XXI ICTAM, 15–21 August 2004, Warsaw, Poland

ANALYSIS OF FLOW-INDUCED, STEP-BUNCHING INSTABILITIES DURING THE GROWTH OF CRYSTALS FROM LIQUID SOLUTIONS

Bing Dai, Yong-Il Kwon, and Jeffrey J. Derby
Department of Chemical Engineering and Materials Science & Minnesota Supercomputer Institute, University of Minnesota, Minneapolis, MN 55455-0132, U.S.A.

Summary We present a novel multi-scale model of the growth of a vicinal crystal surface from a supersaturated liquid solution that couples bulk fluid dynamics with surface step growth. Of particular interest are the effects of fluid mechanics on morphological crystal growth instabilities, such as macrosteps, step bunches, and inclusions. This model is self-consistently solved by an efficient, moving-boundary, finite element method.

INTRODUCTION

Crystal growth is a prime example of an important materials processing operation which is strongly impacted by fluid mechanics. In this presentation, we address solution crystal growth, i.e., the growth of crystals from a supersaturated liquid, a process which is widely employed to produce large, single crystals of materials not amenable to melt growth techniques. In addition, solution growth is very widely employed in crystallization separations and purification processes for high-value materials such as pharmaceuticals. During solution growth, crystal quality is often compromised by morphological instabilities, such as macrosteps, step bunches, and inclusions, which arise from the coupled effects of fluid dynamics, mass transport, and the growth of atomic layers (steps) across a vicinal crystal surface. The main motivation for the work presented here is the need for a coupled, multi-scale, transport-kinetic model which is sufficiently detailed to capture microscopic step growth kinetics and is in a sufficiently general form to be incorporated in a global transport model of fluid mechanics, such as that employed by Vartak *et al.* [1].

MODEL DESCRIPTION

For the work presented here, we consider relatively simple flows within boundary layers adjacent to the macroscopic, vicinal surface of a crystal growing from a liquid solution. This scenario is depicted schematically in Figure 1(a), where the fluid flow over a crystal surface is shown. There is a depletion of solute due to the crystallization at the surface leading to a concentration boundary layer, which is embedded within the momentum boundary layer. At a still smaller scale, we consider a step source, such as a screw dislocation [2] somewhere along the crystal surface (see the yellow arrow) with a train of steps moving away from it (see the blue box). Within this blue box, which is moving with a group of steps on the crystal surface, we construct a growth model involving a series of elementary transport and kinetic processes, starting from material transport in the bulk phase, adsorption and desorption of growth units to and from terraces between steps, followed by surface diffusion and incorporation at discrete step ledges, as depicted in Figure 1(b). This phenomenological approach to describe step motion was first proposed in the classical model by Burton, Cabrera and Frank (BCF) [2] with later extensions by Chernov [3], Bennema [4], and Gilmer, Ghez, and Cabrera [5] for solution growth.

Of particular interest are scenarios whereby the steps within a group (a step train), which are all initially equally spaced and moving at the same speed, begin moving at different speeds to form a feature known as a step bunch. A step bunch contains many closely spaced steps, surrounded by regions with relatively few steps. It is believed that such step bunches degrade the quality of the growing crystal and are a precursor to the formation of liquid inclusions in the crystal. A number of coupled transport-kinetic models have been applied to address this particular issue of morphological instability, most notably the works of Vekilov and co-workers [7] and Chernov, Coriell, and co-workers [8]. These prior efforts employed a number of idealizations. Our approach, first described in [9], rigorously accounts for the interactions of discrete growth steps through surface diffusion fields, adsorption and desorption events, solute incorporation, and surface convection due to step motion. This model is self-consistently coupled with a bulk model that describes the fluid flow and its effects on the convection and diffusion of solute to the surface. The governing equations are solved numerically by an efficient, moving-boundary, finite element method.

SAMPLE RESULTS

A sample result is shown in Figure 1(c), where a snapshot is displayed of the transient response of a train of 51 growth steps under the influence of a boundary-layer flow directed in the same direction as the step motion. Initially, we impose a perturbation to the inter-step spacing of an equidistant configuration of steps. Under these conditions of flow and growth, the step spacing changes in time, leading to the situation depicted in the figure, which shows a step bunch in the middle of the domain. This step bunch moves with its own phase velocity through the simulation box.

Figure 1(c) also shows the instantaneous bulk concentration of solute in the liquid over the crystal surface. A careful examination of the figure reveals depletion regions around individual steps, as the solute in the bulk liquid diffuses to steps and is incorporated due to step motion (i.e., crystal growth). The action of fluid flow on these concentration variations occurs over longer length scales involving dozens of steps and acts, in this case, to destabilize the step train and form

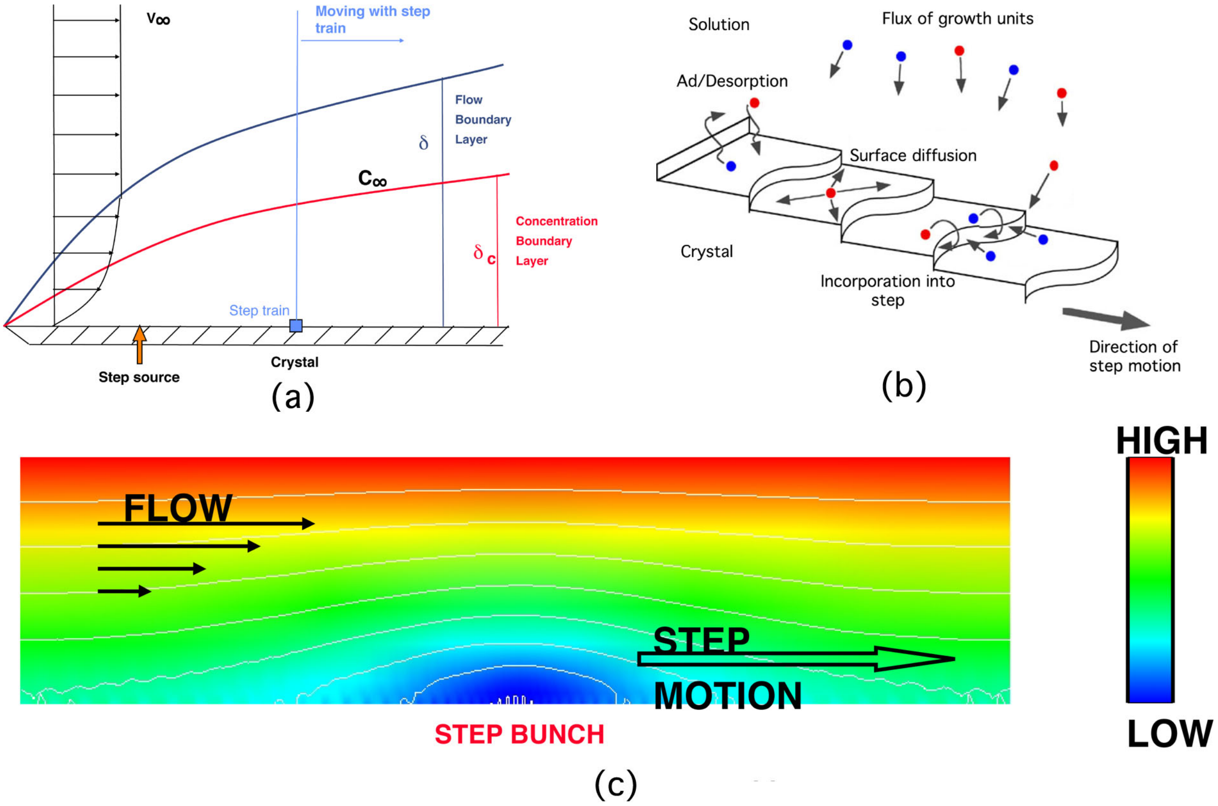

Figure 1. (a) Boundary layer depiction of macroscopic flows and mass transfer across a vicinal crystal surface is shown; the step train is embedded within the blue box moving along the surface. (b) The surface model includes steps, terraces, and growth units. (c) A sample computation of 51 steps under destabilizing conditions. The crystal surface is the bottom of the box; the overlying liquid is colored as a function of its solute concentration. A perturbation in the spacing of the steps results in the evolution of a bunch.

bunches. The lateral concentration profiles across the bulk are in registry with the population of steps along the surface, namely a higher number density of surface steps (a step bunch) is situated below lower-concentration fluid, while higher-concentration fluid regions exists above the surface where there are fewer steps. Thus the lateral variation of the step density couples to the flow, via convection of the bulk solute concentration field, and drives the growth of this step-bunching instability. Under identical conditions, but with the flow direction counter to the direction of step motion, this system is stable to all perturbations and always exhibits equally spaced steps within the train.

SUMMARY

These first-principles computations predict step bunches and allow their underlying mechanisms to be studied. Effects of fluid flow on morphological instability within several growth systems, representing large-molecule organic materials and small-molecule inorganic materials, will be discussed in the presentation and compared to experimental findings.

References

[1] B. Vartak, Y.-I. Kwon, A. Yeckel, and J. J. Derby, “An analysis of flow and mass transfer during the solution growth of potassium titanyl phosphate,” *Journal of Crystal Growth*, **210**, 704–718, 2000.

[2] W. K. Burton, N. Cabrera, and F. C. Frank, “The growth of crystals and the equilibrium structure of their surfaces,” *Phil. Trans. Roy. Soc. London*, **243**, 299–358, 1951.

[3] A. A. Chernov, “The spiral growth of crystals,” *Soviet Physics Uspekhi*, **4**, 116–148, 1961.

[4] P. Bennema, “The importance of surface diffusion for crystal growth from solution,” *Journal of Crystal Growth*, **5**, 29–43, 1969.

[5] G. H. Gilmer, R. Ghez, and N. Cabrera, “An analysis of combined surface and volume diffusion processes in crystal growth,” *Journal of Crystal Growth*, **8**, 79–93, 1971.

[6] F. Rosenberger, H. Lin, and P. G. Vekilov, “Finite-amplitude instability in growth step trains with overlapping step supply fields,” *Phys. Rev. E*, **59**, 3155–3164, 1999.

[7] P. G. Vekilov, F. Rosenberger, H. Lin, and B. R. Thomas, “Nonlinear dynamics of layer growth and consequences for protein crystal perfection,” *Journal of Crystal Growth*, **196**, 261–275, 1999.

[8] S. R. Coriell, A. A. Chernov, B. T. Murray, and G. B. McFadden, “Step bunching: generalized kinetics,” *Journal of Crystal Growth*, **183**, 669–682, 1998.

[9] Y.-I. Kwon and J.J. Derby, “Modeling the coupled effects of interfacial and bulk phenomena during solution crystal growth,” *J. Crystal Growth* **230**, 328–335, 2001.