Journal of Engineering Mathematics, Vol. 14, No. 3, July 1980

Printed in the Netherlands

Transient phenomena in crystal growth systems

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(Received July 30, 1979 and in revised form November 26, 1979)

SUMMARY

In a model of the Czochralski crystal growth system the crystal is represented by a solid rotating plane adjacent to a semi-infinite region occupied by the melt from which the crystal is grown. The melt itself may be subjected to rotation at large distances from the interface. In a co-ordinate system advancing with the interface the crystal growth is modelled by a 'suction' velocity at the interface. A transient analysis is performed following a discontinuous change of solute concentration in the bulk of the melt. Two cases are considered, namely (i) solid body rotation of crystal and melt and (ii) no melt rotation at large distances from the interface. The paper represents a re-examination and re-interpretation of earlier work by Burton, Prim and Slichter [1].

1. Introduction

In an earlier paper Burton, Prim and Slichter [1] (hereafter referred to as BPS) studied transient phenomena in a model of a crystal growth system in which the crystal interface is represented by a plane surface adjacent to a semi-infinite region occupied by the melt from which the crystal is grown. In particular they considered the transient interface solute concentration when a sudden change is made to the solute concentration in the bulk of the melt. Convective effects dominate in the bulk of the melt whose solute concentration is therefore assumed to change instantaneously. It is only within a distance δ from the interface that diffusive and convective effects become comparable. Accordingly BPS apply boundary conditions at the interface and at a fixed distance δ from it. Their analytical solution may then be expressed as an eigenfunction expansion.

The work of BPS has been criticised by Wilson [7], [8]. In [7] Wilson questions the interpretation of δ as a concentration boundary-layer thickness, showing this only to be true at small growth rates.

In [8], the system is modelled by a laterally unbounded region between two parallel disks. Initially the two disks are taken to be stationary, with the solute uniformly distributed throughout the melt. One of the disks is then gradually rotated up to an angular velocity and suction applied at this disk. The resulting steady state achieved by the solute concentration field is compared to that of the BPS model; it is found that the results essentially verify those of BPS. The hydrodynamical aspect of the problem is discussed in [9]. In both [8] and [9] numerical techniques are employed to solve the diffusion and Navier-Stokes equations.

In this paper we reconsider the problem, and in particular by interpreting the outer boundary condition as a matching condition, rather than one to be applied at a finite distance, we demonstrate the inadequacies of the analysis of [1]. We consider the situation in which the solid plane interface rotates and either (i) the whole of the melt rotates with the same angular velocity or (ii) the bulk of the melt is not rotating. Thus case (i), which corresponds to that considered by BPS, is a model of the normal freeze technique whilst case (ii) is a model of the Czochralski process.

In both of the cases considered we use Laplace transform techniques to advantage. In case (i) we show that for $k \geqslant \frac{1}{2}$, where k is the segregation coefficient, the solution is dominated by the presence of a branch point whilst for $k < \frac{1}{2}$ a simple pole is the dominant feature. The exact solution may be expressed as a real integral which is evaluated numerically. A comparison with the work of BPS shows that with the present formulation a much larger response time for the surface concentration is predicted. For case (ii) we extend the analysis of Riley [2] to derive an asymptotic solution, valid at large times, for the large Schmidt numbers associated with the Czochralski crystal growth process. In this case the solution in the transformed plane is determined from simple poles which yield what is effectively an eigenfunction expansion, of value at large times. We supplement this asymptotic analysis with a numerical solution of the governing partial differential equations. The work of BPS is re-interpreted in relation to the results which we have obtained for case (ii).

2. The model equations

As mentioned in Section 1 we consider two different situations. The first is that in which both the liquid and solid phases co-rotate with the same angular velocity Ω about an axis normal to the interface. The interface is assumed to be planar and to move in a direction also normal to the interface. In the second situation, we model a Czochralski growth system in which the solid phase rotates as before but the bulk of the melt does not rotate. In this case the solid-liquid interface is modelled by a rotating disk.

In both cases freezing is assumed to take place and the interface velocity prescribed. This is permitted as the velocity is determined by the thermodynamics of the system. Further in both cases we take our origin of coordinates in the moving interface. This choice gives rise to an effective 'suction' velocity at the interface as it advances into the liquid phase.

We also assume that the ratio of the diameter of the crystal to that of the crucible is small. This then permits us to model the liquid phase by a region of infinite lateral extent. With this simplification the Navier-Stokes equations are reduced to dependence on a single variable. Our model of the system is shown in Fig. 1.

By use of a similarity transformation the radial, tangential and normal velocity components may be written, respectively, as

$$v_r = -\tfrac{1}{2} r\Omega h'(s), \quad v_\theta = r\Omega g(s), \quad v_z = (\nu\Omega)^{\frac{1}{2}} h(s), \quad s = (\Omega/\nu)^{\frac{1}{2}} z \tag{2.1}$$

where ν is the kinematic viscosity of the liquid phase and z is as shown in Fig. 1, we may reduce the Navier-Stokes equations for steady flow to the following pair of coupled ordinary differential equations [3]:

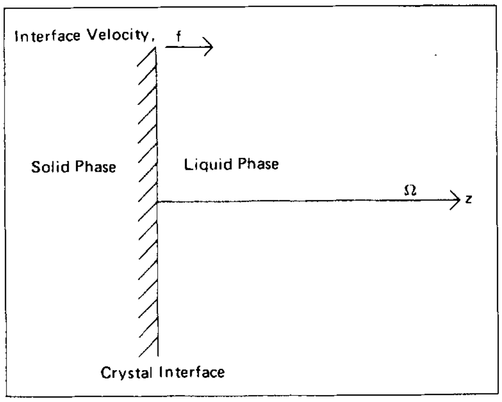

Figure 1. The configuration of the system.

$$
\begin{aligned}
&h''' - hh'' + \tfrac{1}{2}h'^2 - 2g^2 = - 2I^2,\\
&g'' - hg' + h'g = 0,
\end{aligned}
\tag{2.2}
$$

where I is the ratio of the rotation of the bulk of the melt to that of the solid. Thus for case (i) $I = 1$, and case (ii) $I = 0$. The boundary conditions for (2.2) are

$$
h(0) = -\lambda, \quad h'(0) = 0, \quad g(0) = 1, \quad h'(\infty) = 0, \quad g(\infty) = I, \tag{2.3}
$$

where if f denotes the normal component of the interface velocity then $\lambda = (\nu\Omega)^{\frac{1}{2}} f$.

We have modelled the rotation of the bulk of the melt by placing the boundary conditions at infinity. We justify this as follows. Our use of the similarity transformation (2.1) assumes, in effect, that the thickness of the moving layer of fluid, which is $O[(\nu/\Omega)^{\frac{1}{2}}]$ is small compared with the diameter of the crystal which in turn is small compared to a typical dimension d of the crucible. Thus we have that the Reynolds number $R \gg 1$ where

$$
R = \Omega^2 d/\nu. \tag{2.4}
$$

In this high Reynolds number situation the fluid motion is essentially confined to a neighbourhood of the moving boundary with only weak circulation induced in the bulk of the melt and as a consequence the conditions (2.3) may be interpreted as matching conditions with the flow in the bulk of the melt.

We now turn to the diffusion equation. In terms of our similarity transformation (2.1) this may be written as

$$
\frac{\partial^2 c}{\partial s^2} - Sch(s)\frac{\partial c}{\partial s} = Sc\,\frac{\partial c}{\partial \tau}, \tag{2.5}
$$

where c is the solute concentration field, $\tau = \Omega t$, and $Sc = \nu/D$ is the Schmidt number for the system where D is the diffusivity of the solute, and t is the time. The segregation coefficient k for the system under consideration is defined by

$$k = \frac{\text{Concentration of solute in the solid phase at the interface}}{\text{Concentration of solute in the liquid phase at the interface}} \,. \tag{2.6}$$

We assume that k remains constant throughout and that there is no diffusion in the solid phase. By considering the conservation of solute at the interface we obtain for the boundary condition on c at $z = 0$

$$\left.\frac{\partial c}{\partial s}\right|_{s=0} = \lambda Sc(k-1)c\Big|_{s=0} . \tag{2.7}$$

Further we require the concentration of solute in the bulk of the melt to remain constant. Thus as discussed above we place this boundary condition at infinity to give

$$c(\infty) = 1. \tag{2.8}$$

It is at this point that we differ from BPS for they replace the boundary condition (2.8) by

$$c\,|_{z=\delta} = 1, \tag{2.9}$$

where δ is representative of the thickness of the solute boundary layer and thus depends upon the viscous boundary-layer thickness. (For necessarily the solute boundary layer depends on the convective processes and hence the viscous boundary layer.)

They also argue that within a region of thickness δ adjacent to the interface the effect of diffusion becomes important and comparable to the convective effects due to the movement of the interface. Outside this region they consider that convective effects in the bulk of the melt are sufficient to maintain the concentration of the solute at $z = \delta$ at a constant level. They considered the response of the system under the initial condition

$$c = H(z-\delta), \quad t = 0, \tag{2.10}$$

where H denotes the Heaviside unit step function. With these assumptions they give the interface concentration $c(0, t)$ as

$$c(0,t) = \frac{1}{k + (1-k)e^{-\Delta}} - 2\,e^{\frac{\Delta}{2}} \sum_{i=1}^{\infty} \frac{\mu_i\delta \sin\mu_i\delta \exp\left\{-\left[\left(\frac{\Delta}{2}\right)^2 + (\mu_i\delta)^2\right]\frac{Dt}{\delta^2}\right\}}{\left(1 - \frac{\sin 2\mu_i\delta}{2\,\mu_i\delta}\right)\left[\left(\frac{\Delta}{2}\right)^2 + (\mu_i\delta)^2\right]} \tag{2.11}$$

where $\Delta = f\delta/D$ and $\mu_i\delta$ is the ith positive root of

$$\mu\delta \cot\mu\delta = (\tfrac{1}{2} - k)\Delta. \tag{2.12}$$

The solution obtained for $c(s,t)$ by BPS which yields (2.11) is derived by an eigenfunction expansion which is an appropriate technique for the linear parabolic equation (2.6) on a finite interval.

Our primary objections to the model adopted by BPS are:

(i) It presupposes a discontinuous behaviour in the physical processes governing the transport of solute in the liquid phase.

(ii) There is a discontinuity in the gradient of the concentration field at $z = \delta$ for all time, which implies the existence of a solute sink at that point.

(iii) When modelling the co-rotational case, δ is arbitrarily prescribed, as no viscous boundary layer is formed in this case. Hence no estimate can be made of the solute boundary-layer thickness.

(iv) In a situation in which a transient concentration field exists the thickness of the diffusion boundary layer will vary. Hence it is inappropriate to assume that δ is independent of time.

By use of our viscous boundary-layer scaling we overcome these objections by employing a matching condition for the concentration field, in order to model the bulk of the melt, as discussed previously.

In Fig. 2 we reproduce the results of BPS for the interface concentration obtained from equation (2.11) for various values of k and Δ; also in Table 1 we include the calculated eigenvalues for (2.12).

3. The solution procedure

Case (i) I = 1

This is the co-rotational case and equations (2.2) are trivially satisfied by $h \equiv -\lambda$, $g \equiv 1$.

We take the same initial condition upon c as that used by BPS which is given by (2.10). This is so we may compare our results with those of BPS. It is for this reason that we change to a new scaling of z and t. Thus we write $x = z/\delta$, $\alpha = Dt/\delta^2$ and the problem now becomes

$$\begin{aligned}
&\frac{\partial^2 c}{\partial x^2} + \Delta \frac{\partial c}{\partial x} = \frac{\partial c}{\partial \alpha}, \\
&\frac{\partial c}{\partial x} = \Delta(k-1)c \quad \text{at} \quad x = 0, \quad t > 0, \\
&c \to 1 \quad \text{as} \quad x \to \infty, \quad t > 0, \\
&c = H(x-1) \quad \text{at} \quad t = 0, \quad x \geqslant 0.
\end{aligned} \tag{3.2}$$

It should be noted in this case that because there is uniform flow up to the interface, no viscous boundary layer is formed and so the choice of δ is purely arbitrary.

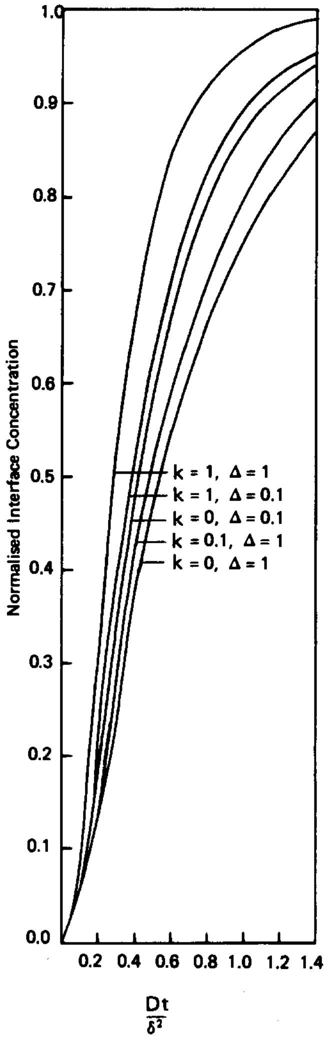

Figure 2. The normalised interface concentration as a function of time for the BPS model, calculated from (2.11).

TABLE 1

Comparison between the eigenvalues of (3.26) and those arising from BPS in (2.12).

k	Δ	$\mu_1 \delta$	ν_0^1	A_{-1}^1
1	1	1.8365	1.2725	−1.3009
1	0.1	1.6019	0.8328	−1.1614
0	0.1	1.5383	0.7740	−1.2674
0.1	1.0	1.2644	0.7111	−2.4936
0	1.0	1.1655	0.6301	−2.8110

We now proceed by taking the Laplace transform of (3.2) with respect to α, where $\bar{c}$, the transform of c is defined by

$$\bar{c} = \int_0^\infty c(x,\alpha)e^{-p\alpha}d\alpha, \tag{3.3}$$

whence the problem for $\bar{c}$ is

$$\begin{aligned} &\bar{c}'' + \Delta\bar{c}' - p\bar{c} = -H(x-1), \\ &\bar{c}' = \Delta(k-1)\bar{c}, \quad \text{at} \quad x = 0, \\ &\bar{c} \to 1/p, \quad x \to \infty, \end{aligned} \tag{3.4}$$

where a prime denotes differentiation with respect to x. We solve this in two regions; $0 \leqslant x < 1$ and $x \geqslant 1$, requiring $\bar{c}$ and $\bar{c}'$ to be continuous at $x = 1$. From the solution obtained in this way we have, for the transform of the solute concentration at the interface

$$\bar{c}(0,p) = \frac{1}{p}\,\frac{\Delta + \sqrt{\Delta^2 + 4p}}{\Delta(2k-1) + \sqrt{\Delta^2+4p}}\,\exp\left(\frac{\Delta - \sqrt{\Delta^2+4p}}{2}\right), \tag{3.5}$$

where a positive square root is intended. From (3.5) the square root terms cause $\bar{c}(0,p)$ to be a multivalued function of p. To overcome this problem we introduce a branch cut into the complex p-plane along the negative real axis from $p = -\dfrac{\Delta^2}{4}$ i.e. $-\pi < \arg\left(p + \dfrac{\Delta^2}{4}\right) \leqslant \pi$. With this restriction upon p we have a simple pole at $p = 0$ and for $k < \frac{1}{2}$ an additional pole at $p = \Delta^2 k(k-1)$. The residues of $\bar{c}(0,p)$ are respectively $\dfrac{1}{k}$, and $\left(2 - \dfrac{1}{k}\right)\exp(-k\Delta)$. The pole at $p = 0$ corresponds to the final steady state. Also the other pole lies between the origin and the branch point moving monotonically from 0 to $-\dfrac{\Delta^2}{4}$ as k varies from 0 to $\frac{1}{2}$.

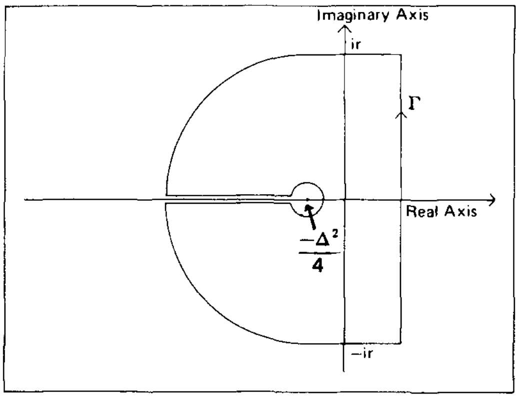

Figure 3. The contour Γ in the complex p-plane.

The Laplace inversion formula is

$$c(0,\alpha) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \bar{c}(0,p) e^{p\alpha} dp, \tag{3.6}$$

where a lies to the right of all the singularities of $\bar{c}(0,p)$. Using the Residue Theorem we may relate this to

$$J = \frac{1}{2\pi i} \int_{\Gamma} \bar{c}(0,p) e^{p\alpha} dp, \text{ in the limit } r \to \infty \tag{3.7}$$

where Γ is as shown in Fig. 3. Then we obtain

$$\begin{aligned} c(0,\alpha) &= \frac{1}{k} + H(\tfrac{1}{2} - k) \exp\left(-k\Delta + \Delta^2 k(k-1)\alpha\right) \\ &\quad - \frac{1}{\pi} \exp\left(\frac{\Delta}{2} - \frac{\Delta^2}{4}\alpha\right) \times \\ &\quad \times \int_0^\infty \frac{[\{\rho + \Delta^2(2k-1)\} \sin \frac{1}{2}\sqrt{\rho} + 2\Delta(1-k) \cos \frac{1}{2}\sqrt{\rho}] e^{\frac{-\rho\alpha}{4}} d\rho}{(\rho + \Delta^2)(\rho + \Delta^2(2k-1)^2)}. \end{aligned} \tag{3.8}$$

Using Watson's lemma we may obtain an asymptotic form for $c(0,\alpha)$ as $\alpha \to \infty$. Thus

$$\begin{aligned} c(0,\alpha) &\sim \frac{1}{k} + H(\tfrac{1}{2} - k)\left(2 - \frac{1}{k}\right) \exp\{-k\Delta + \Delta^2 k(k-1)\alpha\} \\ &\quad - \frac{1}{8c_3c_4\sqrt{\pi}} \exp\left(\frac{\Delta}{2} - \frac{\Delta^2\alpha}{4}\right) \left[(c_1 + c_2)\left(\frac{\alpha}{4}\right)^{-\frac{3}{2}} \right. \\ &\qquad + \frac{3}{2}\left[1 - \frac{c_1}{3!} - \frac{c_2}{2!} - (c_1 + c_2)\left(\frac{1}{c_3} + \frac{1}{c_4}\right)\right]\left(\frac{\alpha}{4}\right)^{-\frac{5}{2}} \\ &\quad + \frac{15}{4}\left[\frac{c_1}{5!} + \frac{c_2}{4!} - \frac{1}{3!} + (c_1 + c_2)\left(\frac{1}{{c_3}^2} + \frac{1}{c_3c_4} + \frac{1}{{c_4}^2}\right)\right. \\ &\qquad \left.\left. - \left(\frac{1}{c_3} + \frac{1}{c_4}\right)\left(1 - \frac{c_1}{3!} - \frac{c_2}{2!}\right)\right]\left(\frac{\alpha}{4}\right)^{-\frac{7}{2}} + O(\alpha^{-\frac{9}{2}})\right] \end{aligned} \tag{3.9}$$

where $c_1 = \frac{\Delta^2}{4}(2k-1)$, $c_2 = \Delta(1-k)$, $c_3 = \frac{\Delta^2}{4}$ and $c_4 = \frac{\Delta^2}{4}(2k-1)^2$.

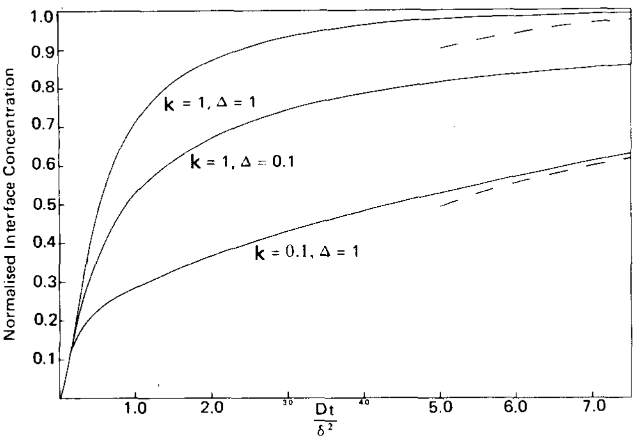

Figure 4. The normalised interface concentration as a function of time for the co-rotational case calculated from (3.8), including the asymptotic representation calculated from the leading-order term of (3.9) which is denoted by the broken line. (It should be noted that for $\Delta = 0.1$, and at the values of Dt/δ^2 shown, the asymptotic result is negative.)

Case (ii) $I = 0$

In this case, in which the non-uniform fluid motion close to the interface is important, we introduce the further realistic assumption that $Sc >> 1$, a consequence of which is that the crystal growth rate is small so that $\lambda << 1$. We follow Riley and Sweet [4] and seek an asymptotic solution of our equations in the limit $Sc \to \infty$. Hence we put

$$\lambda = Sc^{-\beta}\lambda_0, \tag{3.10}$$

where $\lambda_0 = O(1)$, and further expand h and g in terms of the Schmidt number. Thus

$$\begin{aligned} h(s) &= h_0(s) + h_1(s)Sc^{-\beta} + h_2(s)Sc^{-2\beta} + O(Sc^{-3\beta}), \\ g(s) &= g_0(s) + g_1(s)Sc^{-\beta} + g_2(s)Sc^{-2\beta} + O(Sc^{-3\beta}). \end{aligned} \tag{3.11}$$

The leading-order terms, h_0 and g_0, satisfy the original non-linear ordinary differential equations (2.2) but the terms h_i and g_i ($i \geqslant 1$) satisfy linear differential equations.

As BPS point out diffusion is relevant in a boundary layer adjacent to the interface where its effect is comparable to convective effects. Thus we scale the normal coordinate of (2.1) as

$$s = Sc^{-\gamma}\eta. \tag{3.12}$$

The boundary condition (2.7) at the interface then gives

$$\beta + \gamma = 1. \tag{3.13}$$

Also we note that expanding $h_0(s)$ and $h_1(s)$ for $s \ll 1$ gives

$$h_0 = -\mu_0 s^2 + \mu_1 s^3 + O(s^4), \quad h_1 = -\lambda_0 - \mu_2 s^2 + O(s^3). \tag{3.14}$$

Riley and Sweet showed that $\gamma = \frac{1}{3}$ is the most important case corresponding to the situation in which diffusion is comparable to convective effects in the diffusion boundary layer. With $\gamma = \frac{1}{3}$ (2.5) becomes, after expanding h for small values of its argument as in (3.14)

$$\frac{\partial^2 c}{\partial \eta^2} + \{\lambda_0 + \mu_0 \eta^2 + \mu_1 \eta^3 Sc^{-\frac{1}{3}} + \mu_2 \eta^2 Sc^{-\frac{2}{3}} + O(Sc^{-1})\} \frac{\partial c}{\partial \eta} = \frac{\partial c}{\partial \theta}, \tag{3.15}$$

where $\theta = Sc^{-\frac{1}{3}} \tau$.

We must now consider the associated boundary conditions. For small values of growth rate BPS give δ as

$$\delta = 1.6\, Sc^{-\frac{1}{3}} (\nu/\Omega)^{\frac{1}{2}}, \tag{3.16}$$

from a consideration of the steady-state condition for this case. Hence, in order to achieve a comparison with their model we let δ correspond to $\eta = 1.6$. Thus we impose upon the system the following condition

$$c = F(\eta), \quad \text{at } \theta = 0$$

where

$$F(\eta) = \begin{cases} 0.5\, \{1 + \tanh(\exp\{\alpha(\eta - \beta)\} - 1.0)\}, & \eta \geqslant \beta \\ 0.5\, \{1 - \tanh(\exp\{\alpha(\beta - \eta)\} - 1.0)\}, & \eta < \beta, \end{cases} \tag{3.17}$$

rather than a discontinuous step change in solute concentration. The function $F(\eta)$ which models a step change has been chosen to ensure a sufficiently rapid decay to uniform values in order that integrals which subsequently appear in the analysis converge. We put $\alpha = 8.35$ and $\beta = 1.5$ so that the solute concentration achieves 95% of its final value at $\eta = 1.6$.

The boundary condition at $\eta = 0$ given by (2.7) now becomes

$$\left.\frac{\partial c}{\partial \eta}\right|_{\eta = 0} = \lambda_0 (k - 1) c \Big|_{\eta = 0}. \tag{3.18}$$

whilst the boundary condition (2.8) remains unchanged. We are thus required to solve (3.15) with the boundary conditions (2.8), (3.17) and (3.18).

No exact solution is available to us, hence we have numerically integrated (3.15) to leading order in $Sc^{-\frac{1}{3}}$ along with boundary conditions (2.8), (3.17), and (3.18). The appropriate value for μ_0 is 0.51023. From (2.1), (2.11), (3.10) and (3.16) λ_0 and Δ are related by

$$\Delta = 1.6\, \lambda_0. \tag{3.19}$$

Using this relationship we were able to use values of λ_0 that correspond to the cases given by BPS. Further, we have carried out an asymptotic analysis for large time.

It is to the asymptotic solution that we now turn. We shall show that the leading term of c can be given spectrally in the form

$$\sum_{i=0}^{\infty} E^i(\eta)\exp(-e^i\theta), \tag{3.20}$$

where $\{E^i(\eta)\}$ is a sequence of functions, and $\{e^i\}$ is a corresponding positive real sequence.

The appearance of powers of $Sc^{-\frac{1}{3}}$ in (3.15) indicates that we should expand c as a power series in $Sc^{-\frac{1}{3}}$. Thus we write

$$c = 1 + c_0(s,t) + O(Sc^{-\frac{1}{3}}). \tag{3.21}$$

The division of the leading-order term into two parts is purely for convenience at later stages in the analysis. We now take the Laplace transform of (2.8), (3.15), (3.17) and (3.18) to give for $\bar{c}_0$:

$$\begin{aligned}
&\bar{c}_0'' + (\lambda_0 + \mu_0\eta^2)\bar{c}_0' - p\bar{c}_0 = 1 - F(\eta),\\
&\bar{c}_0' = \lambda_0(k-1)\bar{c}_0, \quad \eta = 0,\\
&\bar{c}_0 \to 0 \quad \text{as} \quad \eta \to \infty.
\end{aligned} \tag{3.22}$$

As we wish to show c_0 has the form (3.20) we must demonstrate that $\bar{c}_0$ has a discrete sequence of simple poles along the negative real axis in the complex p-plane. Thus we put

$$p + p_n = \epsilon, \tag{3.23}$$

where $\epsilon \ll 1$. We further allow this pole to be dependent upon the Schmidt number. Hence we write

$$p_n = \nu_0^n + \nu_1^n Sc^{-\frac{1}{3}} + \nu_2^n Sc^{-\frac{2}{3}} + O(Sc^{-1}), \tag{3.24}$$

where $\nu_0^n, \nu_1^n, \ldots$ are non-zero complex constants.

Our aim then is to show that $\bar{c}_0$ can be expanded as

$$\bar{c}_0 = \frac{\phi_{-1}}{\epsilon} + \phi_0 + \phi_1\epsilon + O(\epsilon^2), \tag{3.25}$$

and hence that $\bar{c}_0$ has a simple pole at $p = -p_n$ and further that $\{\nu_0^n\}$ is a positive real sequence. Combining (3.22), (3.23), (3.24) and (3.25) we obtain

$$\begin{aligned}
&\phi_{-1}'' + (\lambda_0 + \mu_0\eta^2)\phi_{-1}' + \nu_0^n\phi_{-1} = 0,\\
&\phi_{-1}' = \lambda_0(k-1)\phi_{-1}, \quad \text{at} \quad \eta = 0,\\
&\phi_{-1} \to 0 \quad \text{as} \quad \eta \to \infty;
\end{aligned} \tag{3.26}$$

$$\begin{aligned}
&\phi_0'' + (\lambda_0 + \mu_0\eta^2)\phi_0' + \nu_0^n\phi_0 = \phi_{-1} + G(\eta),\\
&\phi_0' = \lambda_0(k-1)\left(-\frac{1}{\nu_0^n} + \phi_0\right), \quad \text{at} \quad \eta = 0,\\
&\phi_0 \to 0, \quad \eta \to \infty,
\end{aligned} \tag{3.27}$$

where $G(\eta) = 1 - F(\eta)$.

Equation (3.26) for ϕ_{-1} poses an eigenvalue problem for ν_0^n since for general values of this parameter both boundary conditions will not be satisfied by a non-trivial solution. We consider the eigenvalues ν_0^n generated by equation (3.26). To do this we transform the equation for ϕ_{-1} by defining $\psi(\eta)$ from

$$\phi_{-1}(\eta) = \psi(\eta) \exp \{-\tfrac{1}{2}(\lambda_0 \eta + \tfrac{1}{3}\mu_0 \eta^3)\}, \tag{3.28}$$

so that (3.26) becomes

$$\psi'' + \{\nu_0^n - q(\eta)\}\psi = 0, \tag{3.29}$$

where $q(\eta) = \frac{1}{4}(\lambda_0 + \mu_0 \eta^2)^2 + \mu_0 \eta$. Multiplying (3.29) by ψ^*, the complex conjugate of ψ, and integrating by parts yields, following a little manipulation,

$$\nu_0^n = \left[\int_0^\infty q(\eta) \mid \psi(\eta) \mid^2 d\eta + \lambda_0 (k - \tfrac{1}{2}) \right] \Big/ \int_0^\infty \mid \psi(\eta) \mid^2 d\eta. \tag{3.30}$$

Hence for $k \geqslant \frac{1}{2}$, ν_0^n lies upon the positive real axis in the complex p-plane. For $k < \frac{1}{2}$ no such restriction can be shown for ν_0^n except to say that our numerical searches for these eigenvalues have always given $\nu_0^n > 0$. We also note that with reference to Theorem 5.9 of Titchmarsh [5] we can show that these eigenvalues form a discrete set.

Having considered the eigenvalues we show that such an expansion (3.25) is consistent. Equation (3.24) has two linearly independent solutions, one of which is asymptotic to $\exp\left(-\frac{1}{3}\mu_0 \eta^3\right)$ as $\eta \to \infty$ and the other to $\exp\left(\frac{\nu_0^n}{\mu_0 \eta}\right)$. We require of ϕ_{-1} that $\phi_{-1}(\infty) = 0$. Thus the eigenvalues ν_0^n of (3.26) are such that the eigensolution consists only of the first linearly independent solution. Hence

$$\phi_{-1} = A_{-1} A(\eta), \tag{3.31}$$

where $A(\eta) \sim k_1 \exp\left(-\frac{\mu_0 \eta^3}{3}\right)$ as $\eta \to \infty$, $A'(0) = \lambda_0(k - 1)$, $A(0) = 1$ with A_{-1}, k_0 real constants.

Any other linearly independent solution $B(\eta)$ say will be asymptotic to $\exp\left(\frac{\nu_0^n}{\mu_0 \eta}\right)$. The choice of $B(0)$ and $B'(0)$ will ensure a non-zero Wronskian of $A(\eta)$ and $B(\eta)$ and hence that they are linearly independent. We thus specify

$$B'(0) = 1, \quad B(0) = 0, \tag{3.32}$$

and note that $B(\eta) \sim k_2 \exp\left(\frac{\nu_0^n}{\mu_0 \eta}\right)$ as $\eta \to \infty$.

At this stage A_{-1} is indeterminate and is determined from a consideration of ϕ_0 as follows. By the method of variation of parameters we obtain

$$\phi_0 = A_0A(\eta) + B_0B(\eta) + A(\eta)\int_0^\eta \frac{B(t)}{W(t)}\{A_{-1}A(t) + G(t)\}dt$$

$$-B(\eta)\int_0^\eta \frac{A(t)}{W(t)}\{A_{-1}A(t) + G(t)\}dt, \tag{3.33}$$

where A_0, B_0 are real constants, and $W(t)$ is the Wronskian of $A(\eta)$ and $B(\eta)$. Thus

$$W(\eta) = -\exp\left(-\frac{\mu_0\eta^3}{3} - \lambda_0\eta\right). \tag{3.34}$$

Now

$$G(\eta) = 1 - F(\eta) \sim \exp[-\exp(16.7(\eta - 1.5))], \tag{3.35}$$

as $\eta \to \infty$.

From (3.34) and (3.35) we see that the first integral in (3.33) behaves as $\exp(\lambda_0\eta)$ as $\eta \to \infty$ whilst the second integral converges. Applying the boundary condition at infinity then gives

$$B_0 - A_{-1}\int_0^\infty \frac{A^2(t)}{W(t)}dt - \int_0^\infty \frac{A(t)G(t)}{W(t)}dt = 0, \tag{3.36}$$

whilst the condition at $\eta = 0$ gives

$$B_0 = \frac{\lambda_0(1-k)}{\nu_0^n}, \tag{3.37}$$

so that finally we have

$$A_{-1} = \left[\frac{\lambda_0(1-k)}{\nu_0^n} - \int_0^\infty \frac{A(t)G(t)}{W(t)}dt\right] \Big/ \int_0^\infty \frac{A^2(t)dt}{W(t)}. \tag{3.38}$$

In this way ϕ_{-1} is completely determined and we may go on to determine ϕ_0, ϕ_1, etc. It should be noted that each of ϕ_{-1}, ϕ_0, etc. are only determined at each stage to within an arbitrary multiple of $A(\eta)$. The arbitrariness is removed at the next stage. Hence we have shown that (3.25) is self consistent and therefore that $\bar{c}_0$ has a discrete set of simple poles along the negative real axis. A similar analysis can be applied to higher order terms of c; this would determine ν_1^n, ν_2^n, etc.

From the foregoing analysis we have shown that c_0 has the form (3.20) where $E^i(\eta) = A_{-1}^iA(\eta)$ and $c^i = \nu_0^i$, where A_{-1}^i is the value of A_{-1} corresponding to the ith eigenvalue ν_0^i of (3.26).

Since we have insisted implicitly that ν_0^n is non-zero we have ignored the pole at the origin which yields the final steady state given by the first term of (3.20) with $c^0 = 0$. We calculate the steady-state solution directly from (3.15). Thus with $\frac{\partial c}{\partial \theta} = 0$ and $c = c_{ss}(\eta)$ we have

$$c_{ss}(\eta) = \frac{1}{k + \lambda_0(1-k)\,V(\infty)}\,\{\lambda_0(1-k)V(\eta) + k\} \tag{3.39}$$

where

$$V(\eta) = \int_0^\eta \exp\left[-\left(\lambda_0 u + \frac{\mu_0 u^3}{3}\right)\right] du.$$

Hence the effective segregation coefficient defined by

$$k_{\text{eff}} = \frac{c_{\text{solid}}}{c_{\text{liquid}}} = \frac{k}{k + \lambda_0(1-k)\,V(\infty)}\,, \tag{3.40}$$

whereas BPS obtained for the effective segregation coefficient in their analysis

$$k_{\text{eff}} = \frac{k}{k + (1-k)\exp(-1.6\,\lambda_0)}\,. \tag{3.41}$$

Equations (3.40) and (3.41) illustrate the essential difference between BPS and the present analysis. In the absence of rotation $k_{\text{eff}} = k$, and insofar as the introduction of an artificial sink at $z = \delta$ may model the effects of rotation it is reflected in the value of k_{eff} given in (3.41).

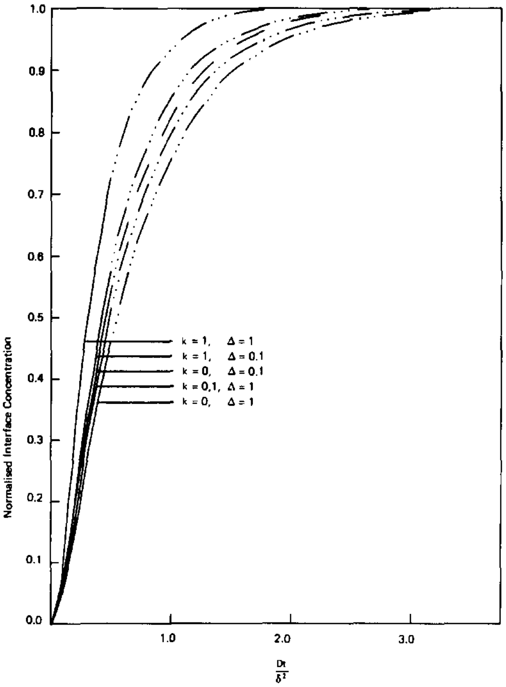

Figure 5. The normalised interface concentration against time for the rotational case obtained by our numerical integration. The asymptotic solution calculated from the first two terms of (3.20) is denoted by the broken line.

This value of k_{eff}, obtained by assuming the form (3.16) for δ is at best an approximation as comparison with (3.40) shows.

In Fig. 5 we display the interface concentration as a function of time, and it is worth remarking that for $t > \dfrac{1.5\,\delta^2}{D}$ the first two terms of (3.20), that is the steady solution and the leading time-dependent solution represent the solution to within 0.01%. Table 1 gives the values of ν_0^t and A_{-1}^1 for the corresponding values of k and Δ.

4. Discussion of results

A comparison of Fig. 2 and Fig. 4 shows that the interface concentration for the co-rotational case varies much less rapidly (by an order of magnitude) that that given by BPS. This is partly due to the fact that BPS introduce a discontinuity in the concentration gradient at $z = \delta$, which has the effect of placing a solute sink there. In turn this causes the interface concentration to rise to a smaller final value and hence with a shorter response time. Further they maintain the concentration level at $z = \delta$ whereas in our model the solute must be brought to the interface from infinity. This also contributes to the shorter response time for the BPS model.

From a detailed comparison between (3.9) and (2.11) we are able to highlight further differences between the solution obtained herein and that given by BPS. We note in particular that the BPS solution (2.11) is the sum of successively smaller terms that decay exponentially. A solution of this type only exists by virtue of the fact that the boundary-value problem is solved by BPS over a finite interval. In our solution we see from (3.9) that when $k \geqslant \frac{1}{2}$ the decay to a steady state is dominated by an exponentially small term whose coefficient also decays with increasing time, through algebraic terms. For $k < \frac{1}{2}$ we see that the response time is much greater than for $k \geqslant \frac{1}{2}$; a similar feature is reflected in the BPS solution through the characteristic equation (2.12). The reason for this change in response time as k passes through the value $\frac{1}{2}$ is not clear. However we note that for smaller values of k large quantities of solute are rejected at the interface. As a consequence large concentration gradients are formed with the result that the diffusive process is more active in opposing convection, leading, in turn, to a longer response time. For $k = 0$ no meaningful solution exists, because in this case no solute is incorporated into the solid phase at the interface. Hence the solute continually builds up at the interface as diffusion is unable to overcome convection.

Comparing Figs. 2 and 5 we see that our results for the interface concentration for the rotational case and those of BPS correspond more closely, although for large time there is still a significant disparity. This can be appreciated in detail from the fact that the eigenvalues generated by (3.26) are smaller by a factor of about two compared with those calculated from (2.12) in the BPS model. See Table 1.

We can identify three stages in time-dependent process. An initial stage where diffusion is the most important factor which acts due to the large concentration gradients imposed on the system. Then after a time convection will have brought the modified concentration jump up to the interface causing a rapid change in concentration there. Lastly when the concentration is near its final value diffusion exists in near equilibrium with convection transient effects now playing a small and diminishing role.

In this final stage the effect of maintaining a fixed concentration at a finite distance $z = \delta$ will be significant as is reflected in the relative sizes of the eigenvalues of BPS when compared to those which we have calculated.

For the reasons outlined above the model adopted by BPS, in which rotational effects are not explicitly included, can only fortuitously give results which are in reasonable agreement with those obtained from a model in which rotational effects are properly incorporated. However it may be noted [6] that the effect of applying the outer boundary condition at the finite distance $z = \delta$ from the interface introduces an artificial solute sink into the system. This sink, which leads to a value of $k_{\text{eff}} > k$, may be thought of as a crude model of the sink effect in the rotation case where solute not absorbed by the solid phase is centrifuged radially away. Of course the strength of the artificial sink cannot be accurately determined in a rational manner and depends on the value of δ. It happens that the value of δ given by (3.16) is close to that required to model rotational effects in a reasonable way, although this point was not made by BPS. As a model of the normal freeze technique the work of BPS is not appropriate. This is due in part to the fact that in the absence of a viscous boundary layer there is no way in which δ may be estimated but largely due to the fact that the introduction of any artificial sink is undesirable as it is known that no solute depletion occurs in this case so that $k_{\text{eff}} = k$.

Acknowledgement

The author acknowledges the receipt of a research studentship from the Science Research Council.

REFERENCES

[1] J. A. Burton, R. C. Prim, and W. P. Slichter, The distribution of solute in crystals grown from the melt, Part 1: Theoretical, *J. Chem. Phys.* 21 (1953) 1987-1991.

[2] N. Riley, Transient heat transfer for flow over a rotating disk, *Acta Mech.* 8 (1969) 285-303.

[3] H. Ockendon, An asymptotic solution for steady flow above an infinite rotating disk with suction, *Q. Jl. Mech. Appl. Math.* 25 (1972) 291-301.

[4] N. Riley and D. A. Sweet, Effect of rotation on Czochralski crystal growth, *J. Cryst. Growth* 47 (1979) 557-567.

[5] E. C. Titchmarsh, *Eigenfunction expansions*, Part 1. Clarendon Press, Oxford, 1962.

[6] D. T. J. Hurle, Private Communication.

[7] L. O. Wilson, On interpreting a quantity in the Burton, Prim and Slichter equation as a diffusion boundary layer thickness, *J. Cryst. Growth* 44 (1978) 247-250.

[8] L. O. Wilson, A new look at the Burton, Prim and Slichter model of segregation during crystal growth from the melt, *J. Cryst. Growth* 44 (1978) 371-376.

[9] L. O. Wilson, and N. L. Schryer, Flow between a stationary and a rotating disk with suction, *J. Fluid Mech.* 85 (1978) 479-496.