

Stabilization and Growth of Polar Ionic Crystal Surfaces

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Abstract

Stabilization of (111) polar surface of NaCl crystal by the deposition of a non-stoichiometric nucleus of Na and Cl atoms has been studied. Monte Carlo simulations were carried out to study the interaction between the nucleus and the surface and the potential of mean force (PMF) was calculated to estimate the equilibrium position of the nucleus above the surface. Umbrella sampling and Ferrenberg-Swendsen histogram reweighting technique was applied to calculate the free energies in the system.

1 Background

Polar surfaces of ionic crystals are known to be unstable due to the presence of an intrinsic electric field perpendicular to the surface. However, polar surfaces do exist in nature and have important applications in the fields of catalysis and photovoltaics. The reduction of surface charge density has been proposed as a mechanism to stabilize the polar ionic surfaces (Tasker, 1979). Under conditions of growth, this would be achieved by the deposition of non-stoichiometric arrangements of ions that would reduce the ratio of positive to negative surface ions and stabilize the electrostatic dipole moment perpendicular to the surface. This mechanism has been studied here for the case of (111) surface of NaCl crystal. The (111) surface of NaCl consists of alternate layers of Na^+ and Cl^- ions. Given the hexagonal planar symmetry of the (111) NaCl surface, a non-stoichiometric nucleus of ions will be triangular-shaped and will consist of Cl ions on the edges of the triangle.

2 Simulation Methods

The polar surface was modeled by a Na-Cl bilayer with the top layer consisting of only Na atoms while the bottom layer has only Cl atoms. The surface atoms interact with each other by a combined Lennard-Jones and coulombic interaction potential as shown in Eqn 1.

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (1)$$

The parameters for Na-Cl system were taken from Smith and Dang (1994) and have been listed in Table 1. Lorentz-Berthelot mixing rules were applied to calculate the σ_{ij} and ϵ_{ij} values for the unspecified pairs of ions.

The surface bilayer consists of 169 Na and 169 Cl atoms. The nucleus has 3 Cl atoms in each of the triangular edges which implies that there are 6 Cl and 3 Na atoms in the nucleus. In order to ensure that the atoms in the nucleus would stay together, a harmonic potential given by Eqn 2 was also applied between the nearest neighbor Na-Cl pairs within the nucleus. This potential was in addition to the potential given in Eqn 1.

$$U_{ij} = \frac{k}{2} (r_{ij} - r_0)^2 \quad (2)$$

Table 1: Force Field parameters for Na^+ and Cl^- (Smith and Dang, 1994).

Atom	q_i	σ_i (nm)	ε_i/k_B (K)
Na^+	1.0	0.235	65.42
Cl^-	-1.0	0.440	50.32

The value of k was taken as $25.0 \text{ eV} / (\text{\AA})^2$ while r_0 was assumed to be 2.82 \AA which is the Na-Cl distance in bulk NaCl lattice. The system was simulated in an NVT ensemble at $T = 300 \text{ K}$. The cut-off distance was set as 25.0 \AA which is just appropriate for the size of the two dimensional surface ($L = 51.8 \text{ \AA}$). A relatively large cut-off radius ($\sim 10\sigma$) was applied since there are strong electrostatic interactions present in the system and Ewald summation technique was not used. Periodic boundaries for the hexagonal unit cell of the surface were assumed, therefore the periodic boundary conditions were appropriately modified for hexagonal symmetry.

3 Results and Interpretation

At first, the surface bilayer alone was simulated for 1 million Monte Carlo (MC) displacement moves (~ 2958 MC sweeps) to equilibrate it without the nucleus. The ions in the bilayer were constrained in the z direction and were displaced only in the plane of the surface. Figure 1 shows the radial distribution function of the bilayer. The Na-Na and Cl-Cl radial distribution functions are symmetric and the maximum in the Na-Cl function was calculated to be close to the bulk distance of 2.82 \AA which implies that the equilibrated surface bilayer structure is close to the ideal (111) NaCl surface. The nucleus was

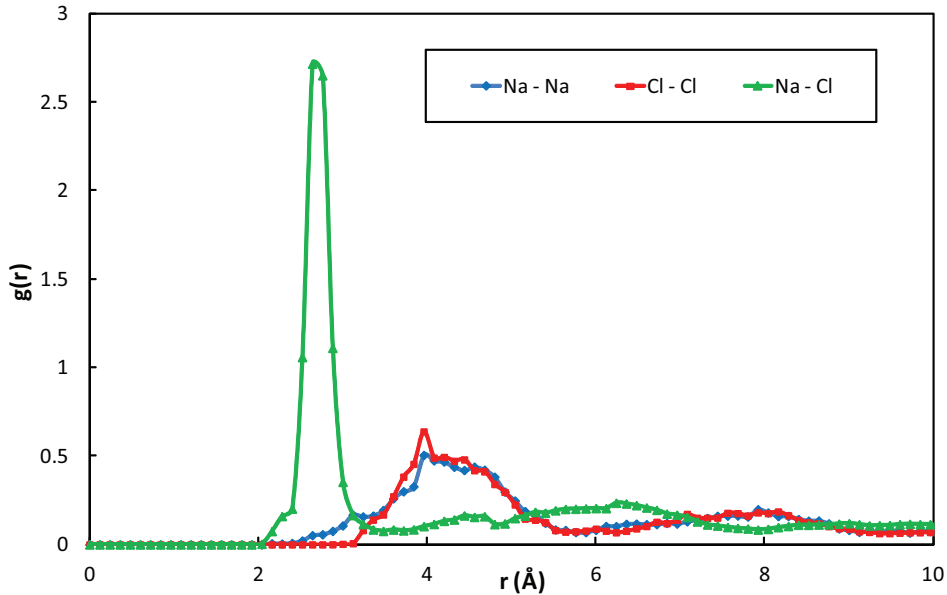


Figure 1: Radial distribution function of the Na-Cl bilayer.

now inserted into the simulation box and the system was then allowed to equilibrate for another 5 million MC moves (~ 14500 MC sweeps). The large number of MC moves required for attaining equilibrium can be attributed to the electrostatic interactions that have a slow rate of convergence. The production runs were carried out for another 14500 MC sweeps. The reaction coordinate was identified as the

height of the centroid of the nucleus above the surface. Histograms of configurations were calculated by constructing bins along this reaction coordinate. 200 evenly spaced bins of bin width 0.02 \AA were used to calculate the counts.

Irrespective of the initial position of the nucleus, the equilibrium position was always very close to the surface. As a result, it became impossible to sample the configurations where the nucleus was away from the surface. Therefore, Umbrella sampling method (Torrie and Valleau, 1977) was used to improve the sampling along the reaction coordinate (distance from the surface along z direction) by biasing the potential energy function. The biasing function used was as shown in Eqn 3. The parameter value of k_U was chosen to be $1.8 \text{ eV} / (\text{\AA})^2$ that ensured that the histograms had sufficient overlap.

$$\eta_j(z) = -\beta \frac{k_U}{2} (z - z_j)^2 \quad (3)$$

An iterative algorithm was developed to calculate the value of PMF $F(z)$ by iterating over the Helmholtz free energies A_j . Figure 2 shows the histograms with 12 different values of z_j . The biased potential is appropriate since adequate overlap between the histograms was obtained. Figure 3 shows the potential of mean force $F(z)$ as a function of the reaction coordinate. We can see that the equilibrium position of the nucleus is around 2.4 \AA which is much larger than the layer spacing of 1.63 \AA for the (111) plane in bulk NaCl. However, we expect the spacing between adjacent layers to be much different than in the bulk since all the interactions in the bulk are not present on the surface. The free energy change of binding of this nucleus is $\sim 2.5 k_B T$. There is also an activation barrier to attachment of the nucleus with a height of $\sim 3.5 k_B T$.

The PMF calculations show that there is a lowering of free energy due to the binding of a non-stoichiometric nucleus to the polar surface modeled here by a Na-Cl bilayer. Thus, a non-stoichiometric surface will be favored over a perfectly flat polar surface which is in agreement with the theory. Also, an activation barrier was also found which could be because of the electrostatic repulsion between the Cl^- ions in the nucleus and in the bilayer. This is also highlighted in the simulation movie where initially the entire nucleus doesn't attach completely and there is at least one Cl^- ion sticking out of the nucleus. It is only after crossing that activation barrier that the entire nucleus is able to attach to the surface.

This simulation can be improved by including more Na-Cl bilayers to better model the polar surface. That should smoothen out the kinks in the PMF values for large z . Also, the variation of the binding energy and the activation barrier with the size and the edge termination (Na-terminated edges) of the nucleus should also be studied to gain further insights into the stabilization mechanism of polar ionic surfaces.

Movie Caption - The movie shows the interactions of a non-stoichiometric nucleus containing more Cl (red) than Na(blue) atoms with the polar surface bilayer with Na (violet) and Cl (green) layers. As the nucleus get closer to the surface and its atoms attach in the appropriate lattice positions above the surface, their color is changed to the original element colors (violet and green). Note that when the nucleus attaches, the Cl atoms lie closer to the surface than the Na atoms due to electrostatic repulsion from the Na atoms in the top surface layer.

4 References

1. Smith, D.E. and Dang, L.X. (1994) Computer simulations of NaCl association in polarizable water, *J. Chem. Phys.* **100**, 3757.
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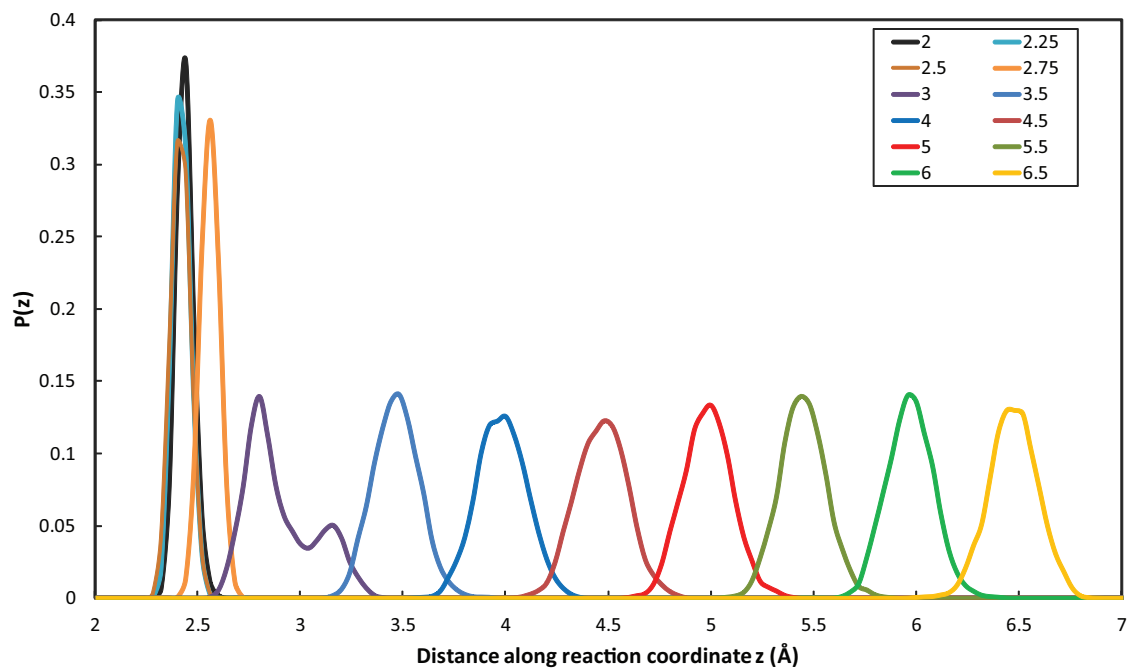


Figure 2: Histograms for the weighted probability $P(z)$ along the reaction coordinate z .

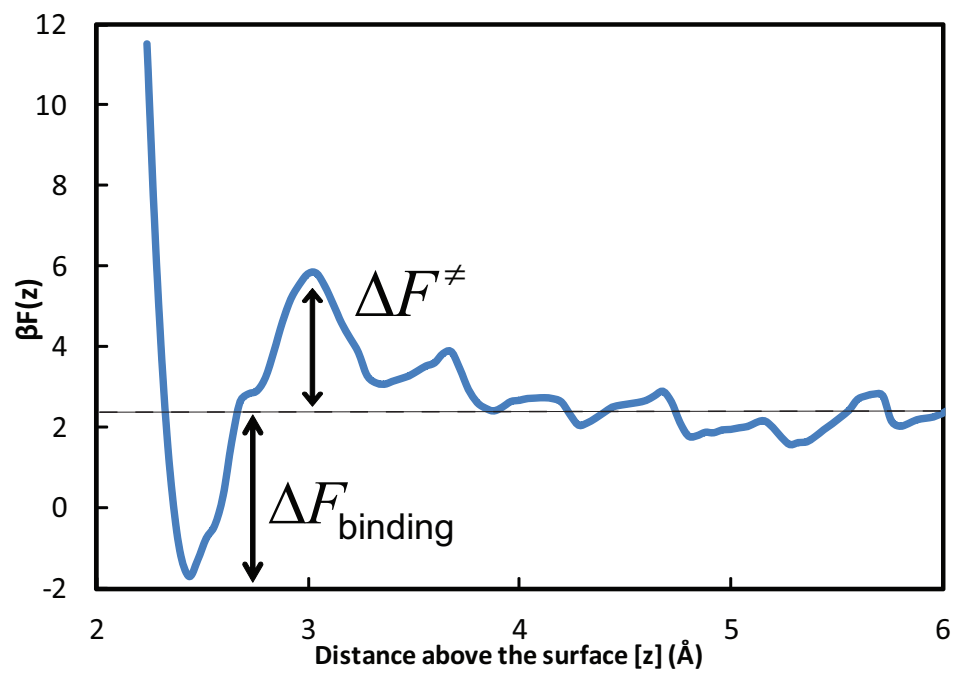


Figure 3: Potential of Mean Force $\beta F(z)$ along the reaction coordinate z .