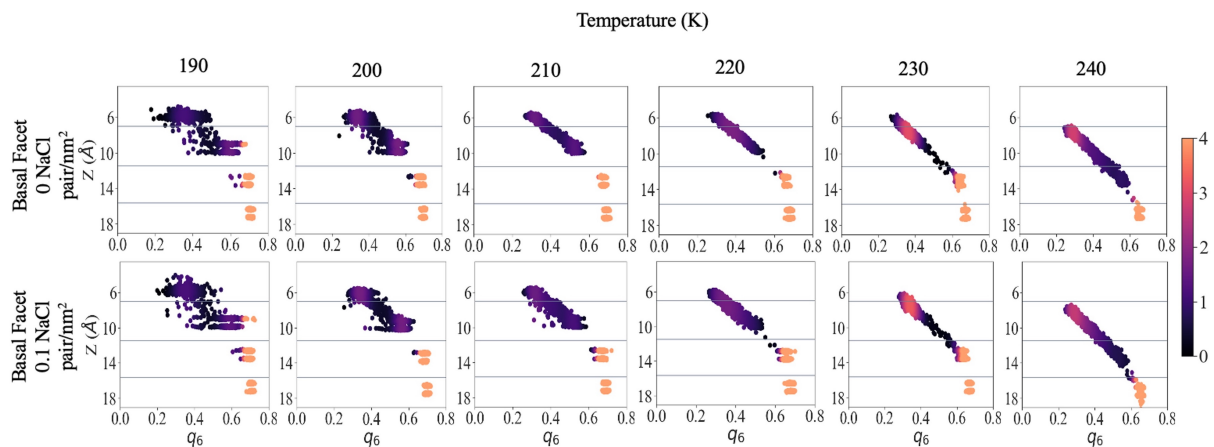

Figure S9: Local Steinhardt q_6 order parameter density map of the first four bilayers as a function of temperature for the basal facet with a NaCl surface density at each surface for pristine ice and the low surface density of NaCl sampled, averaged over 200 ns production runs.
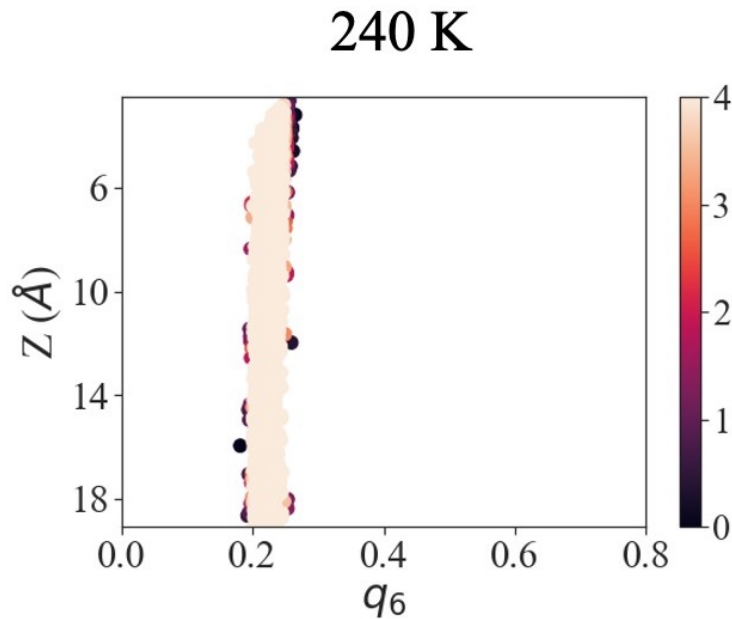
240 K

Figure S10: Local Steinhardt q_6 order parameter density map of supercooled water simulation. A slab of 6144 liquid water molecules with no NaCl present was used to run a NVT simulation utilizing all the same simulation parameters as stated in the main text, at 240 K. The supercooled water slab was allowed to equilibrate for 10 ns and a production run of 10 ns was obtained. Order parameter values are averaged over 10 ns. This indicates that supercooled water tends towards a q_6 value of 2.2.
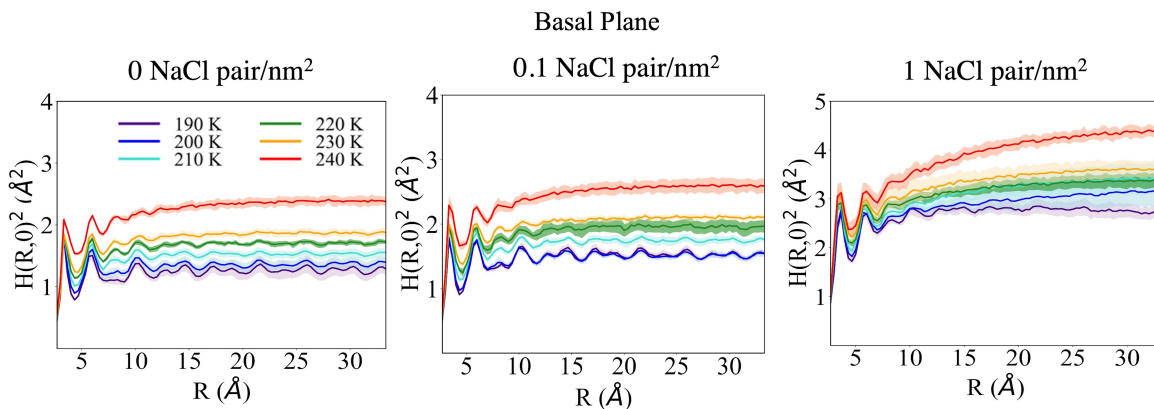

Basal Plane

Figure S11: The structure function of the oxygen atoms as a function of temperature at the surface of the basal facet for each sampled NaCl surface density. The structure function was calculated over the 200 ns production run, using a block averaging over 8 blocks of 25 ns each. The shaded regions corresponds to the standard deviation in the structure function.