

EFFECT OF GRAVITY LEVEL ON THE PARTICLE SHAPE AND SIZE DURING ZEOLITE CRYSTAL GROWTH

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Abstract

A microscopic diffusion model is developed to represent solute transport in the boundary layer of a growing zeolite crystal. This model is used to describe the effect of gravity on particle shape and solute distribution. Particle dynamics and crystal growth kinetics serve as the boundary conditions of flow and convection-diffusion equations. A statistical rate theory is used to obtain the rate of solute transport across the growing interface, which is expressed in terms of concentration and velocity of solute species. Microgravity can significantly decrease the solute velocity across the growing interface compared to its earth-based counterpart. The extent of this reduction highly depends on solute diffusion constant in solution. Under gravity, the flow towards the crystal enhances solute transport rate across the growing interface while the flow away from crystals reduces this rate, suggesting a non-uniform growth rate and thus an elliptic final shape. However, microgravity can significantly reduce the influence of flow and obtain a final product with perfect spherical shape. The model predictions compare favorably with the data of space experiment of zeolites grown in space.

Introduction

The growth of crystals in microgravity has been a potentially attractive means of producing large crystals. This has been attributed to the reduction of density-driven convection and suspension of growing crystals in the nutrient pool¹⁻³. It is generally believed that convection at the interface of the growing particle plays a significant role in determining the growth rate and the final shape of crystals. In the presence of gravity, the density-driven convection that arises from the density difference between the fluid in the depletion zone and that in the bulk, and the forced convection that arises from particle sedimentation during crystal growth from solution affect solute transport across the growing interface and, in turn, the particle shape⁴. In particular, flow towards the crystal enhances the solute transport rate across the growing interface while the flow away from crystal reduces this rate, suggesting a non-uniform growth and an elliptic crystal shape. Microgravity in an orbiting spacecraft could help isolate the effects of natural convection and minimize sedimentation⁵. This is expected to promote larger perfect crystals by reducing the convection and allowing a longer residence time in a high-concentration nutrient field. Although this size increase and shape optimization in microgravity have been observed, our understanding of the underlying mechanism of the influence of variable gravity on solute transport and particle shape is still rather limited. The objective of this paper is to develop a theoretical model to quantify these relationships.

Zeolite crystal growth is a process of transporting solute species from the solution to the crystal surface and then incorporating them into the crystal surface at the kink⁶. As a crystal grows from the solution, it depletes the solute species, producing a concentration-depleted zone around it. In this region, the solute concentration

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changes continuously from the value at the crystal surface to that in the bulk solution. The concentration profile in the depletion zone varies with time as the crystal grows and is controlled by the balance between the flow of solute species towards the crystal surface and the rate of incorporation of these solutes into the crystal lattice. The kinetics of incorporation at the surface is linked to the bond configuration of the crystallographic structure, while the flow towards the surface is highly dependent on the mass transport properties in the bulk solution, which turn out to be crucial for the overall crystal-growth process. The diffusive transport through the depletion zone around a growing crystal is therefore responsible for any observable difference between on-ground and microgravity experiments including crystal quality enhancement.

Although a number of experiments have been performed on crystal growth and shape evolution both under gravity and microgravity, there is no theoretical model to describe particle shape evolution and kinetics of mass transport in the boundary layer of a growing crystal. Carotenuto et al.⁷ performed an order-of magnitude analysis of natural convection during solidification and crystallization in microgravity. This model however does not account for the motion of the crystal and the kinetics of mass transport. The shape evolution as the crystal grows under microgravity is also not addressed.

A model is developed to describe the crystal growth and shape evolution by integrating particle dynamics with the convection-diffusion equation in the boundary layer around the growing crystal. Specifically, particle dynamics is used to obtain the drag force and relative velocity between the particle and the solution, while the convective diffusion equation is used to describe the solute distribution and thus the mass flux across the growing interface. Equally important is studying the impact of variable gravity on evolution of particle shape both on ground and in microgravity. The model is validated by comparison of its predictions with a recent set of experimental data on zeolite crystal growth.

Formulation

Particle Dynamics

We consider a spherical crystal particle growing in an incompressible solution. As shown in Fig.1, the crystal falls down in the presence of gravity due to the difference in density. A boundary layer thus develops around the particle with different solute concentration from the bulk. The integro-differential equation governing the motion of the growing crystal can be expressed as⁸:

$$m_p \frac{dV_p}{dt} = (m_p - m_f)g + F \quad (1)$$

where V_p is the velocity of the particle, m_p is the mass of the particle, m_f is the fluid mass which has the same volume as particle, g is the gravity, and F is the hydrodynamic force associated with the fluid movement. Typically, the first term on the right side of Eq.(1) represents the buoyancy force and the second results from the fluid motion about the particle. For the viscous low Reynolds number flow, the hydrodynamic force can be expressed as⁹:

$$F = 6\pi\mu RV_p. \quad (2)$$

where μ is the viscosity and R is the radius of the particle.

Typically, once nucleated in solution, the crystal will accelerate until it reaches a terminal velocity in the presence of the gravity. The acceleration time and the terminal velocity are strongly dependent on the particle size R , the density ratio of particle to solution δ , and the viscosity of solution μ . For an unbound solution at rest, the acceleration time of a spherical particle can be expressed by¹⁰:

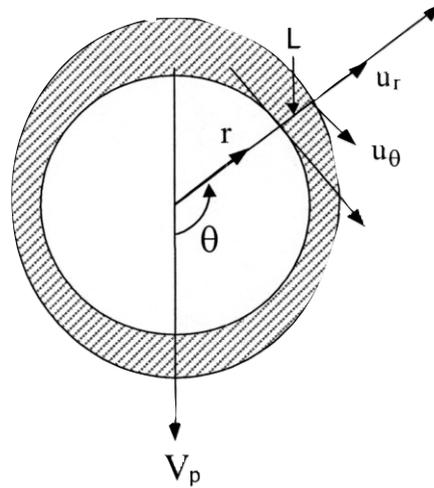


Figure 1. Schematic of the boundary layer or depletion zone around the crystal.

$$\tau_{acc} = \frac{2}{9} \frac{\rho \delta}{\mu} R^2 \quad (3)$$

and the terminal velocity of particle can be expressed by

$$V_p = \frac{2}{9} \frac{\rho g (\delta - 1)}{\mu} R^2 \quad (4)$$

where ρ is the density of the solution. For zeolite particles with a size in the range 0.01-10 μm settling in a solution with a viscosity of 10^{-3} kg/m \cdot s under gravity of 9.81 m/s 2 , the particle acceleration time will be in the range $4.4 \times 10^{-11} \sim 10^{-5}$ seconds. Therefore, it is reasonable to assume that the growing crystal will fall at a steady state.

Governing Equation for Flow in the Boundary Layer

Within this framework, the governing equations for continuity, Navier-Stokes, and convection-diffusion of solute species in the boundary layer of growing crystal can be expressed as¹¹:

$$\nabla \cdot u = 0 \quad (5)$$

$$\frac{\partial u}{\partial t} + (u \cdot \nabla) u = -\frac{1}{\rho} \nabla p + \nu \nabla^2 u + g \quad (6)$$

$$\frac{\partial c}{\partial t} + (u \cdot \nabla) c = D \nabla^2 c \quad (7)$$

where u is the velocity of fluid, p is the pressure, t is time, c is the concentration of the solute species, and D is its diffusivity and ν is the kinematic viscosity of solution. We impose the Boussinesq-Oberbeck approximation in which physical parameters are assumed constant everywhere but in the momentum generation term of the equations above.

This approach amounts to assuming the bulk acts as a nutrient pool for the crystal. When r approaches infinity, the velocity of solution reaches the terminal velocity of particle and the solute concentration is assumed to be a constant c_b . The boundary for the convection-diffusion equation is expressed using the transport rate of solute across the interface between the crystal and the solution thus:

$$J = -D \left(\frac{\partial c}{\partial r} \right)_{r=R} \quad (8)$$

The kinetics of crystal growth dictates that this flux is related to the solute supersaturation as¹²:

$$-D \left(\frac{dc}{dr} \right)_{r=R} = K_e \left(\frac{c_i}{c_s} - \frac{c_s}{c_i} \right) \quad (9)$$

where c_i is the solute concentration at the interface, c_s is the equilibrium concentration and K_e is the equilibrium exchange rate between the solution and crystals. The equilibrium exchange rate can be expressed as a combination of two terms¹², thus:

$$K_e = K_r c_s \sqrt{T} - K_c c_s u_r(L) \quad (10)$$

where T is the temperature, $u_r(L)$ is the radial velocity of solute molecules at the edge of the boundary layer whose thickness is L , and K_r and K_c are two empirical constants. The first term of Eq.(10) is the rate that would exist if the solution were static, and the second term results from the convection due to the sedimentation of growing crystals.

We assume the concentration in the bulk is constant throughout the growth process. Thus, the portion of solution outside of the diffusion layer is approximated as a reservoir that has a given concentration. Since the concentration in the bulk is assumed unchanged by the growth process, strictly speaking the system cannot reach equilibrium.

Crystal Growth and Morphology

The morphology of the crystal strongly depends on the growth rates of the different crystallographic faces. According to Bravais rule, the important faces governing the crystal morphology are those with the highest reticular densities and the greatest interplanar distances. Or, in simpler terms, the slowest-growing and most influential faces are the closed-packed and have the lowest Miller indices. The growth of a given face is typically governed by the crystal structure and defects on the one hand, and by the environmental conditions especially the flow on the other. A reasonable evolution of the crystal size can therefore be written as a function of solute molecule flux across the growing interface, thus:

$$\frac{dR}{dt} = \frac{J}{\rho_c} \quad (11)$$

where ρ_c is the crystal density.

A change in the flow environment can influence the shape of the growing crystal. Due to the symmetry, we consider the shape change along the principal axis in the plane of gravity such that a two-dimensional shape is considered as shown in Fig.1. Therefore, the ratio η of the minor axis (gravity direction) to the major axis (sectional) can be used to describe the evolution of shape of elliptic crystal as it grows, thus:

$$\eta = \frac{R_{\parallel}}{R_{\perp}} \quad (12)$$

where R_{\parallel} and R_{\perp} are the radii of the growing crystal in the gravitational and sectional directions, respectively. Numerically, this ratio equals one when the crystal is spherical.

Computational Details

The equations governing the flow and solute transport are solved with the SIMPLEC algorithm embodied in the CFD-ACE software code. This code uses a control volume based finite difference formulation with upwind difference for convective fluxes.

Having discussed the crystal growth from solution, we shift our attention on the boundary layer around the crystal. We will present a dynamic simulation of crystal growth. To handle this simulation, a structured multiblock scheme is developed with multizone adaptive grid generation (MAGG) algorithm to avoid the stretching and compression of grids. The crystal growth system can be divided into three blocks: crystal, boundary and bulk block. The grids in each block can be generated and moved adaptively independent of other blocks. The crystal block becomes larger and the bulk becomes small as the crystal surface moves outward. The efficiency and accuracy of the dynamic simulation of crystal growth can be improved by using this algorithm. The values of the principal input parameters used in the computation are presented in Table 1.

Table 1. Parameter values used in calculations.

Parameter	Value
Kinematic viscosity ν (m ² /s)	1.12×10^{-6}
Solution density ρ (kg/m ³)	1×10^3
Crystal density ρ_c (kg/m ³)	2×10^3
K_r (m/sK ^{1/2})	6×10^{-11}
K_c	3×10^{-9}

Results and Discussion

Figure 2 shows the solute velocity across the crystal surface as a function of gravity level and solute concentration ratio at interface to bulk for solute diffusion constant (a) 1.0×10^{-5} m²/s, (b) 1.0×10^{-7} m²/s and (c) 1.0×10^{-9} m²/s, respectively. It is seen that the solute velocity decreases as the gravity level decreases and the solute concentration ratio at the interface to the bulk increases. At high diffusion constant as shown in Fig. 2a, variable gravity does not affect the solute flux. However, for a low diffusion constant as shown in Fig. 2b and 2c, microgravity can decrease the solute flux to 20% and 70 % of ground value, respectively. This is due to the fact that the solute transport is mainly controlled by diffusion at high diffusion constant while the convection-controlled transport can compete to the diffusion-controlled transport at a low diffusion constant. In addition, for three diffusion constants tested, gravity levels in the range of 1.0×10^{-2} - 10^{-5} m/s² have no significant effect on solute flux. There are several solute species involved in zeolite crystal growth from solution. The diffusion constants of these species are typically in the range of 10^{-5} - 10^{-12} m²/s. As the gravity level decreases, the transport of solute species with low diffusion constants will play a more significant role in crystal growth.

Two cases are considered for crystal growth dictated by the type of boundary conditions on solute transport. The first assumes a fixed relative solute concentration at the growing interface. This case corresponds to a system in which crystal growth process locks the solute concentration at a fixed value at the growing interface. The predicted results are presented in Fig. 3 to 5. The second uses the boundary conditions expressed in Eqs.(9) and (10) where the parameters are presented in Table 1. This condition implies a diffusion-controlled mechanism of crystal growth. The predicted results are presented in Fig.6 to 8.

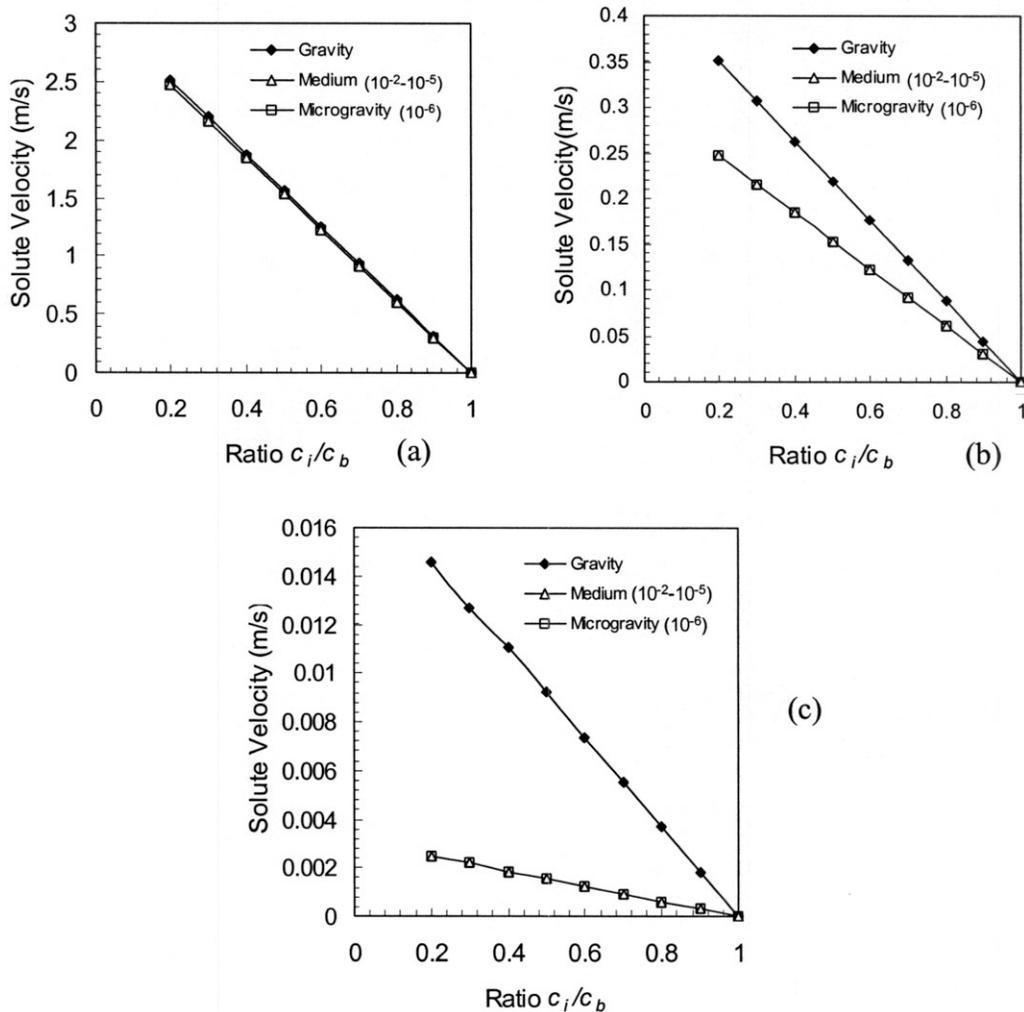


Figure 2. Solute velocity across the growing interface as a function of concentration ratio and gravity level for solute diffusion constant (a) $1.0 \times 10^{-5} \text{ m}^2/\text{s}$, (b) $1.0 \times 10^{-7} \text{ m}^2/\text{s}$ and (c) $1.0 \times 10^{-9} \text{ m}^2/\text{s}$.

Figure 3 shows the evolution of particle shape and solute concentration profile as the crystal grows on ground (a) and in microgravity (b). Buoyancy-induced convection dominates solute transport around the crystal on the ground and induces a thinner concentration-depletion boundary layer around the crystal than in microgravity. On the other hand, mass transport is governed by diffusion in microgravity producing a thicker depletion zone where the concentration gradient is considerably lower than on earth. More importantly, density-driven convection under gravity produces a solute-poor region on the upper position of the crystal. In this region, the flow away from the crystal reduces the frequency with which the solute species collide with the crystal surface. Coupled with the low solute concentration gradient close to the crystal surface, growth in this part is considerably slower than other regions around the crystal.

Figure 4 shows the crystal growth rate in the three directions on the ground (a) and in microgravity (b). The overall growth rate decrease as the crystal grows in both cases. This is due to the progressive decrease in solute concentration gradient close to the crystal surface. The growth rate in microgravity is lower than that on ground by one order of magnitude, consistent with space experiments on zeolite crystal growth. There are significant differences in the growth rate in the three directions on ground. The growth rate in the

direction $\theta = 180^\circ$ is nearly four times that for $\theta = 0$ because of density-induced convection. The difference in the growth rate between the directions is insignificant in microgravity, as would be expected.

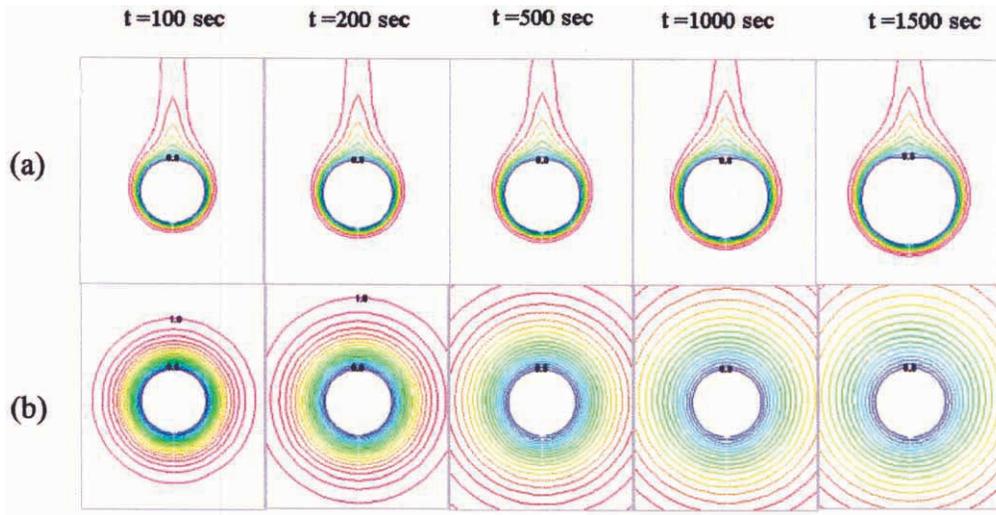


Figure 3. The evolution of particle shape and solute as the crystal grows with a fixed solute concentration ratio of interface to bulk for (a) gravity (9.80) and (b) microgravity (10^{-6}).

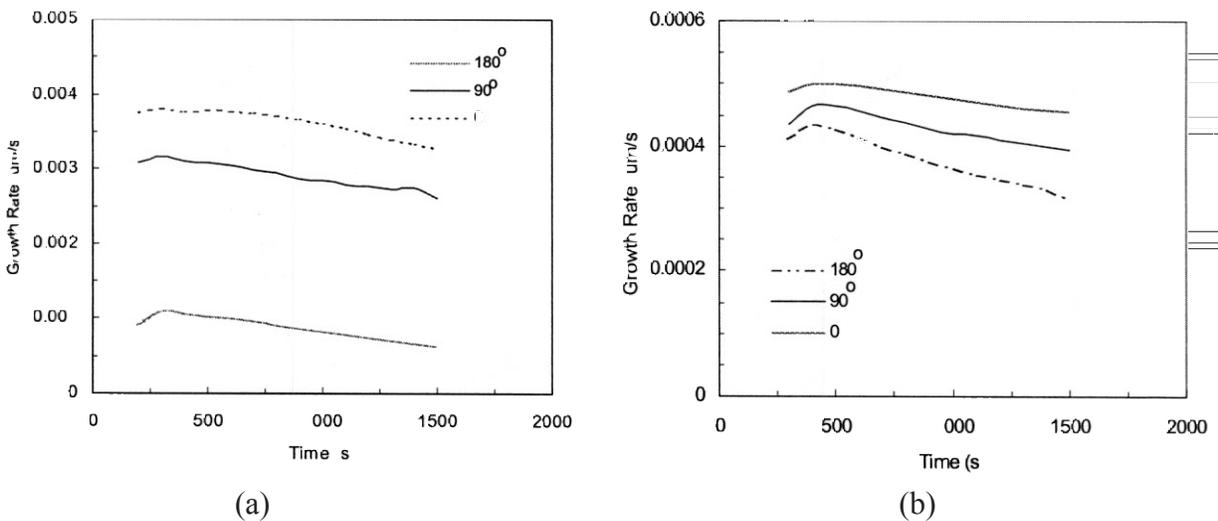


Figure 4. The crystal growth rate in three directions (θ) with a fixed solute concentration ratio of interface to bulk for (a) gravity (9.80) and (b) microgravity (10^{-6}).

The evolution of shape parameter η as the crystal grows on ground and in microgravity is presented in Fig. 5. The curve for $\eta = 1$ representing a spherical shape is also presented for comparison. The crystal that grows in microgravity keeps the spherical shape while the crystals grown on the ground would be predicted to evolve into an ellipsoid. This is largely due to non-uniform growth rate on the ground under the influence of density-driven convection while uniform growth rate is maintained in microgravity.

Figure 6 shows the evolution of particle shape and solute profiles as the crystal grows on the ground (a) and in microgravity (b). Buoyancy-induced convection deeply affects the solute transport in the boundary layer as the crystal falls down on ground. However, this influence is not significant due to the slow growth

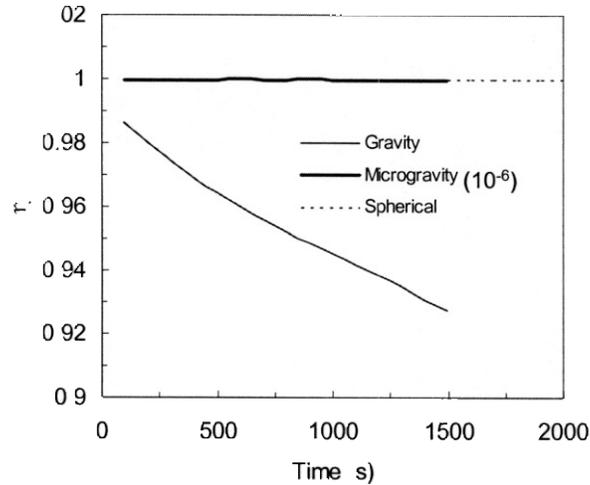


Figure 5. The evolution of parameter η as the crystal grows with a fixed solute concentration ratio of interface to bulk.

rate that is dependent on solute concentration near the crystal surface. Mass transport is governed by diffusion as the crystal grows in microgravity.

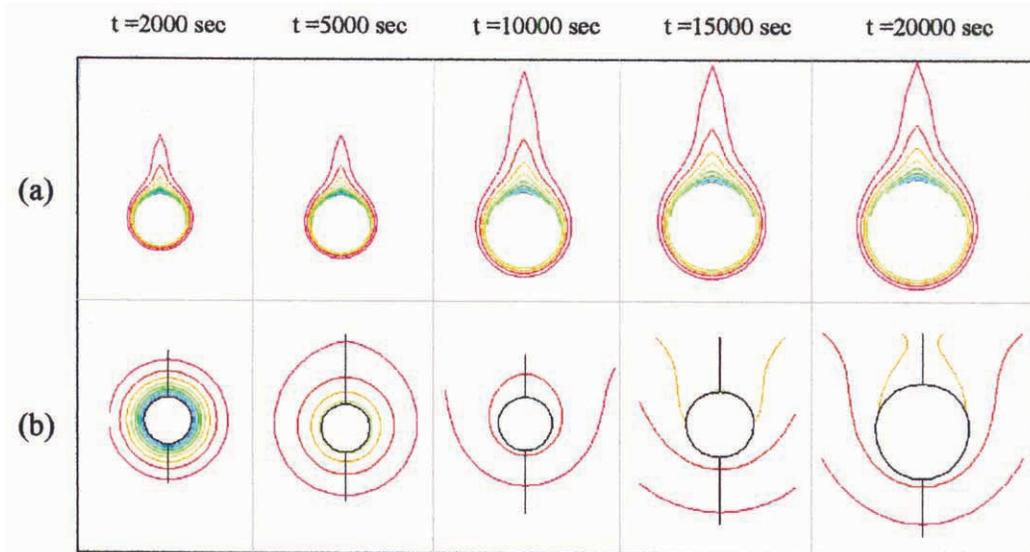


Figure 6. Evolution of particle shape and solute as the crystal grows with $K_I=6.0 \times 10^{-11}$ and $K_C=3.0 \times 10^{-9}$ and $T=100^\circ\text{C}$ for (a) gravity (9.80) and (b) microgravity (10^{-6}).

The growth rates of crystal as a function of θ and gravity level are presented in Fig. 7. The growth rate on the ground varies with θ since natural convection and diffusion jointly govern solute transport in the boundary layer. In microgravity, the variation of the growth rate with θ is relatively small due to the suppression of natural convection.

The evolution of shape parameter η as the crystal grows on ground and in microgravity is presented in Fig. 8. The variation of growth rate with θ results in an elliptic shape on ground and a nearly spherical shape in microgravity.

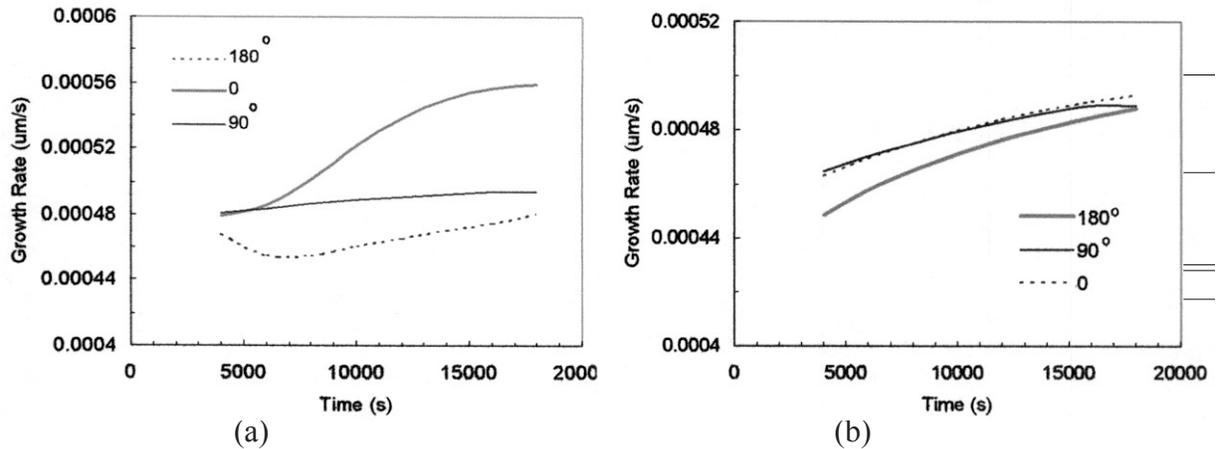


Figure 7. The crystal growth rate in three directions (θ) with $K_R = 6.0 \times 10^{-11}$ and $K_C = 3.0 \times 10^{-9}$ and $T = 100^\circ\text{C}$ for (a) gravity (9.80) and (b) microgravity (10^{-6}).

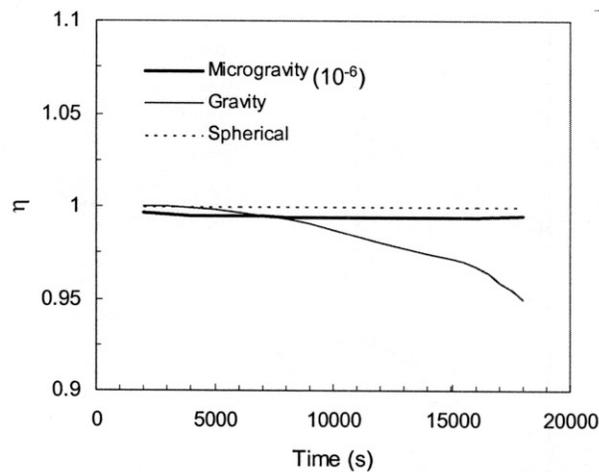


Figure 8. The evolution of parameter η as crystals grow with $K_R = 6.0 \times 10^{-11}$ and $K_C = 3.0 \times 10^{-9}$ and $T = 100^\circ\text{C}$ both on ground (9.80) and in microgravity (10^{-6}).

Conclusions

We developed a microscopic diffusion model for the solute transport in the boundary layer to describe the influence of gravity on crystal shape and solute distribution. The full particle dynamics and crystal growth kinetics are considered in expressing the boundary conditions for the governing equations. A statistical rate theory is used to obtain the rate of solute transport across the growing interface. The latter is expressed in terms of concentration and velocity of solute species. Microgravity can significantly decrease the solute velocity across the growing interface compared to its earth-based counterpart. The extent of this reduction highly depends on solute diffusion constant in solution. Under gravity, the flow towards the crystal enhances solute transport rate across the growing interface while the flow away from the crystal reduces this rate, suggesting a non-uniform growth rate and resulting in an elliptic final shape. Microgravity significantly suppresses the flow, giving a final product with spherical shape.

Acknowledgements

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