An efficient technique for calculating solvation effects on surface structures and energetics

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Wolfgang Pauli famously wrote "God made solids … but surfaces were the work of the Devil". This quote reflects the immense difficulties faced by experimentalists when characterising surfaces. As a result, computer simulations have been at the forefront of surface research. A major triumph was the prediction of extensive surface relaxation on the basal plane of alumina firstly by interatomic potential based calculations and then by quantum mechanical simulations. These predictions were confirmed by experiment very much later. Similar success was obtained for MgO. These simulations were on surfaces *in vacuo* but most surfaces encountered by chemists and mineralogists are formed in the presence of a solvent. Although molecular dynamics simulations can account for the presence of solvent, they are computationally very expensive.

In calculations on molecules, implicit solvation models such as COSMO (the COnductor-like Screening MOdel of Klamt and Schüürmann [1]) have been used extensively. The basis of the COSMO method is that the solvent is assumed to behave as a perfect conductor situated around a solvent accessible surface. The charges induced on the surface due to the electrostatic potential of the enclosed species are then determined, and subsequently scaled to those appropriate to the dielectric constant of the solvent.

We have extended the COSMO scheme to periodic systems. Although for the purposes of a surface calculation only 2-D boundary conditions are required, we have implemented the method (called COSMIC) for 1-, 2- & 3-D periodicity. As well as adapting the scheme for periodic boundary conditions, it was also found beneficial to make several other modifications to the original COSMO algorithm. In this paper will will discuss the algorithm developed and show its utilisation in modelling the surfaces of minerals.

[1] Klamt A. and Schüürmann G. (1993) *J. Chem. Soc., Perkin Trans.,* 799-805.