Ab initio molecular dynamics study of liquid water on NaCl(100) surface

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By employing *ab initio* molecular dynamics (AIMD), we have simulated the liquid water-solid surface interaction of 256 water water on a (4×4) NaCl(100) unit cell, equilibriumed at a time scale of 50,000 fs. In this system, our AIMD results show that these water molecules occupy approximately in four layers. The liquid water density distribution has a maximum peak of 1.40 g/cm^3 in the first layer 2.8 Å above the NaCl surface. The water density decreases to 1.10 g/cm^3 in the fourth layer. The first layer water is about 1 ML on NaCl(100) surface, in which the oxygen atoms mainly occupy Na sites statistically. The liquid water structure appears when water is further away from the NaCl(100) surface by about 7.0 Å from oxygen-oxygen radial distribution function. To understand the dissolving process of NaCl into liquid water, we have calculated the dissolve barriers of Cl^- and Na^+ ions from flat, vacancies,stepped and the corner of the island on the NaCl(100) surfaces using constraint method.

The barrier heights for producing Cl- or Na^+ ions on flat NaCl(100) surface are 0.78 eV and 0.75 eV, respectively. The dissolve barriers for Cl^- and Na^+ ions on stepped surface are 0.19 eV and 0.13 eV respectively. The barriers for producing Cl^- or Na^+ ions from the corners of island on NaCl(100) surface are 0.12 eV and 0.11 eV, respectively. These results indicate that the dissolving process of NaCl crystal starts from the corners of an island or a step surface. Thus, departure of the Na^+ ion has slightly lower barriers than dissolving Cl^- ion at the initial stage. However when more Na^+ ions are dissolved, the Na^+ and Cl^- ions have approximately the same barrier height as tested on the stepped surface.