ATOMISTIC SIMULATION OF MINERAL INTERFACES. S.C. Parker[1], D.J. Cooke and N.H. de Leeuw, Department Of Chemistry, University of Bath, Bath BA2 7AY, U.K. [1]s.c.parker@bath.ac.uk

Introduction: Atomistic simulation techniques represent a powerful complementary tool for studying mineral surfaces. The aim of this presentation is to describe the recent progress in modeling the structure of oxide and mineral surfaces and in particular to review our attempts at studying competitive adsorption at mineral surfaces in contact with water. The basis of these techniques is to use the Born Model of Solids where simple parameterized analytical equations are employed to describe the interactions between atoms. However, increasingly electronic structure calculations are employed to assess and aid in the development of reliable descriptions for the interatomic potential. Once these interatomic forces are specified energy minimization and molecular dynamics techniques can be applied to model mineral surfaces. Energy minimization allows us to evaluate the surface structure and surface energy by adjusting the atom positions until a minimum configuration is obtained. Molecular dynamics gives the effect of temperature by assigning kinetic energy to the atoms in the simulation cell and thus allows us to follow the trajectory of the atoms and molecules with time.

Surface Vibrations: In addition, to probing the surface structure, we are using these simulation techniques to study the vibrational properties. Thus we calculate the phonon density of states from which we can obtain the size of the contribution of the zero point energy and vibrational entropy to the free energy of both point defects and interfaces. For example, work on the surfaces hematite revealed that the zero point energy contribution is a significant component of the surface free energy. For example, the potential energy component of the surface free-energy of the (0001) surface of hematite is 2.5 Jm^{-2}, whereas the surface free-energy is calculated to be 3.1 Jm^{-2}. Surprisingly, 94% of the difference between the surface energy and surface free-energy is not due to the vibrational entropy but to the zero point energy.

Competitive Adsorption: we modeled the competition between protons and surface cations for a number of minerals. The energies of replacing the surface cations by protons were all found to be exothermic and that the magnitude of this replacement energy is highly dependent on cation coordination. For example, with the simple oxides we find that very approximately the energy to replace a five coordinated cation is 50 kJ/mol of protons, four coordinated is 100 and three coordinated 150 kJ/mol. However, this is not the complete picture as the energies do depend on the type of cation replaced, as Mg and Fe are slightly less and Ca more than the crude energies just quoted. Furthermore, there is also a dependence on the details of the surface, which is dramatically exemplified by the non-dipolar forsterite {010} surface, where the Mg ions are in three-fold coordination but are comparatively stable. In the final example we consider the competition between cations at a growing surface and illustrate by considering the growth of calcite steps that the presence of other cations such as magnesium can inhibit the growth of the step. As is observed experimentally.

In summary, atomistic simulation techniques provide a useful complementary tool for modelling mineral interfaces and as the models describing the interactions between surfaces and molecules become more reliable they can be applied to more complex problems.