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# Simulation of Fluid Flows During Growth of Organic Crystals in Microgravity

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DURING GROWTH OF ORGANIC CRYSTALS IN  
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SIMULATION OF FLUID FLOWS DURING GROWTH OF ORGANIC CRYSTALS  
IN MICROGRAVITY

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SUMMARY

Several counterdiffusion type crystal growth experiments have been conducted in space. Improvements in crystal size and quality have been attributed to reduced natural convection in the microgravity environment. One series of experiments called DMOS (Diffusive Mixing of Organic Solutions) was designed and conducted by researchers at the 3M Corporation and flown by NASA on the space shuttle. Since only limited information about the mixing process is available from the space experiments, a series of ground based experiments were conducted to further investigate the fluid flow within the DMOS crystal growth cell. Solutions with density differences in the range of  $10^{-7}$  to  $10^{-4}$  g/cm<sup>3</sup> were used to simulate microgravity conditions. The small density differences were obtained by mixing D<sub>2</sub>O and H<sub>2</sub>O. Methylene blue dye was used to provide flow visualization. The extent of mixing was measured photometrically using the 662 nm absorbance peak of the dye. Results indicate that extensive mixing by natural convection can occur even under microgravity conditions. This is qualitatively consistent with results of a simple scaling analysis. Quantitative results are in close agreement with ongoing computational modeling analysis.

1. INTRODUCTION

Organic crystals have shown considerable potential for use in nonlinear optical devices (ref. 1). The usefulness of these materials in devices is often limited by the inability to grow large crystals with a sufficiently low density of defects. On Earth, temperature and composition gradients result in natural (bouyancy driven) convection, which can interfere with crystal growth (ref. 2). One technique for growing crystals involves the counterdiffusion of two reactants (A and B) and precipitation of the salt (AB) in the interfacial region. This approach is particularly useful when the salt is not sufficiently soluble in common solvents to allow growth by precipitation from a homogeneous

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solution. In the counterdiffusion process natural convection can occur along with molecular diffusion as a result of density gradients within the container. The density gradients are a result of: (1) concentration gradients for components A and B, (2) the density difference between the solution and the solid salt crystal, and (3) thermal gradients resulting from heat released during salt formation and crystallization. These density gradients cannot be eliminated in practical crystal growth experiments. However, the natural convection caused by the density gradients can be considerably reduced if the crystal growth experiment is conducted in space.

Organic crystals were grown by researchers at the 3M Corporation in a series of space experiments called DMOS (Diffusive Mixing of Organic Solutions). Included in DMOS-2 were two experiments designed to measure the extent of solution mixing in microgravity. In order to examine the fluid dynamics more closely, a series of ground based experiments were designed to simulate the fluid flow which occurred during the DMOS experiments. These experiments were conducted at the NASA Lewis Research Center in collaboration with researchers at the 3M Corporation and the NASA Marshall Space Flight Center. This paper describes the details of the ground based experiments and results which apply both to the DMOS experiments and to other similar experiments with horizontal composition gradients.

## 2. EXPERIMENTAL PROCEDURES

The DMOS crystal growth apparatus consists of three cylindrical chambers placed end to end. Between the chambers a sliding gate valve assembly is used to control mixing. For the ground based experiments described in this paper, the simpler two chamber cell shown in figure 1 was used. The chambers of this cell are rectangular for better photographic flow visualization, but the gate valve assembly is identical to that used in the DMOS experiments. In a typical experiment the left chamber is filled with a 0.01 g/l solution of methylene blue dye in water while the right chamber is filled with pure water. The density difference between fluids in the chambers is controlled by adding deuterated water ( $D_2O$ ) to one chamber or the other. Qualitative information about the flow patterns during mixing was obtained using time lapse photography at 2 frames per second. Quantitative results were obtained by photometric analysis using the 662 nm absorbance peak of the methylene blue dye. This was done by closing the gate valve after the desired mixing time, shaking the apparatus to get a uniform dye concentration, and taking samples from each chamber for analysis. At sufficiently long times the mass fraction of dye in each chamber is 0.5. If  $f(t)$  is the mass fraction of dye in the right chamber at any time,  $t$ , the extent of mixing,  $X_m(t)$ , is defined by equation 1.

$$\%X_m = 100X\left(\frac{f}{0.5}\right) \quad (1)$$

Using this definition, the extent of mixing goes from 0 to 100 percent as the mixing time goes from zero to infinity. The temperature was maintained at  $30 \pm 0.1$  °C during the the mixing experiments by immersing the apparatus in a circulating water bath. A quartz thermometer was used to measure the temperature difference between various points in the bath. When the density difference between the solutions was less than  $10^{-5}$  g/cm<sup>3</sup>, heating of the dye solution by the background lighting used for photography began to influence the

fluid flow. Therefore, when quantitative data was taken, no background lighting was used, and the water bath was covered with a black cloth to exclude room light.

The diffusion coefficient of the methylene blue dye in  $D_2O$  was measured by Prof. Ernst von Meerwall at the University of Akron using a pulsed gradient spin echo (PGSE), nuclear magnetic resonance (NMR) technique. Physical properties of  $H_2O$  and  $D_2O$  used in section 3 were obtained from standard tables using values at 30 °C.

### 3. RESULTS AND DISCUSSION

#### 3.1 The Microgravity Environment

Experiments conducted on the shuttle experience both translational and rotational accelerations from many sources (ref. 3). Atmospheric drag causes a steady acceleration of the center of mass antiparallel to the orbit velocity. A steady acceleration perpendicular to the orbit also exists for points not located on the orbital path of the center of mass. Oscillatory accelerations occur as a result of structural vibrations, and transient accelerations occur as a result of attitude maneuvers, satellite deployments, crew motions, etc. An experiment can be run during quiet periods, so that only steady accelerations are important. In this paper only flows resulting from a steady acceleration perpendicular to the initial density gradient are considered.

#### 3.2 Microgravity Simulation-Experiments

It will be assumed for now that the fluid flow which occurs during a space experiment can be simulated in a ground-based experiment if the product of the solution density difference and the effective gravitational acceleration is the same in each experiment. The validity of this assumption will be discussed ~~in more~~ detail in section 3.3. A detailed description of the accelerations which occurred during the DMOS-2 experiments will be published later. Preliminary analysis of accelerometer data indicates that the effective acceleration was on the order of 10-5 times that on Earth. Density differences in ground-based simulations must therefore be smaller than those in the space experiments by the same factor. The solutions used to obtain these small density differences must be different from the solutions used in the space experiments. In some cases solutions very similar to those used in the space experiment can be used in ground-based simulations if isotopic mixtures (such as  $D_2O/H_2O$ ) are used to control solution densities. This allows the density difference between two solutions to be varied over many orders of magnitude with only a minor modification of chemical properties.

An experiment was conducted in the apparatus of figure 1 using a blue solution ( $H_2O$  + dye) in the left chamber and pure water ( $H_2O$ ) in the right chamber. A dye concentration of 0.01 g/l was needed for photographic flow visualization. When the gate valve was opened, the blue solution flowed from left to right through the three bottom channels (counterclockwise flow). This indicates that the dye causes an increase in the density of the water. However, the density change is too small to be measured directly by standard techniques. In order to determine the effect of the dye on the density of the water, a series of experiments were run in which the density of the solution

in the right chamber was incrementally increased by adding various amounts of D<sub>2</sub>O to the water. Each experiment was stopped after 2 hr, and the extent of mixing was determined. Results of these experiments are shown in figure 2. Positive and negative values indicate flow in the counterclockwise and clockwise directions respectively. If ideal mixing is assumed, the density difference between the H<sub>2</sub>O/D<sub>2</sub>O solution and pure H<sub>2</sub>O can be calculated using equation 2.

$$\Delta\rho = v_{D_2O}(\rho_{D_2O} - \rho_{H_2O}) \quad (2)$$

$v_{D_2O}$  volume fraction of D<sub>2</sub>O  
 $\rho_{H_2O}$  density of pure H<sub>2</sub>O  
 $\rho_{D_2O}$  density of pure D<sub>2</sub>O

According to figure 2, the effect of the dye is equivalent to a D<sub>2</sub>O volume fraction of  $3.5 \times 10^{-5}$ . Using this value for  $v_{D_2O}$  and  $(\rho_{D_2O} - \rho_{H_2O}) = 0.108 \text{ g/cm}^3$  in equation 2, the density increase caused by adding 0.01 g/l of dye to H<sub>2</sub>O is calculated to be  $3.8 \pm 0.1 \times 10^{-6} \text{ g/cm}^3$ . Notice that it is possible to prepare solutions with density differences on the order of  $10^{-6} \text{ g/cm}^3$  without knowing the absolute densities of the solutions to the same accuracy. This is possible only if the same source of water is used to prepare both solutions and no significant concentration of impurities is introduced during preparation of the solutions. The consistency and reproducibility of results obtained throughout this work suggest that these conditions were satisfied. Another potential source of error is thermally induced density gradients. The maximum temperature difference measured between any two points in the water bath just outside of the apparatus was 0.007 °C. Using  $3.0 \times 10^{-4} \text{ K}^{-1}$  as the volumetric thermal expansion coefficient of water, the maximum possible thermally induced density difference is  $2.1 \times 10^{-6} \text{ g/cm}^3$ . Since the time averaged temperature difference between any two points outside of the apparatus is much less than 0.007 °C, thermally induced density differences inside the apparatus are probably on the order of  $10^{-7} \text{ g/cm}^3$  or less.

In order to observe qualitatively how mixing occurs, a series of experiments with density differences ranging from  $10^{-6}$  to  $10^{-4} \text{ g/cm}^3$  were conducted. The flow was qualitatively the same throughout this range of density differences. The denser (blue) solution flowed from left to right through the bottom three channels of the gate valve assembly. When the blue solution entered the right chamber, it flowed like a waterfall in a layer about 0.2 cm thick along the vertical wall of the gate valve assembly to the bottom of the chamber. The flow continued until the levels of the blue solution were nearly equal in each chamber.

In some of the DMOS space experiments the density difference between solutions in different chambers was on the order of  $1 \text{ g/cm}^3$ . In order to simulate the flow which occurred in these space experiments, a series of ground based experiments with  $\Delta\rho = 4.9 \times 10^{-6} \text{ g/cm}^3$  were run. The extent of mixing as a function of time is shown in figure 3. Nearly complete mixing is obtained in about 32 hr. At this time each chamber contains the blue solution in the bottom of the chamber and a clear solution at the top of the chamber with a diffuse horizontal interface separating the two solutions. No observable change in the dye distribution was observed between 32 and 56 hr.

### 3.3 Microgravity Simulation-Theory

In order to describe the fluid flow which occurs during experiments conducted in the apparatus of figure 1, it is convenient to consider flow through the valves and flow within the chambers separately. As a simplification, flow through the valves can be described as Poiseuille flow through a rectangular channel. The average velocity of fluid within the valves can then be calculated from equation 3 (ref. 4).

$$\frac{\Delta P}{L} = \left(\frac{\lambda}{d}\right)\left(\frac{\rho}{2}\right)u^2 \quad (3)$$

- u average fluid velocity
- $\Delta P$  pressure difference
- L channel length
- $\rho$  fluid density
- d hydraulic diameter
- $\lambda$  friction factor

The hydraulic diameter is defined as  $4 \times (\text{area})/(\text{circumference})$  for the rectangular channels. Using the Reynolds ( $Re = ud/\nu$ ) number based on the hydraulic diameter, the friction factor is approximately  $\lambda = 64/Re$ . If the hydrostatic pressure difference resulting from a density difference of  $4.9 \times 10^{-6} \text{ g/cm}^3$  is used in equation 3, the fluid velocities through the bottom three channels are  $3.02 \times 10^{-3}$ ,  $2.14 \times 10^{-3}$ , and  $0.73 \times 10^{-3} \text{ cm/s}$  respectively, beginning with the bottom channel. For these velocities the entrance length for fully developed flow [ $Le = (0.035)(d)(Re)$ ] is much less than the channel length. This condition and an assumption of quasisteady flow are required in order to apply equation 3. If the total volume of fluid transferred from the left to the right chamber is calculated using these flow velocities, the extent of mixing after 3162 sec ( $\log t = 3.5$ ) is calculated to be 18.7 percent. This is close to the experimental value of 12.0 percent in figure 3. Numerical computations and computer models are currently being developed to provide a more accurate description of the flow.

Since the denser solution emerging from the channels flows like a waterfall to the bottom of the chamber, the vertical flow velocity must be much larger than the horizontal velocity. This can be explained using simple scaling arguments (ref. 5). The relative importance of various transport processes is determined by calculating the magnitude of appropriate dimensionless parameters. The parameters of interest are the Grashof number, Gr, and the Schmidt number, Sc, which are defined below.

$$Gr = \frac{g(\Delta\rho)L^3}{\rho\nu^2} \quad (4)$$

$$Sc = \frac{\nu}{D} \quad (5)$$

- g    gravitational acceleration
- $\rho$     average density
- $\Delta\rho$     density difference
- L    characteristic length
- $\nu$     kinematic viscosity
- D    diffusion coefficient of dye

Using  $\Delta\rho = 4.9 \times 10^{-6}$  g/cm<sup>3</sup>,  $\rho = 1.00$  g/cm<sup>3</sup>,  $g = 980$  cm/s<sup>2</sup>,  $L = 4.45$  cm,  $\nu = 0.00804$  cm<sup>2</sup>/s, and  $D = 3 \times 10^{-6}$  cm<sup>2</sup>/s in equations 4 and 5 gives,  $Gr = 6.6 \times 10^3$ ,  $Sc = 2.7 \times 10^3$ , and  $ScGr = 1.8 \times 10^7$ . An order of magnitude estimate of the vertical fluid velocity can be calculated from equation 6 or 7 (ref. 5).

$$v = Gr^{1/2} \left( \frac{\nu}{L} \right) \quad (\text{for } Gr \gg 1) \quad (6)$$

$$v = Gr \left( \frac{\nu}{L} \right) \quad (\text{for } Gr \ll 1) \quad (7)$$

Using equation 6 the vertical fluid velocity is 0.146 cm/s. As expected, this is much larger than the horizontal velocities calculated above. A boundary layer thickness ( $\delta$ ) of 0.75 cm is estimated using equation 8 (ref. 5).

$$\frac{\delta}{L} = \frac{1}{Gr^{1/4}} \quad (8)$$

This is within order of magnitude agreement with the observed thickness of 0.2 cm.

So far it has been implicitly assumed that the motion of the dye molecules represents the motion of the fluid. The validity of this assumption depends on  $ScGr$  as described in equations 9 and 10.

$$ScGr \ll 1 \quad \left( \begin{array}{l} \text{diffusion} \\ \text{dominant} \end{array} \right) \quad (9)$$

$$ScGr \gg 1 \quad \left( \begin{array}{l} \text{convection} \\ \text{dominant} \end{array} \right) \quad (10)$$

Since  $ScGr \gg 1$ , transport of the dye by molecular diffusion is much slower than by convection, and the motion of the dye does represent convection of the fluid. Diffusion is not important unless  $(\Delta\rho)g \ll 2.7 \times 10^{-10}$  0/cm<sup>2</sup>-s<sup>2</sup>. This requires matching densities to within  $10^{-7}$  g/cm<sup>3</sup> for a space experiment or  $10^{-13}$  g/cm<sup>3</sup> for a ground based experiment. Use of such small density differences is not experimentally feasible. Furthermore, the time scale of a diffusion controlled experiment would be too long to be of practical interest. Therefore, changes in the geometry of the apparatus in figure 1 would be required in order to conduct a diffusion controlled experiment.

It remains to be determined whether or not matching the  $(\Delta\rho)g$  product is sufficient for simulation of fluid flows. Within the chambers it has been

shown that molecular diffusion is not important, so that the only important dimensionless group is  $Gr$ . For Poiseuille flow between the chambers the mass transfer rate is proportional to  $(\Delta\rho)g/\rho\nu$ . Since flow between chambers depends on viscosity as  $1/\nu$  and flow within the chambers depends on viscosity as  $1/\nu^2$ , the overall process can not be simulated unless the solution viscosities are the same in both ground based and space experiments. However, both the viscosity and density of most organic and aqueous solutions containing moderate concentrations of low molecular weight solutes do not vary by more than one order of magnitude. As a result, matching the  $(\Delta\rho)g$  product should provide reasonable (but not exact) simulation in most cases of interest.

### CONCLUSIONS

The fluid flow which occurs during counterdiffusion type crystal growth experiments in space can be studied using ground based simulations. For isothermal mixing of solutions, approximate simulation can be accomplished by matching the  $(\Delta\rho)g$  product. Density differences as small as  $10^{-6}$  g/cm<sup>3</sup> can be easily obtained using isotopic mixtures. For experiments with a geometry similar to that in figure 1, natural convection is expected to be the dominant mode of transport for both space and ground based experiments if the direction of the gravitational acceleration is perpendicular to that of the initial density gradient. The experimental approach to ground based simulation and the scaling analysis described in this paper can be generally applied to other systems with horizontal composition gradients in a vertical gravitational field.

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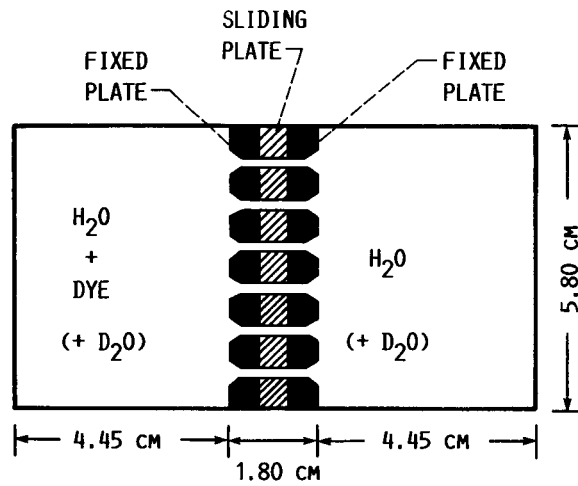


FIGURE 1.- CROSS SECTION OF 2 CHAMBER MIXING CELL USED FOR GROUND-BASED EXPERIMENTS.

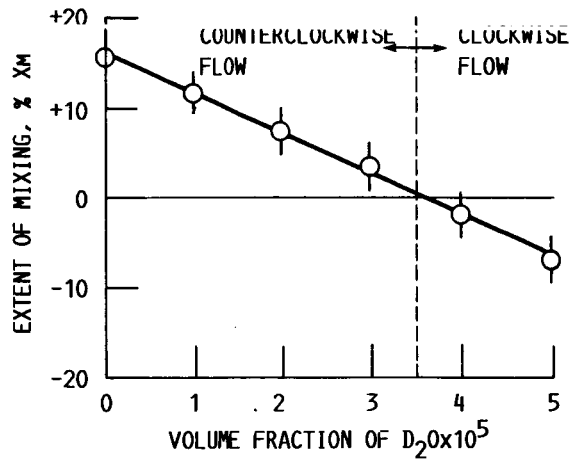


FIGURE 2.- EXTENT OF MIXING AFTER TWO HOURS VERSUS VOLUME FRACTION OF D<sub>2</sub>O IN RIGHT CHAMBER. LEFT CHAMBER CONTAINS 0.01 G/L METHYLENE BLUE DYE. H<sub>2</sub>O IS THE SOLVENT IN BOTH CHAMBERS.

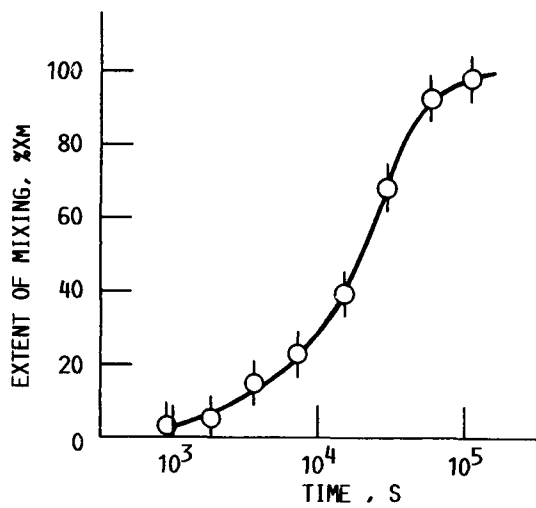


FIGURE 3.- EXTENT OF MIXING VERSUS TIME FOR INITIAL DENSITY DIFFERENCE BETWEEN CHAMBERS OF  $4.9 \times 10^{-6} \text{ g/cm}^3$ .

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