Module 5: Schlieren and Shadowgraph

Lecture 27: Schlieren imaging of crystal growth

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INTRODUCTION

Large crystals with a high degree of perfection are required in a variety of applications. Optical crystals of good quality find utility in critical technology areas such as high power lasers, higher harmonic generation and in nuclear fusion. A class of such crystals can be grown from their supersaturated solution in water, during a slow cooling process. Growth of such crystals from an aqueous solution is one of the commonly used techniques in the industry. The technique can be used for growing optical crystals such as KDP and proteins such as lysozyme. A crystal growing from its aqueous solution creates a three-dimensional solute distribution in its vicinity. The solutal concentration gradients and hence the gradients in the density of the solution are responsible for the evolution of buoyancy-driven convection currents in the growth chamber. The buoyant convection currents influence the magnitude of the concentration gradients prevailing along the growth surfaces. In turn these control the stability of the growth process and the overall crystal quality. The concentration gradients in the growth chamber are significantly altered when the crystal is given rotation. Rotation can hence be viewed as a method of controlling convection during the growth process.

Low temperature solution growth methods are applicable to materials that have moderate to high solubility in temperatures up to $100^\circ C$ at atmospheric pressure. A number of organic and inorganic materials fall in this category and can be crystallized using this technique. The advantages here include relatively low temperature handling of the equipment and a good degree of temperature control to within $\pm 0.01^\circ C$. The grown crystals show full natural morphology. In addition, online studies of surface growth features and growth rate studies of different faces are possible. Since temperature gradients involved in a given process are low, thermally generated strains in the grown crystal are small. The disadvantage of low temperature solution growth is the slow growth rates (0.1 to 10 mm per day). In many cases the ease of solvent inclusion into the growing crystal is a limiting factor. Since many crystals are grown from water as the solvent, the grown crystal is hygroscopic in nature; this limits its use to applications in which water molecules are excluded in the lattice. A large fraction of the crystals produced from low temperature solutions are grown by using water as a solvent owing to its high solvent action, chemical stability, low viscosity, low toxicity and low cost. Other solvents include ethanol, methanol, acetone, carbon tetrachloride, hexane, and xylene. Examples of technologically important crystals grown from a low temperature aqueous solution include potassium di-hydrogen phosphate (KDP), potassium di-deuterium phosphate (DKDP), tri-glycine sulphate (TGS), potassium acid phthalate (KAP), lithium arginine phosphate (LAP), and urea. Recently, low temperature solution growth method has found its applications towards the growth of protein crystals such as lysozymes.

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A crystal growing from its aqueous solution creates a three-dimensional solute distribution in its vicinity. The mechanism involved is the withdrawal of the solute from the solution, causing the solute concentration to decline in the neighboring solution. The solutal concentration gradients, and hence the gradients in the density of the solution are responsible for the evolution of buoyancy-driven convection currents in the growth chamber. The convection currents are the main drivers for the solute from the solution rich in salt as it is transported to the surface of the growing crystal. In the absence of convection, solute transport is mainly by molecular diffusion. Since diffusion coefficients in liquids are small, small fluid velocities greatly increase mass transfer (over the diffusion values) and hence the growth rate of the crystal. It is understandable that changes in the symmetry pattern of the flow field and unsteadiness can lead to a lowering of the crystal quality and the growth rate. Hence an optimum strength of convection currents is desirable to maintain a balance between the quality of the growing crystal and its growth rate. The strength and orientation of buoyancy driven convection currents are intricately linked with the size and morphology of the growing crystal. These in turn depend upon the process parameters namely the supersaturation level of the solution and the rate at which it is cooled. More recently, convection has been found to be quality-limiting mechanism in the growth of protein crystals from their solution. Here, convection has the capability of distorting the effects of mechanisms such as surface tension and magnetic fields and thus influences the crystal growth process.

Buoyancy-driven convection currents influence the magnitude of the concentration gradients prevailing along the growth interfaces. In turn, the gradients control the stability of the growth process and the overall crystal quality. It has been experimentally noted that growth in free convection regime is often limited by density stratification in the vicinity of the growing crystal leading subsequently to unwanted nucleation of solute in the growth chamber. The concentration gradients in the growth chamber are significantly altered when the crystal is given a rotation. An optimum rotation rate tends to stabilize the perturbations along the rotational axis eventually leading to an axisymmetric concentration distribution over the crystal. The stirring of the solution also reduces the natural convection-induced temperature oscillations by homogenizing the bulk solution. Rotation can hence be viewed as a method for controlling convection during the growth process by diminishing the impact of buoyancy.

To ensure the growth of high-quality large crystals, it is important to understand from a fundamental point-of-view, the transport phenomena involved during solute deposition from the solution to the crystal surfaces. Simultaneously, visualization techniques are required to monitor the crystal growth process itself during its progress. Unlike growth from melt and vapor, growth from an aqueous solution is particularly amenable to flow visualization, since it is transparent. It is possible to generate images of the convective field by exploiting changes in the refractive index that accompany changes in the density of the medium. Optical visualization techniques are thus useful for online monitoring of the growth process.

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Optical techniques are ideal for mapping the properties of the solution during a crystal growth experiment. Since a probe need not be introduced in the field of study, they are non-intrusive and practically inertia free. Over the past decade, laser measurement techniques have become popular, though primarily as a flow visualization tool. Recent work however has emphasized the possibility of quantitative measurements as well. A majority of optical techniques are field techniques in the sense that an entire cross-section of the physical region can be mapped. They require the medium to be transparent, and are thus suitable for the measurements in liquids. Optical methods that utilize the dependence of refractive index of light on density (and indirectly on concentration and temperature) can be configured in many different ways. Three available routes are:

- Interferometry, where the image formation is related to changes in the refractive index with respect to a reference environment,
- Schlieren, where light deflection in a variable refractive-index field is captured, and
- Shadowgraph, where the reduction in light intensity on beam divergence is employed.

In the context of crystal growth from an aqueous solution, a unique relationship can be established between the refractive index and the local density of the medium under study. Under normal process conditions, the solution is practically incompressible and the density does not depend on pressure. At any time instant, the solution is also at a spatially uniform temperature. Hence, density changes correlate with those in concentration alone, and the three methods become applicable for concentration field measurement in the fluid medium. The three techniques referred above yield the path integral of the density field in the direction of line-of-sight. The distribution of density in three dimensions can then be extracted from the recorded images using principles of tomography.

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The present lecture reports measurement of the solute concentration distribution around a KDP crystal growing from its aqueous solution under slow cooling conditions. The choice of KDP (molecular mass 136.09) was based on the availability of refractive index and supersaturation data in the literature for image analysis. The solution adjacent to the crystal is depleted of the salt and is close to the saturated state, while it is supersaturated in the far-field. The difference in solute concentrations drives a diffusive mass flux in the initial stages of growth, while the flux is controlled by fluid convection at later times (Figure 5.11). In the context of crystal growth, the present module contains discussions on refractive-index methods, their validation in a buoyancy-driven flow experiment, comparison of interferograms, schlieren and shadowgraph for crystals growing under nominally identical experimental conditions, schlieren imaging and analysis of convection patterns, possibility of control by rotation, and tomographic reconstruction of the concentration field around the growing crystal. The physical problem taken up for *validation* and comparison of the three optical methods is buoyancy-driven convection in a fluid medium confined in a rectangular cavity. The fluid is heated from below, cooled from the top and the cavity has insulating side walls. The flow pattern associated with this configuration shows a sequence of transitions from steady laminar to unsteady turbulent flow.

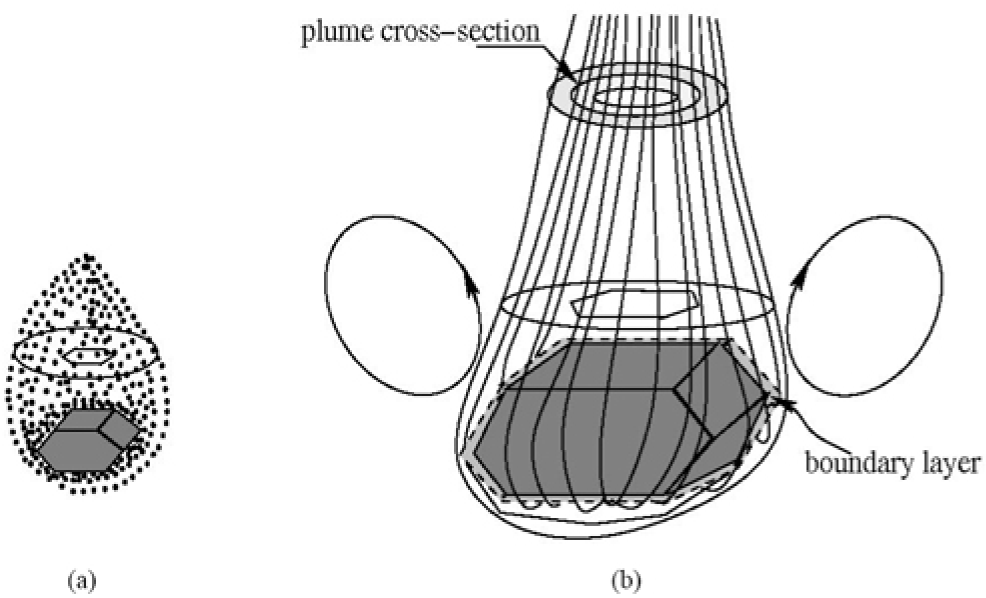

Figure 5.11: Schematic drawing of the concentration distribution around a growing crystal. (a) Diffusion dominated growth shown by dots, (b) Growth in stable convection regime in the presence of a buoyant plume. Arrows indicates fluid motion in the bulk of the solution.

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OBJECTIVES OF THE PRESENT WORK

The importance of convection in determining crystal growth rates and crystal quality has been recognized by a variety of authors. Over the past decade, laser measurement techniques have become popular, though primarily as a flow visualization tool. Recent papers, however, have emphasized the possibility of quantitative measurements using optical methods. Against this background, results are discussed in the present article in the following sequence:

Convection in a rectangular cavity

The literature on refractive index based methods shows that of the three methods, interferometry has been predominantly applied for qualitative as well as quantitative analysis of the thermal fields in buoyancy-driven convection. Schlieren finds potential applications towards qualitative visualization of the flow field and to a limited extent, it has been applied for quantitative studies. Shadowgraph has been extensively used for qualitative imaging. The three techniques, however, have not been jointly compared against a benchmark experimental configuration. The present work compares interferometry, schlieren and shadowgraph techniques for the measurement of temperature distribution in buoyancy-driven convection in a rectangular cavity. The top and bottom walls of the cavity are maintained at uniform temperatures at all times in an unstably stratified configuration. Fluid media considered are air and water. Temperature differences of 5-50 K for air and 3-10 K for water have been employed in the experiments. Over the range of temperature differences considered, flow was seen to become progressively unsteady, finally becoming turbulent.

Comparison of optical techniques for a crystal growing from its aqueous solution

Interferometry, schlieren and shadowgraph are employed to visualize the convection field around a growing KDP crystal from its aqueous solution. Experiments have been conducted under practically identical conditions. The goal of the study is to explore the suitability of these measurement techniques to image, analyze and interpret the convective field around a growing crystal.

Schlieren study of convection around a crystal driven by buoyancy and rotation

The specific goals here are to understand (a) changes in convection pattern at various stages of the crystal growth process, (b) role of convection in creating regions of high/low concentration gradients, (c) possibility of controlling the size of these regions by providing crystal rotation, and (d) to demonstrate the suitability of the schlieren technique for quantitative mapping of solutal concentration around the growing crystal. The process parameters studied are cooling rate of the solution and rotation rate of the growing crystal. Crystal rotation is viewed in this study as a means of diminishing the impact of buoyancy. The crystal size plays an influential role in determining the relative importance of buoyancy and rotation. An independent study of crystal size has also been presented. Schlieren images have been analyzed to correlate the strength of convection currents with the concentration field and its gradients. The crystal quality has been gauged by examining the transparency of the crystal at the end of the experiment.

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Three dimensional concentration contours around a growing crystal

Laser schlieren technique is employed to investigate the three-dimensional concentration field around a KDP crystal growing from its aqueous solution. The convective field is set-up in the growth chamber by inserting a KDP seed into its supersaturated solution followed by slow cooling of the solution. The projection data in the form of two-dimensional schlieren images have been recorded from four different view angles $(0, 45, 90, and\ 135°)$ by turning the crystal growth chamber. Since a circular growth chamber is employed in the present experiments, the entire width of the growth chamber for a given view angle could not be covered. Hence a single view provides only partial data, corresponding to the area localized in the vicinity of the growing crystal. The integrated values of concentration are obtained by analyzing the light intensity data of the schlieren images. Subsequently, the concentration fields at various horizontal planes above the crystal are reconstructed using the convolution back projection (CBP) algorithm. Owing to limitations in the optical system, the projection data required for tomographic inversion is often incomplete. Specifically, the number of view angles is small, and in addition, the entire field of view may not be scanned. The applicability of the inversion algorithms can then be ensured only when additional tests are conducted to validate the result obtained. Validation with numerically simulated data is reported in this work. The focus of the present study is to examine the symmetry of the concentration field in the vicinity of the growing crystal in the initial stages (diffusion-dominated growth) and in the stable growth regime (recognized by the presence of a steady convective plume rising from the crystal surface). Of interest is the relationship between the morphology of the crystal with the solutal concentration field around it, during the growth process.

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