311f Crystal Growth by Spiral Motion

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Modeling crystal growth of organic compounds is of paramount interest to the pharmaceutical, dyes and food products industries. Crystal growth plays an important role in both crystal morphology and polymorph transformations. Steady state and dynamic crystal morphology affect down stream processes such as filtering, washing and drying as well as particle flowability and agglomeration; therefore, the ability to understand and manipulate growth shapes enables process improvements. Furthermore, the quality and efficacy of these materials are affected by crystal shape and polymorph. The shape affects which surface structures are present and their relative sizes. The polymorph can affect the solubility, color, bioavailability, stability and patentability of a crystalline product. Polymorphic phase transformations often take place by a solution mediated mechanism, which is characterized by the growth of a more stable polymorph and the simultaneous dissolution of a less stable polymorph. Thus, predicting growth of the stable polymorph facilitates the calculation of a polymorphic phase transformation rate.

Models of crystal growth shape have evolved from those that depend purely on crystal structure and thermodynamics, such as those of Bravais, Friedel, Donnay and Harker as well as Hartman and Perdok, to those that incorporate mechanistic phenomenon such as solute incorporation at kinks on steps flowing across surfaces. We have focused on a class of these kinetic models in the spirit of Burton, Cabrera and Frank (1951) who pioneered the concept of screw dislocations as a source of spiraling steps. Winn and Doherty (1998) have shown the ability of this class of models to take into account the effect of solvent.

Molecular organic and biological crystals have complex bonding structures, molecular arrangements and energetic interactions. We have developed a spiral growth model to incorporate these important qualities, which result in numerous complicated microscopic features such as non-isotropic spiral shapes, non-uniform kink energy distributions and multiple spiral rotation directions. Some of these features (for example non-isotropic spiral shapes) have previously been measured by experiment; however, existing models do not account for their influence. In combination with an automated method for the determination of periodic bond chains and the inclusion of solvent effects, we demonstrate that these methods are an effective model of crystal growth. Key modeling details will be presented alongside several crystal growth shape predictions and their comparison to experiment, such as □-glycine grown from water and vanillin-I grown from chloroform.

Burton, W.K., Cabrera, N., and Frank, F.C., “The Growth of Crystals and the Equilibrium Structure of their Surfaces,” Phil. Trans. R. Soc., 243, 299 (1951).

Winn, D. and M.F. Doherty, “A New Technique for Predicting the Shape of Solutions-Grown Organic Systems,” AIChE J., 44 (11), 2501 (1998).