

6. Revesz, A.G.; Evans, R.J. J. Phys. Chem. Solids, 1969, 30, 551.
7. Ligenza, J.R.; Spitzer, W.G. J. Phys. Chem. Solids, 1960, 44, 131.
8. Pliskin, W.A.; Gnall, R.P. J. Electrochem. Soc., 1964, 111, 872.
9. Rosenschner, E.; Straboni, A.; Rigo, S; Amsel, G. Appl. Phys. Lett, 1979, 34, 254.
10. Evans, U.R. "The Corrosion and Oxidation of Metals"; Arnold, London, 1960, Chap. XX.
11. Irene, E.A.; van der Meulen, Y.J. J. Electrochem. Soc., 1976, 123, 1380.
12. Hopper, M.A.; Clarke, R.A.; Young, L. J. Electrochem. Soc., 1975, 122, 1216.
13. Irene, E.A.; Ghez, R., J. Electrochem. Soc., 1977, 124, 1757.
14. Irene, E.A. J. Electrochem. Soc., 1974, 121, 1613.
15. Hess, D.W.; Deal, B.E. J. Electrochem. Soc., 1977, 124, 736.
16. van der Meulen, Y.J.; Cahill, J.G. J. Electronic Mater., 1974, 3, 371.
17. Deal, B.E. J. Electrochem. Soc., 1978, 125, 576.
18. Irene, E.A.; Dong, D.W. J. Electrochem. Soc., 1978, 125, 1146.
19. Deal, B.E.; Sklar, M.; Grove, A.S.; Snow, E.H. J. Electrochem. Soc., 1967, 114, 266.
20. Taft, E.A. J. Electrochem. Soc., 1978, 125 968.
21. Irene, E.A.; Dong, D.W.; Zeto, R.J. J. Electrochem. Soc., 1980, 127, 396.
22. Nicollian, E.H. J. Vac. Sci. Technol., 1977, 14, 1112.
23. Eer Nisse, E.P. Appl. Phys. Lett., 1979, 35, 8.
24. Eer Nisse, E.P. Appl. Phys. Lett., 1977, 30, 290.
25. Irene, E.A.; Tierney, E.; Angilello, J. J. Electrochem. Soc., 1982, 129, 2594.
26. Irene, E.A. J. Appl. Phys., 1983, 54, 5416.
27. Ligenza, J.R. J. Electrochem. Soc., 1962, 109, 73.
28. Zeto, R.J.; Thornton, C.G.; Hryckowian, E.; Bosco, C.D. J. Electrochem. Soc., 1975, 122, 1409.
29. Lie, L.N.; Razouk, R.R.; Deal, B.F. J. Electrochem. Soc., 1982, 129, 2828.
30. Ligenza, J.R. J. Appl. Phys., 1965, 36, 2703.
31. Ho, V.Q.; Sugano, T. Jap. J. Phys., 1980, 19, 103.
32. Ray, A.K.; Reisman, A. J. Electrochem. Soc., 1981, 128, 2466.
33. Schafer, S.A.; Lyon, S.A. J. Vac. Sci. Technol., 1981, 19, 494.
34. Boyd, I.W. Appl. Phys. Lett., 1983, 42, 728.
35. Young, E.M.; Tiller, W.A. Appl. Phys. Lett., 1983, 42, 63.

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## Convective Diffusion in Zone Refining of Low Prandtl Number Liquid Metals and Semiconductors

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Several elementary aspects of mass diffusion, heat transfer and fluid flow are considered in the context of the separation and control of mixtures of liquid metals and semiconductors by crystallization and float-zone refining. First, the effect of convection on mass transfer in several configurations is considered from the viewpoint of film theory. Then a nonlinear, simplified, model of a low Prandtl number floating zone in microgravity is discussed. It is shown that the nonlinear inertia terms of the momentum equations play an important role in determining surface deflection in thermocapillary flow, and that the deflection is small in the case considered, but it is intimately related to the pressure distribution which may exist in the zone. However, thermocapillary flows may be vigorous and can affect temperature and solute distributions profoundly in zone refining, and thus they affect the quality of the crystals produced.

The basic idea of zone refining is that a liquid region or zone created by melting a small fraction of the material in a relatively long solid charge, ingot or feed stock. By moving this liquid through the charge in one direction the solid phase can be purified as the forward surface is melting and the rear one solidifies. This is referred to as zone refining. If the liquid zone is passed through the charge in both the forward and reverse directions, uniform distribution of impurities may be obtained. This is zone leveling.

Pfann (1) first described the essential features of zone refining and pointed out its potential as a separation technique in the early 1950's it was used to provide high purity silicon and germanium for semiconductor applications. Since then it has been

used in a variety of applications. The real power of zone refining is that one can pass a molten zone through a solid phase numerous times without difficulty. Up to a limit each pass increases the purity of the solid phase by decreasing the concentration of the solute. It is by means of multipass operation that great purity can be achieved in the solid phase.

Zone refining is a dynamic nonequilibrium separation process. However, to understand its essential features it is important to understand the equilibrium concepts on which it is based. Of central importance is the notion of the equilibrium distribution coefficient,  $k_0 = C_S/C_L$ , where  $C_S$  and  $C_L$  are the concentrations of solute at equilibrium in the solid and liquid phases respectively. Since the value of  $k_0$  may be dramatically different from unity, it is clear that at equilibrium a solute may distribute itself between solid and liquid phases with a great preference for one or the other at a given temperature. On this basis the relative amount of solute in each phase can be controlled, and a separation can be carried out.

Phase diagrams, which describe the equilibrium relations that exist between phases in mixtures, are often very complex as is the case with the nickel-aluminum diagram for example. However, if one restricts attention only to a relatively narrow range of concentration and, in particular, to dilute solutions, then one can simplify this description of these relationships markedly by using straight line approximations as shown in Figures 1(a, b).

Figures 1(a, b) represent phase relationships for cases in which solid solutions exist, a common occurrence in metallic and semiconductor systems. In such cases solidification does not cause complete separation and the degree of separation depends not only on the equilibrium relationships represented by Figures 1(a, b) but also on the convective-diffusive characteristics of the system. If the addition of solute lowers the melting point as in Figure 1a, then  $k_0 < 1$ ; on the other hand if the melting point is raised by adding solute,  $k_0 > 1$  as in Figure 1b.

A solute distribution exists in the melt because the solidification is carried out at a finite rate. For example, if  $k_0 < 1$ , then solute is rejected and accumulates at the surface which is solidifying, and this creates solute gradients in the melt which tend to be relaxed by molecular diffusion and any convection which may exist. The interfacial distribution coefficient,  $k$ , refers to the solid to liquid solute concentration ratio at the interface. It is  $k$  which is used in transport calculations when one is trying to understand the dynamic behavior of zone refining systems. It usually is found that equilibrium exists locally at the solid-liquid interface, in which case  $k = k_0$ .

The concentration,  $C_L$ , of solute in the liquid in the neighborhood of the solid-liquid interface is strongly influenced by  $k$  which thereby affects the concentration in the solid phase after solidification in at least two ways. First, the smaller  $k$  is the faster solute will accumulate on the liquid side of the interface. Second,

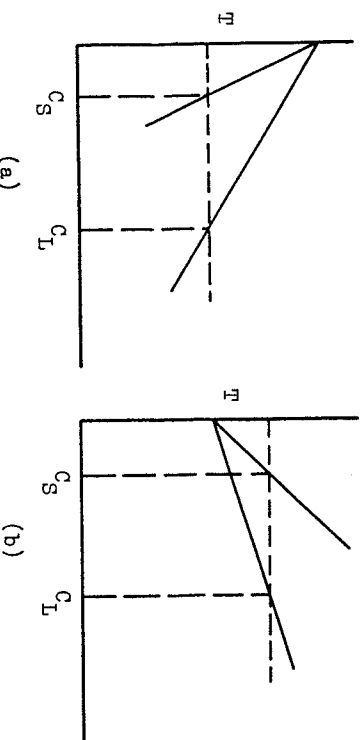


Figure 1. Possible solid-liquid phase diagrams.

It is the value of  $C_L(0)$  which determines  $G_S$  at the interface for a given value of  $k$ . With no convection in the melt, it will be shown that the maximum interfacial concentration is approached as the process progresses and is,  $C_L(0) = C_L(\infty)/k$ , where  $C_L(\infty)$  is the concentration of solute in the solution outside the diffusion boundary layer.  $C_L(0)$  climbs from  $C_L(\infty)$  to the  $C_L(\infty)/k$  asymptote.

The material to be purified often is very reactive, and it is difficult to find container materials which it will not attack. In such cases floating-zone melting is attractive and is used for example to grow oxygen free silicon crystals. In this case the molten zone is held in place by its own surface tension which works against the action of gravity. A molten zone can be established between two rods, one a polycrystalline charge or feed rod and the other a crystalline rod of purified material which is either the product of the separation or may serve as the feed for another pass. The molten zone may be created in several ways including radio-frequency induction heating as is used for silicon or electron beam heating which is favored for refractory materials.

The gravitational field limits the length of the molten zone that can be sustained by surface tension forces, and this also limits the crystal diameter. The possibility of reducing these constraints by decreasing significantly the intensity of the gravitational field has generated considerable interest in performing floating zone experiments in an orbit around the Earth. Heating from an external source creates rather large temperature gradients along the surface of the floating zone which give rise to strong thermo-capillary convective flow which mixes the melt. Furthermore this flow may couple with natural convection flows driven by the gravitational field. These flows give rise to time-dependent behavior which is of considerable theoretical and practical interest because it creates growth striations in semiconductor crystals which affect their performance, and because its origin, and the parameters which characterize it, are not well understood.

A detailed review of zone melting and its applications has been given recently by Shaw (2). In the present paper we shall confine our attention primarily to the convective-diffusive characteristics of such systems, and we shall strive primarily to obtain a sound qualitative understanding of their behavior.

The flow phenomena involved in zone refining will be discussed briefly. In particular we shall consider surface tension driven flow in a cavity containing a low Prandtl number, Pr, fluid (a low Pr number is typical of liquid metals and semiconductors). It will be shown that simplified models of such flow, which simulate the melt configuration in zone refining, predict multiple steady-state solutions to the Navier-Stokes equations exist over a certain range of the characteristic parameter.

#### The Equations of Motion, Energy and Diffusion for Molten Zones

In actual zone refining operations one may encounter three-dimensional simultaneous heat and mass transfer with moving interfaces, and the system also may be time dependent. The mode of heating affects system behavior significantly, as does radiation,

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When materials with high melting points are involved. All of the factors complicate the analysis of the diffusional aspects of this separation process. Therefore we shall treat some rather simplified versions of real systems in an effort to gain some insight into several of the important phenomena which occur.

First, we shall assume the system is two-dimensional and that the physical properties, except surface tension and density (in the body force term of the momentum equations) are constant. With these assumptions the continuity equation, momentum equations, energy equations and the diffusion equation are given by

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (1)$$

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho_\infty} \frac{\partial p}{\partial x} + \nu \left[ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right] + \frac{\rho}{\rho_\infty} g_x \quad (2)$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho_\infty} \frac{\partial p}{\partial y} + \nu \left[ \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right] + \frac{\rho}{\rho_\infty} g_y \quad (3)$$

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] \quad (4)$$

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} = D \left[ \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right] \quad (5)$$

The boundary conditions for Equations 1-5 depend on the mode heating and the way the separation is conducted. To gain some insight into how the separation occurs at the solid-liquid interface we first consider Equation 5. We shall assume that the melt is quiescent so that the process is governed entirely by diffusion and  $u$  and  $v$  are zero. If there is no convection in the melt and directional solidification is occurring only in the  $x$ -direction, then Equation 5 becomes

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} \quad (6)$$

Let us now assume, as is customary, that the charge is being moved through the heater at a constant velocity  $U$ , and that this causes the solid-liquid interface to move at the velocity  $U$ . Then it is convenient to use a coordinate  $X$  which moves with the interface such that

$$X = x - Ut \quad (7)$$

and Equation 6 becomes

$$\frac{\partial C}{\partial t} - U \frac{\partial C}{\partial X} = D_L \frac{\partial^2 C}{\partial X^2} \quad (8)$$

At time  $t = 0$  the solute concentration in the charge was  $C_0$ . Since diffusion in the liquid phase is slow, we can assume the diffusion layer near the interface is thin compared to the length of the melt; and therefore  $C(t, \infty) = C_0$ . Now we must consider the boundary condition at the interface. To do this we equate the fluxes in the solid and liquid phases at  $X = 0$  and remember that with respect to  $X$  there is an apparent convective velocity equal to  $-U$ . Furthermore,  $D_L \gg D_s$  so that solid phase diffusion can be neglected. Therefore

$$-D_L \frac{\partial C_L(t, 0)}{\partial X} = (1-k) U C(t, 0) \quad (9)$$

where  $k = \frac{C_L(t, 0)}{C(t, 0)}$ . If we assume  $k = k_0$  and use the idealized phase diagram with straight lines shown in Figure 1,  $k$  is constant and this makes it much easier to solve the problem posed in Equation 8 and 9 together with the other initial and boundary conditions.

#### Order of Magnitude Considerations

There are various ways of using Equations 8 and 9 to obtain information about the solidification process. The simplest one is to do an order of magnitude analyses, OMA, of these equations. This yields immediately that on a relative basis the first, second and third terms are of order  $l/t$ ,  $U/\delta$  and  $D_L/\delta^2$ , where  $\delta$  is the approximate thickness of the diffusion boundary layer. Equating the first and last terms gives

$$\delta \sim \sqrt{D_L t} \quad (10)$$

and the second and last terms give

$$\delta \sim D_L/U \quad (11)$$

A similar OMA of Equation 9 yields

$$\frac{C(0)}{C_0} = \frac{1}{1 - (1-k) \frac{U \delta}{D_L}} \quad (12)$$

If one combines Equations 10, 11 and 12, one gets

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$$\frac{C(0)}{C_0} = \frac{1}{1 - (1-k) U^2/D_L} \quad t \ll \frac{D_L}{U^2} \quad (13)$$

and

$$\frac{C(0)}{C_0} = \frac{1}{k} \quad t \gg \frac{D_L}{U^2} \quad (14)$$

Equations 13 and 14 provide a qualitative picture of the relationship between the concentration at the solid-liquid interface and that in the bulk of the melt.

We see from Equations 10-14 that two time regimes exist in the problem. The first period is a transient period which exists at  $t \ll D_L/U^2$ . The second period is a steady state one which occurs when  $t \gg D_L/U^2$ . Since  $D_L$  is a physical property which cannot be manipulated, we see that the greater the velocity of solid-liquid interface the more quickly a steady state is reached in the system. This conclusion is of practical importance because one often wishes to distribute the solute throughout the solid with a constant concentration.

#### Exact One-Dimensional Solutions of Diffusion Equation

In the steady state  $\partial C/\partial t = 0$ , and Equations 8 and 9 can be solved easily to give

$$C_L/C_0 = 1 + \frac{1-k}{k} \exp\left(-\frac{UX}{D_L}\right) \quad (15)$$

which gives the steady state solution for the interfacial concentration as

$$\frac{C_L(0)}{C_0} = \frac{1}{k} \quad (16)$$

Equation 16 shows clearly that the solid phase steady concentration is  $C_0$ , the initial melt concentration. It is interesting to note that Equations 14 and 16 are identical.

The solution of Equation 8, if one includes the unsteady state effect is more complex, and was apparently first shown by Smith et al. (3) to be,

$$\frac{C_L}{C_0} = 1 - \frac{1}{2} \operatorname{erfc} \frac{X+Ut}{2\sqrt{D_L t}} + \frac{hD_L}{hd_L - U} e^{-\frac{UX}{D_L}} \operatorname{erfc} \frac{X-Ut}{2\sqrt{D_L t}}$$

$$+ \frac{u-2hd_L}{2(u-hd_L)} e^{-hx + hc(hd_L-u)} \operatorname{erfc} \frac{X + (u-2hd_L)t}{2\sqrt{D_L t}} \quad (17)$$

where  $h = (1-k)u/D_L$ .

Equation 17, evaluated at  $X = 0$ , together with the definition of  $k$ , and setting  $t = x/U$ , enables one to calculate the solid phase distribution as

$$C_S = \frac{1}{2} \left\{ 1 + \operatorname{erfc} \left[ \frac{\sqrt{Ux}}{4D_L} \right] + (2k-1) \exp \left[ -k(1-k) \frac{Ux}{D} \right] \operatorname{erfc} \left[ (2k-1) \frac{\sqrt{Ux}}{4D_L} \right] \right\} \quad (18)$$

where  $x$  is the distance from the point at which the first solid was frozen.

#### Effect of Convection on Segregation

The preceding discussion assumes that no convection exists in the melt, and this is rarely, if ever, the case. Next we shall consider two approaches which account for convection in the melt, a transport mechanism which is especially important in mass transfer because  $D_L$  is small and even weak convection markedly alters solute concentration profiles and may cause macrosegregation. First we shall discuss film theory which is a very simple approach that gives qualitative information and often provides considerable physical insight into the mechanisms involved. Second, we shall discuss a simplified model of zone refining.

In film theory one assumes that the concentration changes near the interface occur in a very thin region of thickness  $\delta$ . In this region the differential equation which describes the concentration is given by the steady state ( $\frac{\partial C}{\partial t} = 0$ ) form of Equation 8. The magnitude of  $\delta$  is determined by the convection which exists in the system. One estimates  $\delta$  by solving simplified convection problems such as natural or forced convection along a flat surface, or two or three-dimensional stagnation flow, etc. From these simple cases one calculates the mass transfer coefficient,  $k_m$ , and  $\delta$  is defined as  $\delta = D_L/k_m$ . In essence, one neglects all convection when calculating  $C$  in the stagnant film, and includes all convection effects in its thickness,  $\delta$ . The stronger the convection the smaller is  $\delta$ .

The steady-state solution satisfying Equations 8 and 9 and  $C = C_0$  at  $X = \delta$  is

$$\frac{C}{C_0} = \frac{k + (1-k) e^{-\frac{U}{D_L} X}}{k + (1-k) e^{-\frac{U}{D_L} \delta}} \quad (19)$$

Therefore, one obtains the well known Burton-Prim-Slichter (4) equation

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$$\frac{C_S}{C_0} = \frac{k}{k + (1-k) e^{-\frac{U}{D_L} \delta}} \quad (20)$$

and the problem is reduced to choosing an expression for  $\delta$  which represents a realistic estimate of the convective patterns which exist in the melt. Let us use a few relevant examples to illustrate how film theory may be applied to zone refining.

By definition, the mass transfer coefficient is given by

$$j = -D_L \frac{\partial C(0,y)}{\partial x} = k_m (C(0) - C_0)$$

where  $y$  is the distance parallel to the surface and  $x$  is normal to it. Therefore the definition of  $\delta$  is,

$$\delta = \frac{D_L}{k_m} = \frac{C(0) - C_0}{k_m} = \frac{y}{Sh_y}$$

where  $Sh_y$  is the Sherwood number defined by  $\frac{k_m y}{D_L}$  and  $\frac{\partial C(0,y)}{\partial y}$  is calculated from a problem similar to the one to which we are applying film theory, but one that can be analyzed more easily. For example, to calculate  $\frac{\partial C(0,y)}{\partial x}$ , one would not include the moving boundary because that is included in the film model, the steady state form of Equation 8. One might also use a constant concentration or constant gradient boundary condition at the interface rather than Equation 9 which also is included in the film model.

Suppose natural convection is the dominant convection mode in the melt. If a natural convection boundary layer created by convection gradients exists, then its behavior depends on whether the interface is vertical or horizontal to the earth. If it is vertical, one can show that,

$$Sh_y = 0.54 Ra_y^{1/4} = 0.54 \left( \frac{\rho g \Delta T y^3}{\nu D_L} \right)^{1/4} \quad (21)$$

may be a reasonable approximation, Kays and Crawford (5), and

$$\delta \approx \frac{1}{0.54} \left( \frac{\nu D_L y}{\rho g \Delta T} \right)^{1/4} \quad (22)$$

If it is horizontal, Stewartson (6) and Gill et al. (7) showed that

$$\text{Sh}_y \approx 0.75 \text{ Ray}^{1/5} \quad (23)$$

may apply if the interface faces upward and the density of the fluid adjacent to it increases with distance from the interface; or if it faces downward and the density relationship is reversed. In this case

$$\delta \approx \frac{4}{3} \left( \frac{\nu D_L y}{\text{Rg} \Delta C} \right)^{1/5} \quad (24)$$

The important point made by Equations 20, 22 and 24 is that  $\delta$  is a function of  $y$ , the distance parallel to the interface, and this leads to segregation in the  $y$  direction (a nonuniformity of solute concentration) in the solid phase as given in Equation 20.

It is most desirable for  $\delta$  to be constant, and there are ways to make this happen. If the solid-liquid interface is circular, which is most often the case because the charge is a rod, then  $\delta$  can be controlled by rotating the rod so that the interface behaves as a rotating disk with angular velocity  $\omega$ . This configuration is widely used in analytical and electrochemistry because  $\delta$  is essentially constant if this mechanism controls. Levich (8) has shown that for a rotating disk

$$\delta = 1.61 \left( \frac{D_L}{\nu} \right)^{1/3} \sqrt{\nu/\omega} \quad (25)$$

Equation 25 shows that  $\delta$  is constant and its magnitude can be controlled by changing  $\omega$ .

Natural convection to blunt bodies such as cylinders (2-dimensional) and spheres (3-dimensional) has been studied by Acrivos (9) and from his analysis one can show that these configurations are characterized by constant boundary-layer thicknesses. For 2-dimensional bodies,

$$\delta = \frac{1}{0.54} \frac{R \nu D_L}{\text{Rg} \Delta C} \quad 1/4 \quad (26)$$

and for 3-dimensional ones,

$$\delta = \frac{1}{0.54(2)} \frac{1}{\Gamma^{1/4}} \left( \frac{R \nu D_L}{\text{Rg} \Delta C} \right)^{1/4} \quad (27)$$

where  $R$  is the radius of curvature of the surface. Note that Equation 26 is identical to 22 except that the length scale is  $R$  which is a constant, and thus  $\delta$  is a constant. This implies that the interfacial concentration of solute is uniform across the stagnation region. These results may apply to an interface which faces downward (in the direction of the gravity vector) into a fluid whose density increases with distance from the interface or one

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which faces upward into a fluid of decreasing density with distance from the interface.

When strong temperature gradients exist, natural convection may be primarily induced thermally or both heat and mass transfer may play comparable roles. In these cases the situation is more complex, because the number of parameters increases. In liquid metals and semiconductors the Schmidt number,  $\nu/D_L$ , is several orders of magnitude greater than the Prandtl number,  $\nu/\alpha$ , and this enables one to solve for the concentration profile in a rather general way without great difficulty as will be discussed next.

The number of alternative configurations of the melt and modes of heating it that may exist in zone refining is very large. Therefore it seems desirable to have a method which enables one to estimate macrosegregation under a wide variety of flow conditions. Such an approach is not available now, but some progress toward it can be made by noting that liquid phase diffusion is characterized by a large Schmidt number, which implies that diffusion boundary layers are thin compared to momentum boundary layers. It seems that Lighthill (10) was the first to suggest that one can restrict attention to the velocity field near the interface under these conditions, and by doing this one can derive the expression

$$\delta = 0.894 (9D_L \mu)^{1/3} \tau_w^{-1/2} \left[ \int_0^y \tau_w^{1/2} dy \right]^{1/3} \quad (28)$$

Equation 28 is a general result for high  $Sc$ , two-dimensional flows in which the diffusion boundary layer thickness is zero at  $y = 0$ . It includes Equations 22 and 24 as special cases, but it does not apply to systems in which  $\delta \neq 0$  at  $y = 0$ , such as stagnation regions, and also it does not include Equation 25. Equation 28 can be applied to flows which are driven by temperature differences regardless of the magnitude of the Prandtl number.

To use Equation 28 for thermally driven free convection boundary layers one simply calculates  $\tau_w = -\nu \frac{\partial u}{\partial x}(0, y)$  from known solutions. Then this result is inserted in Equation 28 and  $\delta$  in Equation 19 or 20.

Unfortunately, because of the variety of factors, such as shape, mode of heating and orientation, that is possible in melts, and the complexity of the flow patterns which may exist, it is extremely difficult to offer general rules, a priori, on how to estimate  $\delta$ . One needs to examine each particular case carefully to obtain even a qualitative understanding of the macrosegregation that may occur in the crystals being produced. However, one procedure which seems to yield generally beneficial results is crystal rotation as predicted by Equation 25.

#### Simplified Model of Surface Tension Driven Flow in a Two-dimensional Molten Zone Supported on the Bottom

The preceding discussion showed that steady-state natural convection often leads to undesirable macrosegregation. It also has been shown by Gill (11) that natural convection flows may become unstable, and

Carruthers (12) and Milson and Pamplin (13) have discussed the implications of the resulting oscillations on crystal growth. In this section we shall examine exact solutions of the Navier-Stokes equations for a two-dimensional simplified model of a molten zone which is in the form of a cavity or slot of liquid of depth  $d$ , supported on the bottom, but with a free surface on top. The zone is heated over the length,  $-\ell < x < \ell$ , by a flux,  $q$ , and cooled on its ends at  $x = \pm \ell$ , where  $L > \ell$ . We shall study the core region inside  $-\ell < x < \ell$  for which a similarity solution exists. Thus we are neglecting end-effects.

One can show that Equation 4 is satisfied by a temperature distribution in the form

$$\theta = \frac{T - T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}} = g_1(\eta) + g_2(\eta) \left(\frac{x}{\ell}\right)^2 \quad (29)$$

where  $g_1$  and  $g_2$  are functions which are determined from

$$g_1'' + 2A^3 Ma \int_1^2 g_1' = -2A \int_2^2 g_1 \quad (29a)$$

and

$$g_2'' + 2A^3 Ma [ \int_2^2 g_2' - 2 \int_1^2 f' g_2 ] = 0 \quad (29b)$$

with the initial conditions (See Appendix I)

$$g_1(0) = g_1'(0) = 0 \quad (29c)$$

$$g_2(0) = -g_2'(0) = 1 \quad (29d)$$

and  $\eta = y/d$ . Here  $f(\eta)$  and  $f'(\eta)$  are functions related to  $u$  and  $v$  which will be determined later;  $Ma$  is the Marangoni number  $\frac{\Delta T \ell |d\alpha/dT|}{\mu \sigma}$ ; and  $A$  is the aspect ratio  $\frac{d}{\ell}$ . In the limit  $Pr \rightarrow 0$ , the

solution given by solving Equations 29 implies a constant heat flux along the bottom of the cavity,  $\eta = 1$ , and a zero heat flux from the free surface,  $\eta = 0$ , into the vacuum surrounding the liquid zone. For non-zero  $Pr$  the flux at  $\eta = 1$  varies with  $x$ . Obviously Equation 29 implies that the liquid surface temperature varies as

$$T(x, 0) = T_h - (T_h - T_c) \left(\frac{x}{\ell}\right)^2 = T_h - \Delta T x^2 \quad (29e)$$

where  $T_h$  is the temperature at  $x = 0$  and  $T_c$  is that at  $x = \pm \ell$ .

Gill et al. (14) have shown by numerical computation that Equation 29e is a good approximation to a constant heat flux for fluids with finite values of  $Pr$  which are typical of liquid metals. The following discussion applies to all  $Pr$  fluids, but low  $Pr$  is the category that includes essentially all fluids of interest in semiconductor technology as well as all liquid metals. On the other hand, the most complete data on thermocapillary flows in molten zones has been reported by Preisser, Scharmann and Schwabe (15) and Schwabe and

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Scharmann (16) for  $\text{NaNO}_3$  which has a Prandtl number of 9 and  $T$  heating from the side which is not consistent with the present theory.

Levich (8) has discussed capillary motion in two-dimensional creeping flows in which the surface was flat. Yih (17) pointed out inconsistencies in Levich's analysis which were associated with assumptions of a linear distribution of surface tension with distance along the interface, and with the deflection of the surface which inevitably occurs when capillary flow exists. He noted under certain circumstances steady flows may not exist. Ostrea (18, 19) has discussed scaling problems in capillary flows.

Recently, Sen and Davis (20) studied capillary flow in bounded tubes in which  $d/\ell$  is small, and effects are present, and the flow is very slow and the cavity is heated from the side. Cowley and (21) studied the high Marangoni number "Thermocapillary analog" a buoyancy driven convection problem solved by Roberts (22). We shall make some comparisons between our results for the deflection of the surface and those of Sen and Davis (20).

The boundary conditions for Equations 1-3 which will be satisfied at  $x = 0$  and the solid bottom are straightforward, but the free surface are rather complex and call for some discussion. At  $x = 0$  we have a stagnation condition and at  $y = d$  is no slip and no penetration of fluid through the solid bottom. Therefore

$$u(x, d) = v(x, d) = 0, \quad (0 < x < \ell) \text{ and } u(0, y) = 0, \quad (0 < y < d)$$

The free surface is not flat in general and the boundary conditions on this surface require careful consideration. The kinematic condition at  $y = -h(x)$ , where  $h(x)$  is the deflection from flat surface at  $y = 0$ , is

$$\frac{dh}{dx}(x, -h) = -\frac{dh}{dx} u(x, -h)$$

Equation 31a is the steady state form of the kinematic condition which also is used to describe wave motion as discussed on page 10 of Levich's book, *Physicochemical Hydrodynamics*. One also must equate the normal and tangential components of the forces in the phase at the free surface. Since we consider a gas-liquid interface, we neglect gas phase resistance due to its viscosity and include only the pressure it imposes on the interface on the side. Therefore, at  $y = -h(x)$  the tangential component of the stress tensor for the liquid phase is equal to the tangential created by the change in surface tension with temperature in the direction. Thus the tangential force balance at the interface becomes

$$\frac{-\mu}{1 + h^2 x} \left[ \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) - 2h x \left( \frac{\partial v}{\partial y} - \frac{\partial u}{\partial x} \right) \right] = \frac{\sigma}{x} \frac{\partial T}{\partial x}$$