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Theory and simulations of crystal growth

Fundamental steps in morphology prediction

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Summary

The morphology or outer shape of a crystal is an important crystal property and has as such received much attention in the literature. The aim of the present thesis is to contribute to the study of crystal morphology by integrating the methods of three sub-disciplines within the field of crystal growth to come to a better understanding of the underlying mechanisms that determine the morphology. These are the study of atomistic models, continuum descriptions of growth mechanisms and morphology prediction methods. The thesis can be divided into two parts. The first part discusses classical microscopic models in detail to arrive at a better fundamental understanding of the crystal growth mechanisms. The second part studies “real” crystal structures.

The first five chapters study crystal growth on an atomic level. Fluctuations in growth steps on crystal surfaces are considered using a statistical mechanical approach. We start by studying kink and step kinetics of the simple cubic or Kossel crystal in Chapters 2 and 3. For this very simple one-particle crystal model we were able to obtain analytical expressions which are in close agreement with Monte Carlo simulation results, for both the kink density and the step propagation velocity. For a slightly more complicated two particle crystal, referred to as a non-Kossel model, it is however not possible to obtain a general expression for these quantities as is shown in Chapter 4. For each step different kinetics apply which are determined by the local structure and interactions between the growth units.

Based on this knowledge of kink kinetics, the phenomenon of kinetic roughening is studied. For the Kossel crystal, an expression for the step free energy of an infinitely long step is derived in Chapter 5 based on the previously found expression for the kink density. The non-equilibrium step free energy vanishes beyond a critical value of the driving force. We propose to define the onset of the kinetic roughening regime by this point, which is found to agree with earlier phenomenological criteria for this transition.

However, since the kink density is the basis of the step free energy, this method cannot easily be applied to more complicated structures like the non-Kossel model. Chapter 6 therefore

uses an alternative method based on an analysis by Leamy and Gilmer to estimate the onset of the kinetic roughening regime without prior knowledge of the structure. This is done by determining the vanishing point of the step energy, which is roughly defined as the difference in surface energy between faces with a zero and non-zero misorientation angle. The estimate found in this way for the Kossel model is very close to the onset previously found and the method is therefore also applied to two steps in the non-Kossel model. Both steps are found to show very different growth behaviour as compared to the Kossel step.

Chapter 7 has a topic which in a sense bridges the atomistic approach of the previous chapters and the more continuum approach of the next chapters. It discusses the influence of the size of 2D nuclei on the edge (free) energy of the nucleus. The edge free energy is a variable often used in continuum expressions for birth-and-spread growth as is discussed in Chapter 8 and is usually considered to be independent of the nucleus size and the driving force. Chapter 7 tests this assumption. It is found that the step free energy is a function of both quantities, but that the step free energy of a critical nucleus is approximately constant given a constant bond strength. These findings are used in Chapter 8 to derive a birth-and-spread model for an anisotropic crystal and fit it to growth data obtained from Monte Carlo simulations of an isotropic and anisotropic Kossel surface and a non-Kossel surface. Besides the 2D nucleation mechanism spiral growth is an as important phenomenon in crystal growth. Chapter 9 studies the interaction between spiral growth, 2D nucleation and step flow for a wide range of driving forces by means of Monte Carlo simulation. The last chapter of the first part, Chapter 10, deals with crystal structures with orientations that have connected nets, but nevertheless have zero step energies in at least one direction which makes them grow rough.

Part II consists of five chapters that study some particular phenomena encountered in the growth of real crystals. These are studied using Monte Carlo simulations based on crystal graphs as models for these real crystals. Chapter 11 studies the influence of the force field on the morphology prediction using Monte Carlo simulations. Monoclinic paracetamol is used as a model structure. Small differences in interaction energies are found to give huge differences in the simulation results. Chapter 12 studies the morphology of polycenes like naphthalene, anthracene and tetracene both experimentally and by computer simulations. The results show that at moderate conditions crystals of these compounds growing with a 2D nucleation mechanism would be extremely thin platelets. Only crystals with screw dislocations on the basal faces can be formed. Chapter 13 discusses the polar morphology of crystals growing in spacegroups without inversion symmetry. It shows that the morphology of a polar crystal can be polar as a result of differences in kinetic pathways for opposite faces. This results from bulk interactions instead of external factors like the solvent or impurities. Finally, Chapters 14 and 15 explain the needle-like morphology of aspartame forms II-A and I-A, respectively. The extreme aspect ratios of these crystals stems from the unexpectedly small edge energy for steps on the fast growing top faces as compared to those of the side faces.