

Film thickness and convection coefficient formulations of k_{eff}

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Abstract

The Burton, Prim and Slichter's BPS model published in 1953 is considered to be of the most useful equations in crystal growth and is presented in most textbooks on solidification. It relates the effective segregation coefficient k_{eff} as a function the stagnant film thickness δ . During the past decades, the shortcomings of the BPS model have been recognized and several new film-thickness based models have been proposed. Here we revisit the film-thickness based models and compare to the recently proposed model, where k_{eff} is a function of the effective convection coefficient h_{eff} .

Keywords: BPS, segregation, convection, Czochralski process.

1 Introduction

During plane front solidification used to grow single crystals, the concentration of a solute in the solid C_S , is different from the concentration in the melt, C_L . In *equilibrium segregation*, the concentration in the melt is uniform because (a) the freezing rate is low, $f \rightarrow 0$, and/or, (b) melt is homogenized by perfect mixing. The equilibrium segregation coefficient k_0 is,

$$C_S / C_0 = k_0 \quad (1)$$

where $C_0 = C_L$ [atoms/cm³] is solute concentration at the interface, see Fig. 1a).

During actual crystal growth, a finite freezing rate is used, while mixing is not perfect. Thus, an enriched concentration layer builds up ahead of the interface. Referring to Fig. 1 b), the thickness of the layer is δ . The effective segregation coefficient is,

$$C_S / C_L = k_{eff} \quad (2)$$

The Burton, Prim and Slichter's BPS model published in 1953, gives k_{eff} as a function of δ (Burton et al. 1953). It is considered to be of the most useful equations in crystal growth (Hurle and Rudolph, 2004), and is presented in most

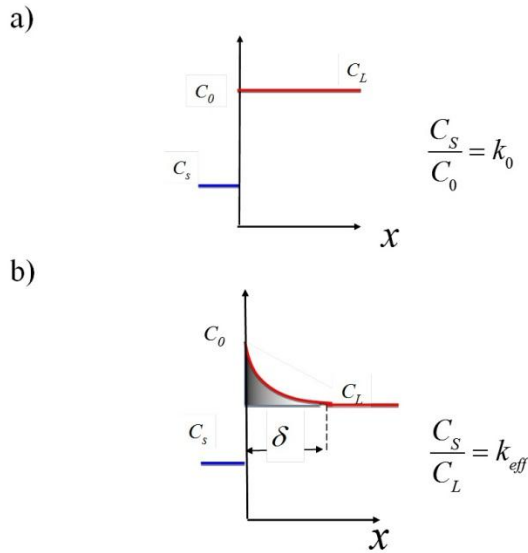


Fig. 1. a) Equilibrium and b) effective segregation coefficients

textbooks on solidification¹. For example Glicksman (2011) states: “The model, now referred to as BPS theory, captures with astounding simplicity several of the major features to be considered when the melt ahead of the solid–liquid interface is stirred“. Rosenberger (1979) describes the model as a “hybrid of the stagnant film model, and a full-fledged fluid dynamic boundary layer treatment”.

During the past sixty years, the shortcomings of the BPS model have been recognized. Several models for k_{eff} have been proposed (Wilson 1978; Ostrogorsky and Muller 1992; Yen and Tiller 1992; Garandet 2008). Yet, these models give k_{eff} is a function of layer thickness δ . Here we revisit the film models and compare to the recently proposed model, where k_{eff} is a function of convection coefficient h (Ostrogorsky 2012), or its dimensionless form, $Nu \equiv hL/D$ where Nu is Nusselt number, $D[cm^2/s]$ is diffusion coefficient and $L[cm]$ is characteristic length.

2. Film-thickness formulations

2.1 k_{eff} vs. static film thickness δ^{static} (BPS model)

The starting point of the BPS model is the assumption that a stagnant-film exists between the solid-liquid interface and the perfectly mixed region (Fig. 2 a). Within the static film, the concentration profile is exponential, and equal to the steady-state diffusion-controlled profile (Tiller et al. 1953),

$$\frac{C(x) - C_S}{C_0 - C_S} = \exp\left(-\frac{f}{D}x\right) \quad (3)$$

¹ According to Google Scholar, the BPS model has been cited over 1000 times.

$D[cm^2/s]$ is diffusion coefficient, and $f[cm/s]$ is the rate of crystallization. The static-film thickness is introduced by imposing $C(\delta^{static}) = C_L$,

$$\frac{C_L - C_S}{C_0 - C_S} = \exp\left(-\frac{f}{D}\delta^{static}\right) \quad (4)$$

Here we use superscript “static” to distinguish the static film. Rearranging and using $k_0 = C_S / C_0$, gives the BPS formula,

$$k_{eff}(\delta^{static}) = \frac{C_S}{C_L} = \frac{k_0}{k_0 + (1 - k_0)e^{-\Delta}} \quad (5)$$

$$\Delta = \frac{f\delta^{static}}{D}$$

Note that static films do not exist on Earth². Thus, δ^{static} is a fictitious parameter, and as such it can not be calculated (Levich 1961, Wilcox 2004). For small enough values of $f[cm/s]$, the BPS model makes the unjustifiable assumption,

$$\delta^{static} = \delta_{f=0}^{grad} = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \quad (6)$$

where superscript “grad” is used because δ^{grad} is distance between $x=0$ and the point where the gradient $dC/dx|_{x=0}$ intersects C_L , see Fig. 2 b). Equation (6) was derived by Levich in (1942) and (1961). It is based on the exact flow solution³. Levich derived the mass flux j from the surface of the impermeable rotating disk to be (see p.69, Levich 1961)

$$j_{f=0} = 0.62D^{2/3}\nu^{-1/6}\omega^{1/2}(C_0 - C_L) \quad (7)$$

where $\nu[cm^2/s]$ is kinematic viscosity, and $\omega[1/s]$ is disk rotation rate. Levich defined the film thickness as,

$$\delta^{grad} = D \frac{C_0 - C_L}{j} = \frac{C_0 - C_L}{-D[dC/dx]_{x=0}} \quad (8)$$

Substituting eq. (7) into (8) gives eq. (6),

$$\delta_{f=0}^{grad} = 1.61\sqrt{\nu/\omega}(D/\nu)^{1/3} \quad (9)$$

Furthermore,

$$\delta_{f=0}^{grad} \approx 0.5(D/\nu)^{1/3}\delta_{Hydraulic} \quad (10)$$

$$\delta_{f=0}^{grad} \approx 0.5\delta \quad (11)$$

² Static films are presumed to exist in steady-state diffusion-controlled segregation in space laboratories (Witt et. al. 1975)

³ von Karman’s (1921) and Cochran’s (1934) similarity solution of Navier-Stokes equations for laminar flow near an infinite rotating disk.

where $\delta_{Hydraulic}$ and δ are respectively the actual velocity and concentration boundary layer thickness, unrelated to δ^{static} (see Fig. 2b).

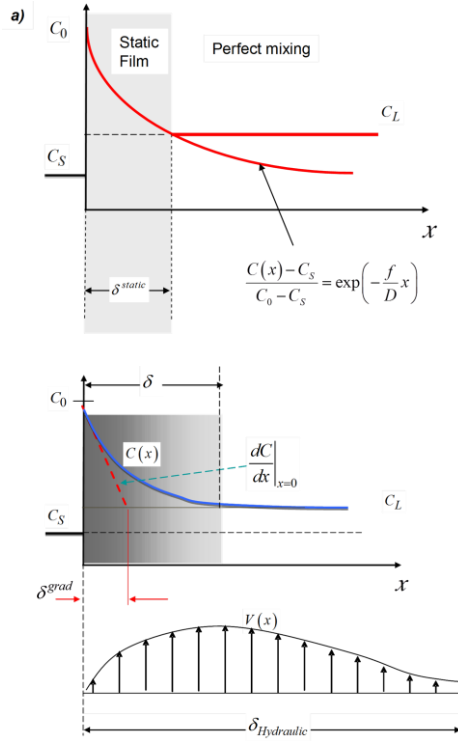


Fig. 2.a) Static film and perfect mixing regions in BPS. b) Actual concentration profile and its gradient used by Levich.

2.2 k_{eff} vs. dynamic film thickness, δ^{grad}

Wilson (1978) and Garandet (1993) recognized the shortcomings of the stagnant film formulation, and the exponential concentration profile used in BPS. Wilson and Garandet defined film thickness as Levich, equ. (8), and proceeded to show that the correct formula for k_{eff} is,

$$k_{eff}(\delta^{grad}) = \frac{k_0}{1 - (1 - k_0)\bar{\Delta}} \quad (12)$$

where $\bar{\Delta}$, is based on gradient thickness,

$$\bar{\Delta} = f \delta^{grad} / D = \int_0^{\infty} \exp(-z - Bz^3) dz \quad (13)$$

where $B = 0.17 f^{-3} \omega^{3/2} \nu^{1/2} D^2$. Equations (12) and (13) will be referred to as the *Wilson-Garandet's exact solution*.

Wilson(1979) proposed the following approximation,

$$\bar{\Delta} = 1.61 \frac{\xi}{1 + \xi} \tag{14}$$

$$\xi = D^{-2/3} v^{1/6} \omega^{-1/2} f$$

and determined that it yields less than 0.8 % if $0 < \xi < 0.5$. Equation (12) with (14) will be referred to as Wilson’s approximation-model.

3. Convection coefficient formulation

In steady-state, mass conservation requires that all solute released at the crystal-melt interface, is swept away by convection (Ostrogorsky 2012), see Fig. 3,

$$j_{in} - j_{solid} = j_C$$

where the convective mass flux is expressed via the convection coefficient $h_{eff} [cm/s]$,

$$j_C = h_{eff} (C_0 - C_L) \tag{15}$$

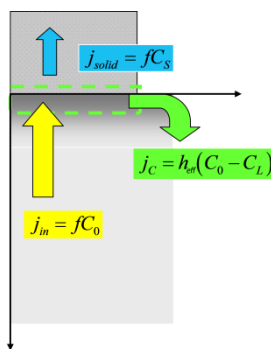


Fig.3. Solute fluxes

The heat transfer analog of equ. (15) is known as the Newton’s law of cooling. Referring to Fig. 3,

$$f (C_0 - C_S) = h_{eff} (C_0 - C_L)$$

Rearranging and using $k_0 = C_S / C_0$, and yields,

$$k_{eff} (h_{eff}) = \frac{C_S}{C_L} = \frac{k_0}{1 - (1 - k_0) \frac{f}{h_{ff}}} \tag{16}$$

Comparing eqs. (12) and (16) gives,

$$\bar{\Delta} = f / h_{eff}$$

Here, $\bar{\Delta}$ represents the ratio of the growth velocity $f[cm/s]$ and effective velocity of solute removal, i.e. convection coefficient $h_{eff}[cm/s]$.

3.1 Impermeable Interface

The interface can be considered impermeable for $f < 0.1h_{mix}$. (Ostrogorsky 2012).

Numerous analytical and empirical correlations for h (i.e. Nu) have been developed for impermeable interfaces (Incropera and DeWitt 1985; Cengel and Ghajar 2010). For forced convection,

$$Nu_{FC} \equiv \frac{h_{FC}L}{D} = f(\text{Re}_L^n, Sc^{1/3}) \quad (17)$$

where Re is Reynolds number and Sc is Schmidt number. $n=0.5$ and $n=0.8$ for laminar and turbulent flow respectively. It is interesting to note that Levich did not provide a formula for h , although it is obvious from the flux (7) and the eq. (15),

$$h_{FC} = 0.62D^{2/3}v^{-1/6}\omega^{1/2} \quad (18)$$

The dimensionless form of eq. (18) is,

$$Nu_{FC} = \frac{h\sqrt{v/\omega}}{D} = 0.62Sc^{1/3} \quad (19)$$

where $L = \sqrt{v/\omega}$ is the characteristic length scale. Equations (18) and (19) are valid only for steady laminar flow, forced convection from impermeable rotating disk ($f=0$), for $Sc \rightarrow \infty$.

The general form of the correlations for natural convection is,

$$Nu_{NC} \equiv \frac{h_{NC}L}{D} = f(Gr_L, Sc)^n \quad (20)$$

where Gr is Grashof number. $n=1/3$ and $n=1/4$ for laminar and turbulent flow respectively. For mixed convection,

$$Nu_{mix} = h_{mix}L/D = (Nu_{FC}^m \pm Nu_{NC}^m)^{1/m}$$

or,

$$h_{mix} = |h_{FC}^m \pm h_{NC}^m|^{1/m} \quad (21)$$

where $m=3$ for a vertical surface and $m=3.5$ for a horizontal surface. h_{mix} is mass transfer coefficient which accounts for “mixed convection”(Incropera and DeWitt 1985; Cengel and Ghajar 2010), and the sign is: + when forced and buoyant convection act in the same direction, or - when forced and buoyant convection act in the opposite direction.

3.2 Permeable interface with uniform or suction

Using the fluid mechanics terminology, the flow velocity perpendicular to the porous interface is “uniform suction” velocity (Schlichting 1968; White 1991). The effect of suction is to stabilize the boundary layers⁴ by reducing their thickness (Schlichting 1968).

Reducing boundary layer thickness also enhances convection. Since correlations for interfaces with suction are not available, it has been proposed to use an effective convection coefficient defined as (Ostrogorsky 2012),

⁴ prevent boundary layer separation on airfoils (Schlichting 1968).

$$h_{eff} = (h_{mix}^n + f^n)^{1/n} \quad (22)$$

where n is to be determined from experiments or theory. Combining eqs. (16) and (22) gives,

$$k_{eff}(h) = \frac{C_s}{C_L} = \frac{k_0}{1 - (1 - k_0) \frac{f}{(h_{mix}^n + f^n)^{1/n}}} \quad (23)$$

Comparing eqs. (12) and (23) gives,

$$\bar{\Delta} = \frac{f}{h_{eff}} = \frac{f}{(h_{mix}^n + f^n)^{1/n}} \quad (24)$$

3.4 Czochralski growth

In most CZ melts, natural convection and/or turbulence are significant. Since forced and buoyant convection act in the opposite direction, $h_{mix} = (h_{mix}^{3.5} + f^{3.5})^{1/3.5}$. The convection coefficients to be used in eq. (21) are (Ostrogorsky 2012):

for laminar flow and $10 < Sc < 100$,

$$\begin{aligned} h_{FC} &= 0.485 D \sqrt{\omega / \nu} Sc^{0.373} \\ h_{NC} &= 0.54 (D / L) (Gr \cdot Sc)^{1/4} \end{aligned} ;$$

or for turbulent flow,

$$\begin{aligned} h_{FC} &= (D / r) 0.0267 Re_r^{0.8} Sc^{0.6} \\ h_{NC} &= 0.15 (D / L) (Gr \cdot Sc)^{1/3} \end{aligned} .$$

4. Assessment of the models applied to forced laminar convection

For forced laminar convection near a rotating disk, and $Sc \rightarrow \infty$, the Wilson-Garandet's Model, eqs. (12) with (13), provides accurate reference values for k_{eff} , because it is based on the exact solution of the concentration field near the disk. To assess the precision of the models, k_{eff} was calculated for the properties and parameters used for the BPS experiments with Ga-doped Ge: $\nu = 0.0013 \text{ cm}^2/\text{s}$, $D = 2.8 \times 10^{-5} \text{ cm}^2/\text{s}$, 60 RPM^5 , while the range of growth rate is $0 < f < 0.008 \text{ cm/s}$ ($= 80 \text{ } \mu\text{m/s} = 28.8 \text{ cm/hr}$).

Figure 4 shows k_{eff} as a function of the growth rate f , calculated using:

- (i) BPS model, eq.(5) with (6), assuming $\delta^{static} = \delta_{f=0}^{grad}$ (squares)
- (ii) Wilson-Garandet's exact model eqs. (12) and (13), where $\bar{\Delta}$ is obtained by numerical integration (full line).
- (ii) Wilson's Approximate-model, eqs. (12) and (14) for $\bar{\Delta}$ (triangles),

⁵60 RPM is the lowest crystal rotation rate used by Burton et al. (1953). The lower is RPM, the lower is h_{FC} , and thus the effect of suction flow f is more pronounced.

- (iii) Ostrogorsky's model, eq. (23); $h_{mix}=h_{FC} = 0.0045$ cm/s is calculated using eq. (18). Crosses are for $n=1$; circles for $n=1.4$.

Figure 4. verifies the validity of the convection coefficient model, for laminar forced convection in CZ growth. $n=1.4$ gives a perfect fit for $0 < f/h_{FC} < 1.3$, or $f < 0.006$ cm/s \sim 21 cm/hr. $n=1$ is useful up to ~ 0.001 cm/s = 3.6 cm/hr.

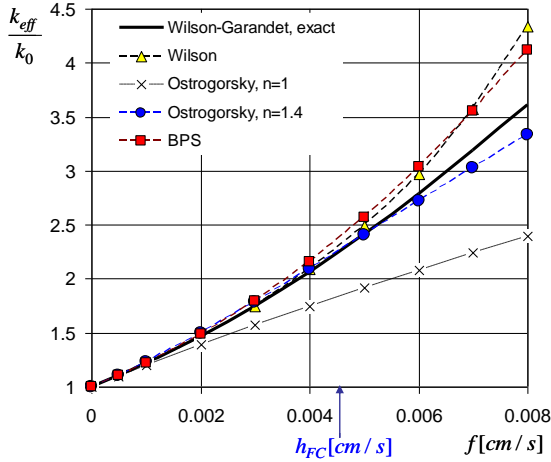


Fig. 4. k_{eff} / k_0 vs. growth rate. Full line: exact Wilson-Garandet's model eqs. (12) and (13). Triangles: Wilson's model, eqs. (12) and (14). Circles, and crosses are respectively $n=1$, $n=1.4$ in eq. (23). Squares: BPS model.

5. Discussion

The stagnant film concept is unsatisfactory, because their thickness can not be calculated a priori (Levich 1961). In the **BPS model**, the exponential profile within the stagnant film thickness leads to a great deal of confusion. Assuming $\delta_{eff}^{static} = \delta_{f=0}^{grad}$ has no foundation, since $\delta_{f=0}^{static}$ corresponds to the exponential profile, while $\delta_{f=0}^{grad}$ corresponds to the linear profile (Fig. 2).

Fig. 4 reveals that the BPS model is accurate for $1 < k_{eff} / k_0 < 2$ or $f < h_{FC}$. In typical CZ system, convection leads to thin solute layers while the f is low. For small $\Delta = f \delta_{f=0}^{grad} / D$, the one term Taylor series expansion, transforms fictitious exponential profile into linear,

$$e^{-\Delta} \approx 1 - \Delta$$

and turns the BPS formula into eq. (12) or (16). For $\delta_{f=0}^{static} \rightarrow 0$, the exponential and linear profiles nearly overlap, Fig. 2). This, Wilson's (1979) comment: "the right answer has been obtained for the wrong reason" appears justified.

Kodera's (1953) use of the BPS model to determine the diffusion coefficients in Si is problematic. Kodera grew Si crystals at 5, 55 and 200 RPM. Note that at 5 RPM, convection is dominated by buoyancy forces, while at 200 RPM it is likely to be of turbulent. Kodera did not provide the dimensions of the crystals and melts, but according to Ristorcelli and Lumley (1992) even relatively small silicon melts are expected to be turbulent. In turbulent flow,

momentum, heat, mass transfer are dominated by eddy-mixing (Muller and Ostrogorsky 1994), while molecular transport weak. In turbulent flow, a concentration gradient $\partial C / \partial x$ induces an apparent mass flux,

$$j_{\text{apparent}} = -(D + \varepsilon_D) \frac{\partial C}{\partial x} \quad (25)$$

where ε_D is turbulent eddy-diffusivity. Typically, $\varepsilon_D \gg D$. Thus, Kodera's high diffusion coefficient for indium, $D_{In} = 6.9 \times 10^4 \text{ cm}^2/\text{s}$ compared to that of boron $D_B = 2.4 \times 10^4 \text{ cm}^2/\text{s}$ may be explained by the presence of eddy-diffusivity, not by high molecular diffusivity. Furthermore, to fit the data, Kodera used viscosity three times higher than the actual. Kodera's diffusion coefficients are listed in most handbooks. Diffusion coefficients should not be measured in turbulent melts.

The **Wilson-Garandet's formulation** based on the linear profile is consistent, and exact. Its limitations originate in the von Karman's/Cochran's similarity solution: it is applicable exclusively to laminar flow near a rotating disk, and $Sc \rightarrow \infty$.

The **Wilson's approximation**, (using eq. (14) for $\bar{\Delta}$) is precise for $1 < k_{\text{eff}} / k_0 < 2$, or $f < h_{FC}$.

The **Convection Coefficient Formulation** (Ostrogorsky 2012), is based on mass conservation, and as such, equation (16) is exact. For steady laminar flows, the formula $h_{\text{eff}} = (h_{\text{mix}}^{1.4} + f^{1.4})^{1/1.4}$ gives a solid agreement with the exact solution. For impermeable interfaces, well established correlations for h_{FC} and h_{NC} are available. Thus, Convection Coefficient Formulation can be applied to a variety of melt-flow conditions, including: (a) turbulent flow; (b) natural convection/mixed convection; (c) finite Sc numbers.

The remaining issue is the lack of correlations for convective coefficients h along interfaces with suction. More data are needed to determine n for turbulent flow with suction.

6. Conclusions

The film-thickness based models are limited by the restrictions carried over from the von Karman's/Cochran/ Levich solution. They are valid only for steady laminar flow near a rotating disk.

The recently proposed convection-coefficient formulation (Ostrogorsky 2012), is more general than the models based on Levich's film thickness. It is based on mass conservation and as such is exact. It is applicable to turbulent flow, natural and mixed convection, finite Sc numbers. This is a principal advantage considering that (i) most semiconductor melts are turbulent (Ristorcelli and Lumley 1992), and (ii) natural convection on Earth is unavoidable.

For steady laminar flow near a rotating disk, $n=1.4$ should be used in eq. (23).

Diffusion coefficients should not be measured in turbulent melts.

Извод

Дебљина слоја и формулација конвективног коефицијента k_{eff} **A. G. Ostrogorsky**

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Резиме

Burton, Prim и Slichter's (BPS) модел публикован 1953. год. се сматра најкориснијим моделом за раст кристала и приказан је у већини књига за очвршћавање. Овај модел карактерише коефицијент сегрегације k_{eff} као функција константне дебљине филма δ . Последњих година се уочавају недостаци BPS модела и предлажу се нови модели који се заснивају на дебљини слоја. У овом раду поново се разматрају модели засновани на дебљини слоја и пореде са недавно предложеним моделом где је коефицијент k_{eff} функција конвективног коефицијента h .

Кључне речи: BPS, сегрегација, конвекција, Czochralski процес**References:**

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