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Computational Nanoscience (COMP)

AIMD study of liquid water on NaCl(100) surface

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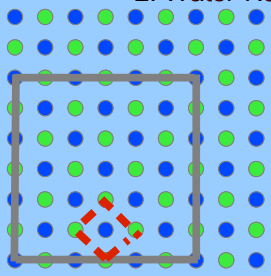
1. Abstract

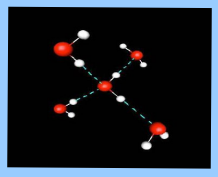
By employing ab initio molecular dynamics (AIMD),we have obtained liquid water density distributions on NaCl(100) surface. To understand the dissolving process of NaCl into water, we have calculated the dissolving barriers of Cl- and Na+ ions on NaCl(100) surface models using constraint method.

After the barrier search of Cl- and Na+ ions departure from the NaCl(100) surface, the system is scaled up to a "real" situation "a grain of salt" which contains 2 000 --1 000 000 atoms by employing the kinetic Monte Carlo (kMD) method.

2. Water-NaCl(100) interface models



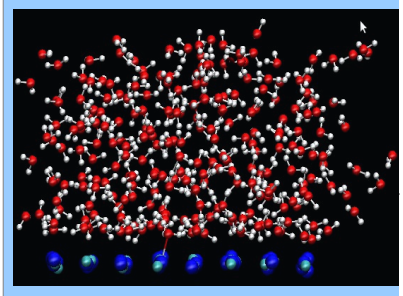
Unitcell: (√2x√2) or c(2x2) R45°
Supercell: (3x3)
Supercell: (4x4)

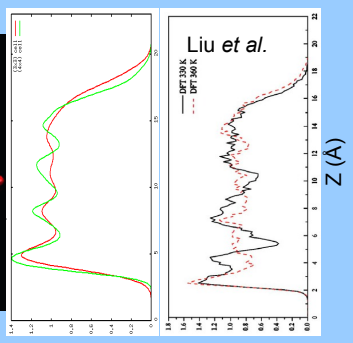


Unsolved liquid water structure

Lliquid water has an instantaneous tetrahedtron structure, one water molecule connects with four other water moleculesby H-bonds. The tetrahedron distorts, breaks and reforms on a time scale of 500 fs. O--O peak distance is 2.85 Å by X-ray diffraction experiments.

3. Density distribution



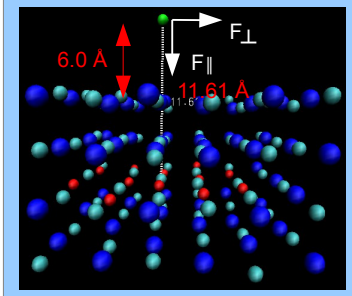


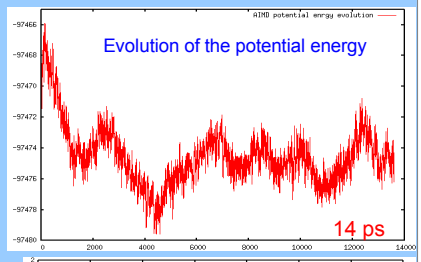
$$\rho(z) = \sum_{i=1}^{m} \frac{M_{H_2O}}{2\sigma N_A a^2 \sqrt{2\pi}} e^{-\frac{(z-z_i)^2}{\sigma}}$$

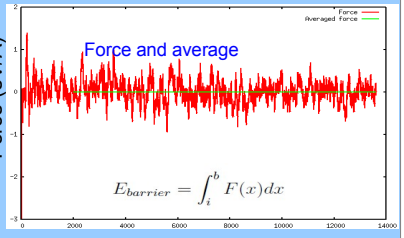
Water density (g/cm³)

***M*: water mass, N_A: Avogadro constant, n: number of water molecules and *σ*: width of Gaussian expansion. The first layer is important to simulate the barriers of dissolving Cl^- and Na^+ ions.**

4. Constraint method for barrier search





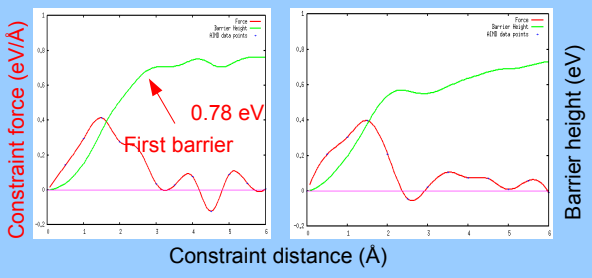


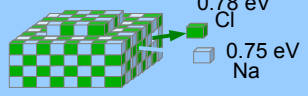
Step 1: Set target distance w.r.t. collective coordinates defined by 12 Na atoms in the slab.

Step 2: Calculate the constraint artificial force acting on the target Cl atom by average.

Step 3: Integrate the force according to a series of target distances.

5. Dissolve Cl^- and Na+ ions on NaCl(100) surface





Na^- and Cl^- ion experiences the largest force before it enters the first water layer. Force becomes zero when ions enter the liquid water. The barrier for Na^+ ion is earlier than Cl- ion, because one H_2O molecule also occupies the Na vacancy but with H atom down

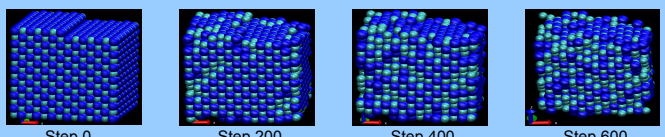
	Surface type	Barrier (eV)	Freq (cm^{-1})	Rate const. (s^{-1})	Initial weight
1	Flat Cl^-	0.87	141.94	2.17 x 10	1.06 x 10^{-9}
2	Flat Na^+	0.75	146.94	6.12 x 10	2.98 x 10^{-9}
3	Vacancy Cl^-	0.26	150.93	7.79 x 10^{8}	0
4	Vacancy Na^+	0.10	174.64	1.86 x 10^{11}	0
5	Step Cl^-	0.25	150.93	1.08 x 10^{9}	8.83 x 10^{-3}
6	Step Na^+	0.13	174.64	6.87 x 10^{10}	0.55
	Step 2nd Na+	0.19	With a neighbor Na+ vacancy		
7	Step Cl-	0.17	With two neighbor Na+ vacancies		
	Step Cl-	0.16	With three neighbor Na+ vacancies		
8	Corner Cl^- (3x3)	0.17	140.15	1.45 x 10^{10}	6.56 x 10^{-3}
9	Corner Na^+ (3x3)	0.05	166.78	9.44 x 10^{11}	0.42
	Corner Cl- (4x4)	0.11	(4x4) cell with one-layer (2x2) island		
	Corner Na+ (4x4)	0.12	(4x4) cell with one-layer (2x2) island		
10	Corner Cl-	0.30	(4x4) cell with two-layer (2x2) island		
	Corner Na+	0.21	(4x4) cell with two-layer (2x2) island		

6. kMD study of NaCl dissolving

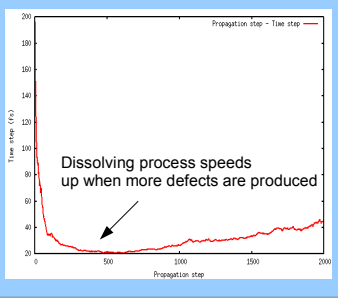
The dissolving nano meter size NaCl crystal is described by the master equation

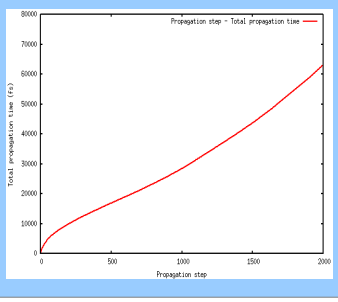
$$\frac{dP(r,t)}{dt} = -\sum_{r'} \pi(r,r')P(r,t) + \sum_{r'} \pi(r',r)P(r',t)$$

***P(r, t)*: probability of a state at time *t*, *π(r, r')*: transition probability from state *r* to state *r'* at a unit time.**



Step 0 Δt = 202 fs | Step 200 Δt = 26 fs | Step 400 Δt = 22 fs | Step 600 Δt = 20 fs





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