

MedeA Morphology: From Atomic Arrangement to Crystal Shape

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1 Overview

The macroscopic shapes or morphologies of crystals and crystallites are governed by interatomic interactions. When crystals are grown under equilibrium conditions the crystal shape adopted by the crystal minimizes the total surface free energy of the crystal. The *MedeA Morphology* module employs the lattice parameters and space group symmetry of a given crystal and information about the relative energies of low index crystal faces to simulate the morphology of crystals. *MedeA Morphology* can be used to predict the morphology of crystals based on computed surface energies and to determine the atomistic consequences of experimentally observed morphologies.

The morphologies of crystals and crystallites are readily observed macroscopically. *MedeA Morphology* allows crystal morphology information to provide insights into the atomic details of materials.

For example, scanning electron microscopy (SEM) images are widely employed in the analysis of materials samples, typically at the scale of microns. In addition to providing information on the presence of impurities and particle size, SEM images also reveal information on the morphology adopted by individual crystallites and the small size of such particles increases the likelihood that thermodynamic stability determines their adopted shapes, as small agglomerations of matter reach equilibrium with their environment with the greatest ease.

As originally proposed by Wulff [1], the length of a surface normal from a given crystal face to a common point within the crystal interior is proportional to its surface energy and indeed a crystal shape constructed in this manner minimizes its surface free energy. Wulff's proposal can be readily and intuitively appreciated, stable surfaces have the smallest surface normal vectors and dominate the morphology of the crystal.

However, when crystals grow under kinetically or partially kinetically controlled conditions the analysis of crystal morphologies is more challenging because the crystal shape is governed not by equilibrium surface stability but by the expression of the slowest growing crystal faces. Under kinetic control, fast-growing surfaces typically disappear from the morphology, being subsumed by the junctions between slower growing surfaces.

Hence here the kinetics of the addition of atomic or molecular addition to key surfaces must be evaluated, and the slowest growth surfaces are dominantly expressed in the kinetically controlled morphology. Predicting the rate of crystal growth through the deposition of atoms or molecules requires an analysis of the key rate-determining steps in deposition and potentially an evaluation of solvent and environmental effects, which are currently challenging targets for atomistic simulation. However, the *MedeA Morphology* module allows experimentally observed morphologies to be indexed by adjusting surface lengths to match observation, and this provides information on the character of dominant surfaces for subsequent simulation. Hence, when kinetic control of crystallite morphology applies, *MedeA Morphology* module provides insights that can focus the application of atomistic simulation methods.

[1] G Wulff, "Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen," *Zeitschrift für Kristallographie* 34, no. 1 (1901): 449-530.

2 Theory

The *MedeA Morphology* module employs the lattice parameters (a, b, c, alpha, beta, gamma), space group, and surface stabilities of a given system to determine the possible terminating faces and morphology of that crystal. These data determine the possible crystal faces and their relative orientations. The overall shape of the crystal is determined by the relative importance of each crystal face, which is obtained from information on the normal lengths from the centroid of the crystal. In order to generate an initial crystal morphology, the *MedeA Morphology* module employs the Bravais-Friedel [2] [3] rule, which relates surface stability to the inverse lattice spacing for a particular set of planes. The *MedeA Morphology* module accounts for the space group symmetry of the system in selecting sets of planes to include in the morphology and hence encompasses the observations of Donnay and Harker [4] who developed growth selection rules based on crystal symmetry.

Given the set of possible crystal faces and their relative surface normal lengths based on the Bravais, Friedel and Donnay, Harker approximations, *MedeA Morphology* computes the crystallite morphology based on a geometrical analysis of the resulting set of plane intersections. This geometric analysis is recomputed interactively whenever adjustments to the surface normal lengths are made, or choices are made about the planes included in the model, allowing interactive indexing of observed morphologies. The relative areas of crystal faces are also reported interactively as surface normal lengths are updated providing information on the importance of a given surface in determining interfacial properties, for example.

Computed in this way the morphology is a starting point for more detailed analysis. The Bravais, Friedel and Donnay, Harker approximations do not account for interatomic or bonding interactions. Some surfaces are particularly stable (typically indicating few broken chemical bonds or significant reconstruction) and tend to dominate equilibrium morphologies more than would be anticipated based on inverse lattice spacing alone and conversely some surfaces are particularly high energy (indicating significant bonding disruption that cannot be relieved through restructuring) and are disfavored under equilibrium conditions. The initial Bravais, Friedel and Donnay, Harker approximation provides a useful starting point for further analysis. To employ *MedeA Morphology* using computed surface energies, for example as computed using VASP with surface models leading to energies typically expressed in J/m^2 , these energies can be entered directly in the `Relative length` field replacing the initial BFDH value. The resulting computed morphology will be dominated by the most stable faces, as expected.

MedeA Morphology is initiated using the `Tools >> Crystal Morphology` command. This command creates a crystal morphology view window within the *MedeA* graphical interface. This view supports several commands. These are:

Load : loads a morphology (*.morpho*) file into the current morphology view.

Save : saves a morphology (*.morpho*) file including visualization options to disk for future use.

Set from crystal structure : sets interface options based on either an existing *MedeA* system or a supplied *.sci* file. The input data (space group and lattice parameters) taken from the supplied system are shown in the *Morphology view*.

Define manually : allows direct entry of lattice parameters and space group symmetry. This option can be used to explore the morphology for systems for which crystal structures are not available.

Reset to default : erases **all** entries for the facets, i.e. values for

- `h`, `k`, and `l`,
- `Relative length`, i.e. `surface energy`
- `Relative area`
- `color`

[2] Auguste Bravais, "Mémoire Sur Les Systèmes Formés Par Les Points Distribués Régulièrement Sur Un Plan Ou Dans L'espace," *J. Ecole Polytech.* 19 (1850): 1-128.

[3] M G Friedel, "Etudes Sur La Loi De Bravais," *Bull. Soc. Franc. Miner.* 9 (1907): 326.

[4] JDH Donnay and D Harker, "A New Law of Crystal Morphology Extending the Law of Bravais," *American Mineralogist* 22 (1937): 446.

- transparency

to show the default shape of a crystallite, namely an octahedron

Warning: Reset to default cannot be undone! All previously entered values are gone and have to be entered again!

Cell Parameters : reports the current cell parameters and space group employed in generating the morphology view. With the feature **Define manually** you may enter updates to cell data using these fields.

Show symmetric indices : shows symmetry-related faces directly so that, for example, 001 and 00-1 are shown explicitly. If this option is not selected, 001 will be the label applied to both the 001 and 00-1 faces, so that only symmetry unique labels are employed.

Lines/Labels color : sets the color employed for lines and labels.

Update shape : applies the current settings to the morphology view.

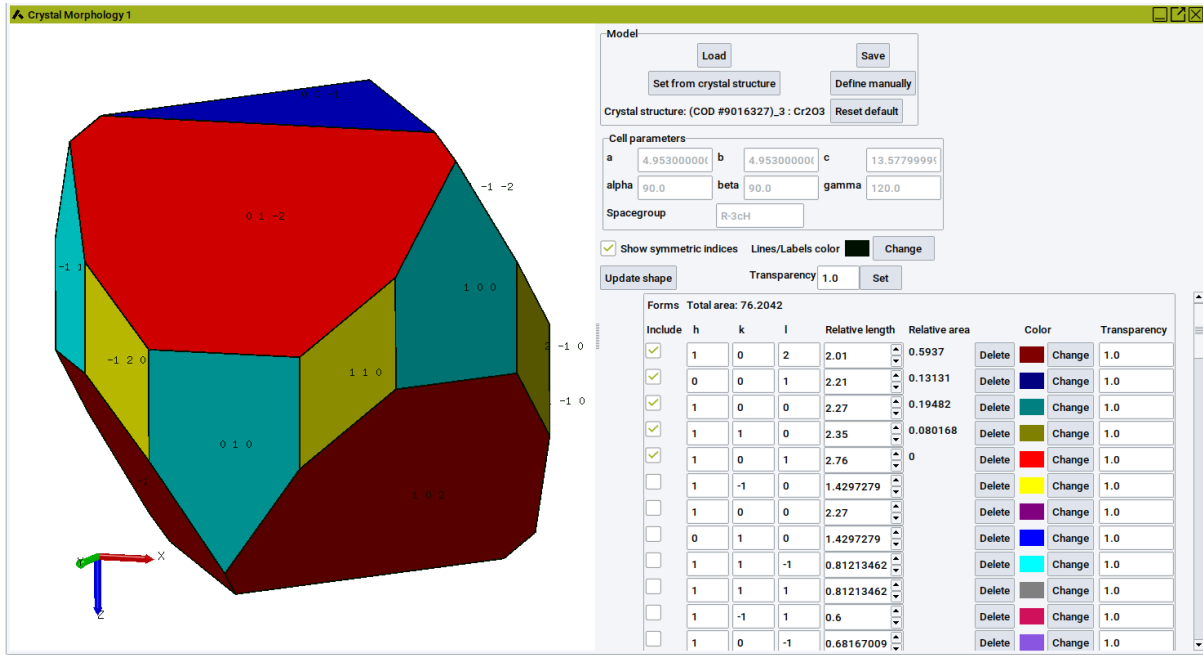
Transparency : applies transparency to the planes of the morphology view so that obscured planes and labels may be viewed.

For each plane in the current morphology model, you can select whether that plane is included in the morphology calculation, the relative length of that particular plane, its color, and an individual transparency setting for that plane. Planes can also be added and deleted, using the appropriate buttons.

The morphology view context menu is available via right-click in the canvas on the left side and can be used to adjust the current mouse mode, and the background color employed in the morphology view. Additionally, when a morphology has been created using a *MedeA* system as a starting point, the context menu associated with a given face of the displayed crystallite provides an access point, for example, **Build (1 0 0) surface** (where (1 0 0) is the surface index), that initiates the *MedeA* surface builder for the construction of an atomistic model for this particular surface.

Typical applications:

- Simulation of the morphology of equilibrium crystal morphologies based on computed surface energies.
- Analysis of experimentally derived morphologies to determine surfaces for further atomistic simulation.
- Analysis of the effect of impurities on morphology, using computed surface energies for surface impurity coverage models.
- Exploration of the effect of crystallite shape on crystallite packing before interface model construction.



The computed morphology of Cr₂O₃ based on reported surface energies: [5]

Surface	Energy (J/m ²)
001	2.21
102	2.01
100	2.27
110	2.35
101	2.76

[5] M J Davies, P R Kenway, P J Lawrence, S C Parker, William C Mackrodt, and P W Tasker, "Impurity Segregation to the Surfaces of Corundum-Structured Oxides," *Journal of the Chemical Society, Faraday Transactions 2* 85, no. 5 (January 1, 1989): 555-563.