2.1.33

Grand-Canonical simulations for the growth and the stability of nanostructures

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We consider the formation of nanostructures on surfaces by deposition from a solution. Usually such processes occur at a constant chemical or electrochemical potential. Therefore, it is convenient to use a grand-canonical ensemble for their simulation, in which the particle number is variable and the chemical potential is kept constant.

For the investigation of nanostructure formation we have devised a molecular-dynamics simulation method in which the following particles are considered explicitly: several top layers of the surface, the nanoparticle ensemble, and the particles in the solution that are to be deposited. The solvent molecules are not treated explicitly; however, they affect the motion of the solutes by providing a Langevin force, so that the solute undergoes Brownian dynamics Typical ensemble sizes are of the order of 5000 – 10000 particles. Conceptually, the system consists of two parts:

(1) A bath of particles (the solution) that move stochastically in a constant background potential; the density of particles in this bath is kept constant.

(2) The solid part of the system which follows standard microcanonical molecular dynamics. The interactions between these particles are calculated from a semi-empirical potential.

The two subsystems are in contact and exchange particles. The (electro-)chemical potential in the bath can be varied by adjusting the particle density and the background potential.

We have used this method to investigate the deposition of metal structures on metal surfaces. For this purpose the interactions between the metal particles have been calculated from the embedded atom method. In this way, it is possible to determine the critical cluster size as a function of the chemical potential, to study the growth mechanism and the rate of particle deposition. Another application is the simulation of the growth of a nanowire that is formed with the aid of a scanning tunneling microscope.

Grand-canonical Monte-Carlo simulations give fewer details than grand-canonical molecular dynamics, but are usually faster. We have used this method to determine the stability of metal clusters of various compositions.

2.1.41

Non-stoichiometric surfaces of minerals: *Ab initio* phase diagrams

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Traditional theoretical techniques for surface energy calculations usually are limited to considering stoichiometric surfaces. But there is no requirement that stoichiometric terminations are inherently more stable than their non stoichiometric counterparts, especially if in contact with a realistic environment.

We present an *ab initio* methodology to model non-stoichiometric surfaces of oxide minerals in equilibrium with a mixed vapour of oxygen, hydrogen or water. The stability of surfaces of different stoichiometry are compared in terms of general surface phase diagrams, function of the oxygen and hydrogen chemical potentials, which are dependent on temperature and partial pressures of oxygen and hydrogen. Thus, the stable structures and compositions can be evaluated at specific experimental conditions.

We apply this methodology to the low index surfaces of α-alumina, namely the (00.1), (01.2), (11.3), (11.0), (10.0), (10.1) and (22.3). surfaces We also compare the relative stoichiometric surface stability by generating a Wulff construction. The predicted morphologies compare very well with recent high temperature pore optical microscopy measurements, with the exception of the (10.1) surface.

We show that under ambient conditions there are only two types of surfaces that are thermodynamically stable: either fully stoichiometric (low partial pressures, high temperature) or fully hydroxylated (high pressures, low temperature).

Comparing our results with two recent experimental studies, we first suggest that the observed lack of reactivity of the (11.0) surfaces with hydrogen is due to the fact that the surface is already hydrogen terminated. We also confirm that of the two proposed structure for the (01.2) surface (stoichiometric relaxed bulk termination and Al poor) it is indeed the Al poor structure which is the most stable and also that it is hydroxylated (while the experiment could not identify the presence of hydrogen atoms).

We will also discuss preliminary results concerning the surface thermodynamics of other minerla, namely ZnO and $CaCO_3$.