

603a Detailed Analyses of Transport Limitations during Afm Measurements of Solution Crystal Growth

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Atomic force microscopy has emerged as the preeminent experimental tool for real-time, in situ measurements of solution crystal growth. This technique has been used to examine the microscopic events associated with crystal growth of various organic and inorganic crystals. Its use allows for the direct imaging of terraces, ledges, and kinks, and the direct measurement of kink and step velocities. From such measurements, thermodynamic and kinetic properties of the crystal surface can be estimated.

Impressive as these techniques may be, however, there are currently no independent means of determining the crystallization conditions present while AFM measurements are being conducted. Of particular importance is knowledge of potential mass transport limitations being experienced by the crystal. Such limitations have been clearly identified in many AFM studies of crystallizing systems. To overcome these, flows must be increased above a threshold level. However, simply carrying out measurements at high flow rates through an AFM cell is not a guarantee of good images for these systems. Interestingly, the effect of the hydrodynamic forces on the AFM tip has also been postulated as a source of measurement error in liquid environments. Clearly, a detailed understanding of flow and mass transfer is required for the unambiguous interpretation of in situ AFM growth measurements.

In this presentation, we present initial work on the development of a model for continuum transport through an AFM flow cell employed for measurements of the growth of calcium oxalate monohydrate. These are the first three-dimensional computations of such detail for flow and mass transfer through an entire AFM cell and are enabled by the parallel, finite element codes previously developed by us for continuum computations in solution crystal growth.

Analyses address conditions under which flow is expected to significantly impact AFM measurements and address suitable strategies to minimize such effects. We also study the effect of nearby crystals on measurements. These growing crystals are surrounded depletion zones that are convected by flow around the crystal into a downstream plume. We simulate conditions of crystal placement, flow strength and direction, and supersaturation under which one expects interference effects in AFM measurements. Finally, we discuss the general utility to "model the experiment," i.e., to employ modeling in conjunction with measurements to obtain accurate interpretations of kinetic data from specific systems.