Modeling of Crystal Morphology
-Growth Simulation on Facets in Arbitrary Orientations-

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Abstract

Many aspects of crystal morphology modeling are studied in this thesis. Most important of all, is the dependence of crystal growth on supersaturation--the driving force for crystallization--which not only influences the crystal morphology, but also polymorphism and nucleation.

It is shown that an unusual type of epitaxial growth can take place beyond a threshold supersaturation in the crystallization of a model steroid. The same compound shows pseudomorphism upon crystallization from the vapor phase. Modeling studies show that the two structures are related polytypically.

The experimental morphology of gibbsite could be explained through the analysis of effective edge energies of two-dimensional nuclei on the crystal surfaces.
For this, the program MONTY is extremely useful. It uses the concept of the crystal graph, a description of the interactions between the growth units in the crystal. It allows Monte Carlo crystal growth simulations in any crystallographic direction.

The analyses on three fat morphologies support the idea that not the attachment energy is the relevant parameter for the growth rate of a crystal surface, but rather the edge energy of two-dimensional nuclei on the surfaces. Needle formation is explained by the systematic absences of barriers for 2D nucleation in all but a few crystallographic orientations. For paracetamol, growthsimulations show that a supersaturation dependence can be reproduced quite convincingly using the experimentally determined growth mechanisms for the respective surfaces.

Finally. a hypothesis is studied that the morphology of the (sub-)critical nucleus resulting from a certain polymorphic structure must determine the effective barrier of formation of that nucleus, therefore determining the probability of formation of that polymorph. A model is derived and tested on a series of well-known polymorphic structures. It is shown that, indeed, a small majority of the compounds studied produce crystal structures with relatively high levels of isotropy.