

Predicting Crystal Morphologies With *Crysalis* and *MetaMorph*

Many industrial problems in chemistry and chemical engineering demand an understanding of particle flow and aggregation, for which a knowledge of the crystal morphology and crystal growth is important. The shape of crystals can have significant implications for their packing and flow behaviour.

For ionic crystals, applications include such diverse areas as ceramics, scale development (for example, in oil pipelines), and sintering. Even properties like conductivity are important, since in a macroscopic system these are influenced by the intergrain contacts, and so by particle shape.

Crystal growth is affected by a variety of factors, including the presence of solvent, of impurities, and of habit modifiers which adsorb preferentially at certain surfaces. In relatively pure materials, it is often the surface energies of the different crystal faces which have a dominant effect.

A new approach - *Crysalis* with *MetaMorph*
Surface energy and crystal growth are areas which are ideally suited to a computational approach.

Crysalis takes crystal data available from databases and allows you to generate bulk and surface crystal structures on your Silicon Graphics workstation. Surface energies are calculated simply by determining the energy needed to create a new surface from the bulk.

The simulation engine in ***Crysalis*** consists of a static lattice code, which quickly calculates defect energies and lattice relaxations around defects. Visualization

and manipulation of the resulting structure can be carried out within ***Crysalis*** in a variety of display styles.

Static lattice simulations have been tested both in academe and industry over the past few years, and have a well-established track record of producing useful results with minimal computational time. They use 2-body and higher potentials to describe the interactions between the ions; ***Crysalis*** is supplied with a standard database of potentials which have been tested and validated in the published literature.

MetaMorph can use the Donnay Harker method to predict morphologies from d-spacings or Wulff's Theorem to predict crystal morphologies using surface energies calculated with ***Crysalis***.

THE RESULT? Improved understanding of hard-to-measure surface energies and how they affect crystal morphology.

Example: Crystal Morphologies in Corundum and Haematite

The shape in which a crystal grows depends on the relative growth velocities of the various faces, which determine the relative centre-to-face distances. Wulff's theorem has often been used to relate the surface energies to the centre-to-face distances and therefore to the morphology.

Surface	Unrelaxed energy	Relaxed energy
(111)	5.95	2.03
(-211)	6.46	2.23
(011)	3.63	2.29
(01-1)	4.37	2.50
(100)	5.58	2.52

Table 1. Low-index surfaces of Al_2O_3

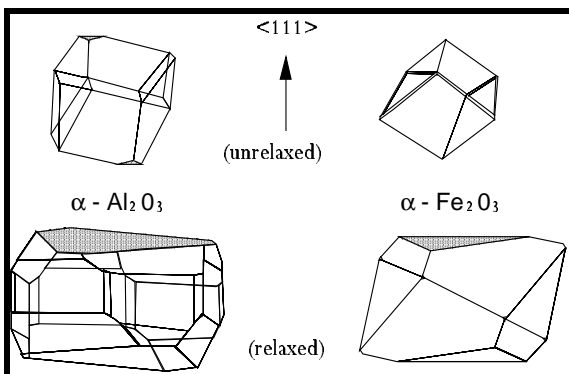
Determining the relative growth velocities or surface energies therefore becomes very important in determining crystal morphology.

Theories advanced by Donnay and Harker suggest that the predominance of a crystal face described by Miller indices (hkl) is inversely proportional to the spacing, d_{hkl} , between the surface planes, using crystallographic information for the perfect crystal.

Alternatively, surface energies can be estimated (usually assuming a bulk termination for the crystal) and used in predicting the equilibrium crystal morphology. Various ways of getting surface energies have been described in the literature, including the static lattice methods which underlie **Crysalis**.

Neglecting the important role of surface relaxation can have marked consequences. Both corundum (α -Al₂O₃) and haematite (α -Fe₂O₃) have similar hexagonal structures, and simple arguments based on d-spacings would suggest that they have very similar morphologies. However, experimentally, it is known that they do not.

Mackrodt, Davey, Black and Docherty from ICI's New Science Group investigated this using static lattice calculations like those used in **Crysalis**, and have shown conclusively the role of surface relaxation in determining the crystal morphology (*J Crystal Growth*, **80** 441, 1987).



Their calculated surface energies are given in Tables 1 and 2 for corundum and haematite respectively. Energies are given in J m⁻². The effect of lattice relaxation is clear from the numbers. These surface energies can be used in **MetaMorph** in order to generate crystal morphologies.

Mackrodt and coworkers reached four main conclusions:

- > in all cases, the surface energy for relaxed surfaces is lower than that for the unrelaxed (bulk termination) case
- > the degree of relaxation varies from surface to surface
- > relaxation gives changes in *relative* surface stability - an important result for morphology prediction
- > relaxation reduces the energy differences between different surfaces.

Surface	Unrelaxed energy	Relaxed energy
(011)	2.88	1.47
(111)	5.26	1.53
(01-1)	3.79	2.03
(-211)	5.34	2.36
(100)	4.79	2.41

Table 2. Low-index surfaces of Fe₂O₃

Using their relaxed surface energies, Mackrodt and coworkers were able to predict crystal morphologies for the two materials which are seen to be in good agreement with experiment - without the need to invoke impurity ions or solvent effects to account for the geometry, as had been required in earlier studies where the effect of lattice relaxation was neglected. For both materials, the correct morphology can be predicted on *structural* grounds alone.

Of course, the effect of having dopants to lower surface energy could also be calculated with **Crysalis**, so that their effect on crystal growth can be understood.

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