The effect of imposed homogeneity on inhomogeneous surfaces

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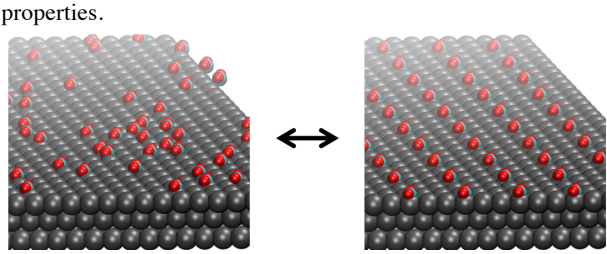
All geological materials that are exposed to air or aqueous solutions have adsorbed organic compounds, whether the surface is in nature or in the laboratory, and this contamination influences surface behaviour. The organic material is inhomogeneous in extent, degree of coverage and composition, which makes surface behaviour complex and difficult to understand at the nanometre to atomic scale. Therefore, we usually make simplified model systems so we can study the effect of various parameters on the physical and chemical properties.



Surfaces with a random and homogeneous distribution of ionizable sites behave differently, even for identical surface charge densities.

To be computationally viable, modelling has dimension limits but by using a periodic cell with a single ionizable group and periodic boundaries one can extend the dimension to infinity. This, however, forces the surface charge to be homogeneously distributed and imposes constraints on the surface charge density, which must be comensurate with the single cluster dimension. These constraints violate the natural system and introduce an artefact in the model. We used a recently developed technique on a 15×15 nm^2 surface to see how homogenization of ionisable groups affects its properties, i.e. 1) how clustering vs. homogeneously dispersed functional groups affect surface charge density at various pH and ionic strength values and 2) how the in plane interactions between surface ionizable groups interact compared to standard, simplified Coulomb interactions.

The homogenization works well when the surface charge density is low and the ionizable sites are randomly distributed, whereas the homogenized surface charge density deviates significantly when surface sites are clustered or when the surface charge density is large. This suggests that models using a homogeneous surface charge density give an idealized and sometimes over simplified view on surfaces.