

The object of this column is to enhance our readers' collection of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professors James O. Wilkes and Mark A. Burns, Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

CZOCHRALSKI CRYSTAL GROWTH MODELING

A Demonstrative Energy Transport Problem

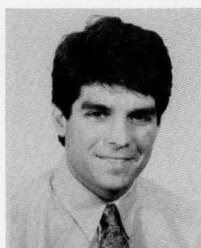
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The development of new and interesting transport phenomena examples and problems that can be solved using relatively simple mathematical tools can be a challenge. This is especially true when teaching an undergraduate course in transport phenomena where the students have little or no experience solving partial differential equations. There are, unfortunately, a finite number of physically meaningful problems one can formulate that lead to linear, ordinary differential equations (even with three coordinate systems and several types of boundary conditions to choose from).

This paper presents an energy transport problem that is both instructive and interesting; it can be used to demonstrate

- the use of dimensional analysis
- the quasi-steady state approximation
- the fin approximation

As the example progresses, students see an "intimi-



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dating" PDE transformed into an innocent ODE through the introduction of several physically reasonable assumptions. The novelty of the example arises from the fact that it applies to a technology not traditionally associated with chemical engineers, although it is one that virtually all engineers use.

INTRODUCTION

The example arises from an energy transport analysis of a process widely used in the semiconductor device industry. The process, known as Czochralski Crystal Growth (CZCG), is used to produce single-crystal, defect-free ingots of Si (and similar materials) which are subsequently sliced into thin disks (or "wafers"), polished, and used as substrates in the fabrication of microelectronic devices, or "computer chips." The example or problem might be introduced by giving a short description of the process.

CZCG is a batch process initiated when a seed crystal is dipped into a melt of the same material so that the liquid wets the seed crystal. As solidification occurs, the seed is slowly withdrawn from the melt so that a neck and shoulder are grown. Once the desired radius is achieved, a nearly cylindrical crystal is grown by manipulation of the pull rate and/or melt temperature.

It should be noted that even for the simplified description of CZCG given above, a high level of complexity is required to develop detailed transport models. The presence of a number of free bound-

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aries (at the crystal-melt, crystal-ambient, and melt-ambient interfaces), radiative heat transfer, and temperature-dependent physical properties all make the problem highly non-linear. Detailed transport models which account for these phenomena require numerical solution on large computers. An excellent review of the CZCG and other crystal growth processes along with discussions on the importance of various transport processes can be found elsewhere.^[1]

PROBLEM FORMULATION AND ANALYSIS

Before they are presented with this example, students should have been exposed to the appropriate energy transport phenomena fundamentals: conservation laws (either by the shell balance^[2] or Reynolds Transport Theorem^[3] approach), constitutive equations, and boundary conditions.

For the example, we will consider a relatively simple model of the CZCG process that describes energy transport within the cylindrical crystal. A schematic diagram of the process is shown in Figure 1, which indicates the position of the coordinate system. Results from this analysis could be used to estimate thermoelastic stresses (due to temperature gradients), which can lead to crystal defects, or used to find relationships between crystal length, growth rate, and melt temperature. The assumptions to be used in the development of the model are

1. Axial symmetry in the crystal.
2. All physical properties are isotropic and independent of temperature.
3. Heat transfer between the crystal and the ambient

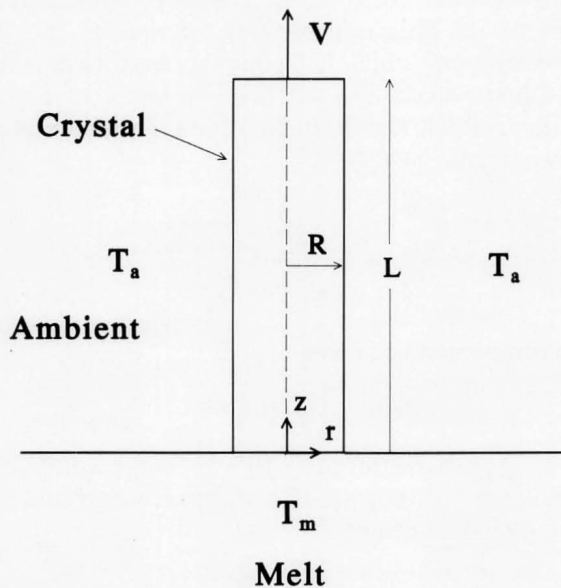


Figure 1. Schematic diagram of Czochralski Crystal Growth (CZCG) process.

can be described by a convective heat transfer law to an ambient temperature that is independent of time and position.

4. Heat transfer between the crystal and the melt can be described by a convective heat transfer law to a melt temperature that is independent of position.
5. The velocity of the crystal (pull rate) is constant.
6. The crystal-melt interface is planar and fixed at the origin of the coordinate system.

Assumptions 1 to 6 lead to the following for the thermal energy equation and boundary conditions:

$$\frac{\partial T}{\partial t} + V \frac{\partial T}{\partial z} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] \quad (1)$$

$$T(r, z, 0) = T_f \quad 0 \leq r < R; 0 < z < L(0) \quad (2)$$

$$T(r, 0, t) = T_f \quad 0 \leq r < R; t > 0 \quad (3)$$

$$-k \frac{\partial T}{\partial z}(r, L(t), t) = h_a [T(r, L(t), t) - T_a] \quad 0 \leq r < R; t > 0 \quad (4)$$

$$-k \frac{\partial T}{\partial r}(R, z, t) = h_a [T(R, z, t) - T_a] \quad 0 < z < L; t > 0 \quad (5)$$

where $\alpha = k / \rho C_p$. The (jump) energy balance at the crystal-melt interface gives

$$-k \left\langle \frac{\partial T}{\partial z}(r, 0, t) \right\rangle = h_m [T_m(t) - T_f] + \rho V \Delta H_f \quad t > 0 \quad (6)$$

where $\langle \rangle$ indicates a radially averaged quantity. A list of the dimensional variables that appear in this set of equations can be found at the end of this paper.

Equations (1) to (5) define the linear boundary value problem (BVP) for $T(r, z, t)$. The boundary conditions given by Eqs. (4) and (5) simply relate the conductive and convective energy fluxes at the crystal-ambient interfaces according to assumption 3. Equation (6) is an energy balance for the crystal-melt interface that must be satisfied so that a constant radius crystal is grown by manipulation of the melt temperature, $T_m(t)$. If T_m is made constant, then the crystal velocity V , rather than the melt temperature, is manipulated to maintain a constant radius crystal. In this case, Eq. (6) would be solved for the crystal velocity which would be a function of the temperature gradient at $z = 0$ rather than a constant. Hence, Eqs. (1) to (6) would constitute a non-linear BVP since Eq. (1) would be non-linear (due to the convective term) and because the moving boundary $L(t)$ would be a function of the dependent variable rather than some external influence. In this case, assumptions 4 and 5 would, of course, be modified.

Although the problem defined by Eqs. (1) through (6) can be solved analytically, we will try to find

ways to simplify it using several additional assumptions. To begin, we first put the equations in dimensionless form using

$$\xi = \frac{r}{R} \quad \sigma = \frac{z}{R} \quad \tau = \frac{\alpha t}{R^2} \quad \phi = \frac{T - T_a}{T_f - T_a}$$

Substitution of the above definitions into Eq. (1) gives

$$\frac{\partial \phi}{\partial \tau} + Pe \frac{\partial \phi}{\partial \sigma} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial \phi}{\partial \xi} \right) + \frac{\partial^2 \phi}{\partial \sigma^2} \quad (7)$$

where Pe is a dimensionless group

$$Pe = \frac{VR}{\alpha} \quad \text{Peclet No.}$$

The problem at hand would be much simpler if it were a steady-state problem, but unfortunately no steady-state exists because the length of the crystal is a function of time: $V = dL(t)/dt$. Suppose, however, that we could neglect the unsteady term in Eq. (7) but still allow the length of the crystal to change. Under what conditions would this be a good assumption? To answer, let us consider the time scale for energy transfer (t_E) and the time scale associated with a change in the length of the crystal (t_L). If $t_E \ll t_L$, i.e., conduction along the length of the crystal is instantaneous compared to the time required for the length to change, then neglecting the unsteady term in Eq. (7) would seem reasonable. Of course, what we are saying is that the quasi-steady state approximation (QSSA) would be valid. If we let $t_E = L^2/a$ and $t_L = L/V$, then we have

$$\frac{t_E}{t_L} = \frac{VL}{\alpha} \ll 1 \quad L \ll \frac{\alpha}{V}$$

For CZCG growth of Si, $\alpha \sim 10^{-1}$ cm²/sec and $V \sim 10^{-3}$ cm/sec, so that the QSSA will be valid if $L < \sim 100$ cm. We will later see the QSSA will also be valid for much greater crystal lengths. Thus we will add the following assumption to our list:

7. The quasi-steady state approximation is valid.

The complete problem in dimensionless form is now given by

$$Pe \frac{\partial \phi}{\partial \sigma} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial \phi}{\partial \xi} \right) + \frac{\partial^2 \phi}{\partial \sigma^2} \quad (8)$$

$$\phi(\xi, 0) = 1 \quad 0 \leq \xi < 1 \quad (9)$$

$$\frac{\partial \phi}{\partial \sigma}(\xi, A) + Bi_a \phi(\xi, A) = 0 \quad 0 \leq \xi < 1 \quad (10)$$

$$\frac{\partial \phi}{\partial \xi}(1, \sigma) + Bi_a \phi(1, \sigma) = 0 \quad 0 < \sigma < A \quad (11)$$

$$\left\langle \frac{\partial \phi}{\partial \sigma}(\xi, 0) \right\rangle + Bi_m [\phi_m - 1] = Pe St \quad (12)$$

which includes the following dimensionless groups:

$$A = \frac{L}{R} \quad \text{Aspect Ratio}$$

$$Bi_i = \frac{h_i R}{k} \quad \text{Biot No. for ambient (i=a) or melt (i=m)}$$

$$St = \frac{C_p \Delta H_f}{T_f - T_a} \quad \text{Stefan No.}$$

The solution to Eqs. (8) through (11) can now be found by the separation of variables method for $\phi(\xi, \sigma)$, and Eq. (12) can be evaluated for the dimensionless melt temperature, ϕ_m . For the case when $Pe \rightarrow 0$, one might have the students find the solution in the literature.^[4]

Let us see if there are other physical arguments that will further simplify our CZCG model. For stages of the process when the crystal is long ($A \gg 1$), it would seem reasonable to expect the temperature variation in the z-direction to be much greater than in the r-direction. Does this mean that neglecting the radial conduction term in Eq. (8) would be a good assumption? While this seems like a good idea at first glance, we remind the students that in doing so we are in effect saying that the cylindrical surface of the crystal is insulated and no energy is transferred across it. For large A, this surface is much larger (2A times) than the surface of the top of the crystal and neglecting the heat transfer from it would be a poor assumption.

Our original argument, however, still seems valid, and it would be nice if we could find some way of simplifying the radial conduction term. Since the variation of T in the r-direction is probably small, suppose we use an average radial temperature to represent it? This approach is, of course, the "fin approximation" which is frequently used to describe finned heated transfer surfaces. In terms of dimensional variables, the definition for average temperature we use is

$$\langle T(z) \rangle = \frac{\int_0^R \int_0^R T(r, z) r dr d\theta}{\int_0^R \int_0^R r dr d\theta} = \frac{2}{R^2} \int_0^R T(r, z) r dr$$

or, in dimensionless form

$$\langle \phi(\sigma) \rangle = 2 \int_0^1 \phi(\xi, \sigma) \xi d\xi \quad (13)$$

Since A can be large ($\sim 10^2$) in a typical CZCG process, we will pursue this approach and add the following assumption:

8. The fin approximation is valid.

Of course, the fin approximation can also be incorporated into the governing equations by the shell

balance approach.^[2]

Integration of Eq. (8) according to Eq. (13) gives

$$Pe \frac{\partial \langle \phi \rangle}{\partial \sigma} = 2 \frac{\partial \phi}{\partial \xi}(1, \sigma) + \frac{\partial^2 \langle \phi \rangle}{\partial \sigma^2} \quad (14)$$

and substitution of the boundary condition given by Eq. (11) in Eq. (14) leads to

$$Pe \frac{\partial \langle \phi \rangle}{\partial \sigma} = -2 Bi_a \phi(1, \sigma) + \frac{\partial^2 \langle \phi \rangle}{\partial \sigma^2}$$

which, since $\phi(1, \sigma) = \langle \phi(\sigma) \rangle$, can be written as

$$\frac{d^2 \langle \phi \rangle}{d\sigma^2} - Pe \frac{d \langle \phi \rangle}{d\sigma} - 2 Bi_a \langle \phi \rangle = 0 \quad (15)$$

Equations (9), (10), and (12), in terms of the radially

averaged temperature, $\langle \phi(\sigma) \rangle$, can be written as

$$\langle \phi \rangle(0) = 1 \quad (16)$$

$$\frac{d \langle \phi \rangle}{d\sigma}(A) + Bi_a \langle \phi \rangle(A) = 0 \quad (17)$$

$$\frac{d \langle \phi \rangle}{d\sigma}(0) + Bi_m [\phi_m - 1] = Pe St \quad (18)$$

Hence, utilization of the quasi-steady state and fin approximations has transformed the original problem (Eqs. 1-6) to the problem given by Eqs. (15) through (18), which the typical junior or senior chemical engineering student can solve.

SOLUTION AND APPLICATIONS

For the sake of space, we present only the solution to the last model, Eqs. (15) through (17), which is given by

$$\langle \phi(\sigma) \rangle = \exp\left[\frac{Pe}{2} \sigma\right] \frac{\cosh\left[\frac{\lambda}{2}(A - \sigma)\right] + \frac{Pe + 2 Bi_a}{\lambda} \sinh\left[\frac{\lambda}{2}(A - \sigma)\right]}{\cosh\left[\frac{\lambda}{2} A\right] + \frac{Pe + 2 Bi_a}{\lambda} \sinh\left[\frac{\lambda}{2} A\right]} \quad (19)$$

where $\lambda = \sqrt{Pe^2 + 8 Bi_a}$. The gradient at the crystal-melt interface is given by

$$\beta = \frac{d \langle \phi \rangle}{d\sigma}(0) = \frac{-Bi_a \cosh\left[\frac{\lambda}{2} A\right] + \frac{Bi_a (Pe - 4)}{\lambda} \sinh\left[\frac{\lambda}{2} A\right]}{\cosh\left[\frac{\lambda}{2} A\right] + \frac{Pe + 2 Bi_a}{\lambda} \sinh\left[\frac{\lambda}{2} A\right]} \quad (20)$$

which can be used in Eq. (18) to find ϕ_m .

This solution can be used to demonstrate various aspects of the heat transfer processes in CZCG. Students can see how the temperature distribution and pull rate depend on the dimensionless groups that arise in the model, which always provides physical insight into their meaning. The temperature distribution predicted by Eq. (19) is shown in Figure 2 for typical values of Bi_a and Pe . One might also point out that a crystal length A_c can be found beyond which the crystal has an effectively infinite length. For $A > A_c$, we can infer that $t_L \rightarrow \infty$, so that the QSSA will be valid for long crystals as was mentioned earlier. A_c can be estimated by plotting the interfacial temperature gradient β from Eq. (20) as a function of crystal length A , as shown in Figure 3.

Another interesting exercise is to have students find the range of Bi_a for which the fin approximation is valid (this turns out to be $Bi_a \sim 0.2$). This can be done by comparing β from Eq. (20) to the radial average of the crystal-melt temperature gradient determined from the two-dimensional model, which

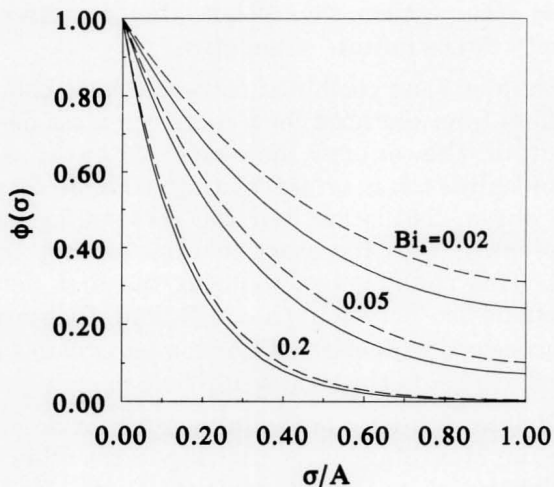


Figure 2. Dimensionless axial temperature distribution from Eq. (19) for the indicated values of Bi_a .

Solid lines: $Pe = 0$; dashed lines: $Pe = 0.1$.

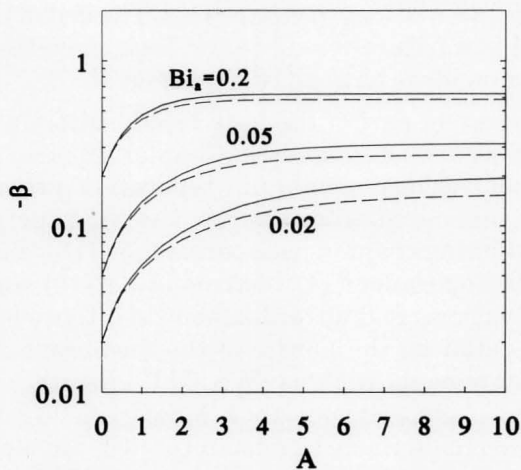


Figure 3. Dimensionless temperature gradient at the crystal-melt interface from Eq. (20) versus crystal length for the indicated values of Bi_a .

Solid lines: $Pe = 0$; dashed lines: $Pe = 0.1$.

can be given in class or derived from results found in the literature.^[4]

The simple model and its solution that have been presented in this paper are most appropriate for an undergraduate-level transport phenomena course. When used in a lecture, it is a compact example that demonstrates the use of two important engineering approximations. At the graduate level, the two-dimensional models (both unsteady and steady) could provide the basis for a good homework or exam problem. The validity of the QSSA can be determined by comparing results from the transient and quasi-steady models. A more realistic transient model could be developed by allowing the crystal-melt interface to move according to a mass balance on a melt of finite volume. In this case, the crystal pull rate and crystal velocity will not be the same.

This type of problem can also be useful to demonstrate techniques for boundary immobilization. There are, of course, many other ways to look at or use this example; they are left for the reader to ponder.

ACKNOWLEDGMENT

The author is grateful to Daniel White, Jr., for bringing the CZCG modeling problem to his attention during an excellent course Dr. White taught at Penn State University in the fall of 1986.

NOMENCLATURE

C_p	specific heat capacity of crystal
h_a	convective heat transfer coefficient to ambient
h_m	convective heat transfer coefficient to melt
ΔH_f	specific enthalpy of fusion
k	thermal conductivity of crystal
L	crystal length
r	radial position
R	crystal radius
t	time
T	crystal temperature distribution
T_a	ambient temperature
T_f	melting temperature of crystal
T_m	melt temperature
V	crystal velocity or pull rate
z	axial position
α	thermal diffusivity of crystal
ρ	density of crystal

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REVIEW: Mass Transfer

Continued from page 117

some problems in using Fickian theories of diffusion when more than two species are present. Chapters 3 and 4 start formulating the M-S theory, but with little mention of it by name. Chapter 3 discusses driving forces for mass transfer, while Chapter 4 considers friction effects. The idea of a "bootstrap" relationship to provide an absolute level of velocity in the M-S equations is introduced in Chapter 4 and is explained with examples in Chapters 5 and 6.

Chapter 5 shows several binary ideal solution examples and notes that the M-S theory gives the same results as Fickian diffusion and is no more difficult to use. Ternary examples are the subject of Chapter 6. The example for distillation is a particularly clear explanation of how the Murphree efficiency can be infinite or negative.

Chapter 7, on combined mass and heat balances, suffers from the need for a more complete description of the energy balance. Chapter 8, on nonidealities, has an interesting example on ethanol water distillation, but the reasons for lack of agreement with the exact solution are not spelled out. This chapter also contains the first detailed comparison between the M-S and Fickian approaches. Moving parts of this comparison to a place much earlier in the book would help many readers.

Chapter 9 briefly presents theories for determining the M-S diffusivities. Driving forces other than activity gradients are the topic of Chapter 10. These include pressure gradients, centrifugal force, support forces (from solid matrices), and electrical forces. With these additional forces, Chapter 11 can look at the diffusion of ions in electrolytes. The end of Chapter 11 is a natural break in the book since the fundamental ideas have all been presented.

The second part of the book briefly covers a variety of separation processes. Chapter 12 is an overview of various membrane separation processes, while individual processes are covered in detail in the following chapters: gas permeation (13), dialysis and pervaporation (14), electrodialysis (15), and reverse osmosis and ultrafiltration (16). There is very little detail on the nature of the membrane itself, and statements such as "We shall treat the membrane as homogeneous," (p. 125, referring to reverse osmosis) could easily be misinterpreted. Supplementation of these sections with a book such as R.E. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective* (2nd ed., Wiley, New York, 1985) is

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