

Role of ions in solid-liquid interfaces investigated by molecular simulations

Lidija Zivanovic¹, Peter Spijker¹, Kei Kobayashi², and Adam S. Foster^{1,3}

¹ COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland

² Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan

³ Division of Electrical Engineering and Computer Science, Kanazawa University, Kanazawa 920-1192, Japan

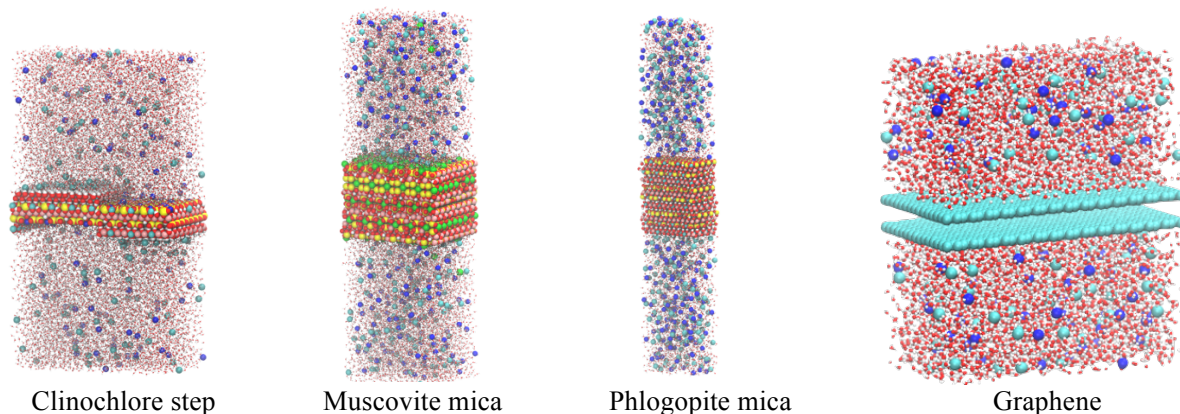
Natural occurring materials composed primarily of fine-grained minerals are commonly referred to as clay minerals, of which sheet silicates (phyllosilicates) are important to industry. Examples include aluminum silicate minerals such as kaolinite, pyrophyllite and muscovite, as well as the corresponding magnesium silicate minerals, antigorite, talc and phlogopite. In their natural environment, these clay minerals are exposed to electrolyte solutions, and typically an electrical double layer (EDL) forms near the solid-liquid interface. This distribution of charge in the solid-liquid interfaces plays an essential role in a wide range of processes in biology, geology and technology. Ions are also expected to play a role in high-resolution atomic force microscopy (AFM) imaging in liquids, although the mechanism remains unclear. Standard theories describing the EDL, such as DLVO theory, break down near the interface where the molecular size plays a role. Instead, molecular simulations are a prime technique to investigate the influence of ions on solid-liquid interfaces at this molecular level.

To investigate the influence of ions on the different types of solid-liquid interfaces, we used MD simulations to study clinocllore and muscovite mica, and, as control systems, calcite and graphene, in the presence of high ion (NaCl) concentrations ($>1\text{M}$). On charged surfaces, solvated ions tend to accumulate close to the surfaces creating a clear EDL, reflecting the surface charge distribution in which ions are binding to specific surface sites. Furthermore, ions not only affect the water ordering within the first hydration layer but they are also increasing water ordering up to third and fourth hydration layers as ion concentration is increased.

In order to investigate this, we compared our results to recent AFM measurements on clinocllore, where ordered patterns on different terraces were found, but no regular patterns were seen at the step edge region. Our simulations of different clay steps show that ions tend to avoid the step region, leaving the interfacial water structure near the step edge strongly ordered [1]. On the other hand, away from the step regions the ions interact with the hydration layers. It is likely that the formation of the EDL and the increased water ordering could be the reason for the increased contrast in AFM observation.

On the other side, it is also important to investigate effects of ions on the mobility of hydration layers. By calculating diffusion coefficient for each hydration layer on different type of surfaces, one can link mobility of hydration layers with nature of surface-water interactions.

To explore this further, we calculated diffusivity of hydration layers on muscovite mica and graphene surfaces. As expected, layers created above graphene surface are more mobile then layers created on muscovite mica surface, assuming repulsive nature of interactions between water and graphene and attractive one with muscovite mica surface. Increased ion concentration has also affect on the mobility of each hydration layer.



Reference:

[1] K.Umeda, L.Zivanovic, P.Spijker, K. Kobayashi, A S.Foster, and H. Yamada, *submitted* (2016)