



ANALYTICAL MODELLING OF FLOATING ZONE CRYSTAL GROWTH

I. Martínez, J. Meseguer, and J. M. Perales
IDR/UPM, Universidad Politécnica de Madrid, Madrid, Spain (isidoro.martinez@upm.es)

(in *Advanced Space Research* 29, p. 569-574, 2002)

ABSTRACT

An analytical model for predicting the outer shape evolution of a crystal grown by the floating zone technique is developed. The analysis is axisymmetric and linear in the departure from a cylindrical evolution, thus it only applies to crystal growth under negligible external force fields (e.g. under microgravity), when the seed and feed sizes do not differ too much, and when radial deformations are not pronounced. In spite of these limitations, the analytical model clearly shows that, depending on the slenderness of the molten bridge, the processing may give rise to steady growth (after some transients) or just to a breakage by capillary forces.

INTRODUCTION

In the floating zone technique of crystal growth, a molten zone is established between two rods: a charge or feed rod of polycrystalline material, and a seed rod (monocrystalline in the ideal case). The molten zone can be established in a variety of ways depending on the material to be crystallised; for example radio frequency induction heating using a single turn coil or radiation heating in mirror furnaces are commonly used with silicon, whereas electron beam melting is employed in the case of refractory metals (Cröll et al. 1988).

The equilibrium shapes and stability limits of the floating zone melt under the large variety of disturbances that could arise either accidentally or intentionally during the growing process is a matter of great concern. Its study involves a formidable task both because of the material characteristics of the melt, whose properties are strongly temperature dependent, and because of the complexities associated to the disturbances which could be imposed on the zone. Thence, several simplifications must be introduced in the model. The simplest approach consists in disregarding phase changes, considering an isothermal liquid zone held between two parallel solid disks, the so-called liquid bridge model of the floating zone process (Martínez and Cröll, 1992).

Of course there are many differences between isothermal liquid bridges and real floating zones. The behaviour of the melt in a real floating zone is driven by many effects (dynamics, convection, diffusion, phase changes, electric and magnetic effects, reactive processes...) which are not accounted for in the liquid bridge problem. However, in spite that the real solid-liquid interfaces are rather different between liquid bridges (where supports are assumed to be flat) and floating zones (where protruding solid ends appear), it is of no importance at all for the mechanical stability of the melt. Thus, to a first approximation, assuming that the interest is focussed on the hydrostatic behaviour of the molten zone (equilibrium shapes and their stability), the above-mentioned effects can be considered negligible, valid results are obtained (Martínez and Eyer, 1986), and consequently its use has widespread.

Equilibrium shapes and stability limits of capillary liquid bridges have been extensively analysed from both the theoretical and the experimental point of view during the last decades, and as already said many papers dealing with such fluid configurations have been published (a review of the state of the art in the field can be found in Meseguer et al. (1999)).

An analytical method to compute the temporal evolution of the molten zone and the melting and resolidifying solid boundary is devised in this paper. The model allows not only to predict the shape of the molten zone at any time and the shape of the grown crystal, but also to monitor the stability of the process. This way it is possible to select appropriate parameters to ensure a stable growing process.

MODELLING

Although the modelling might have been extended to account for many other details, to make it clearer we restrict it here to an initial circular solid rod (e.g. $R_0=10$ mm) made of silicon, and a very simple heating law (not so simple to achieve in practice, however): the heating is such that the length of the molten zone is constant with time (e.g. $L_0=40$ mm).

Because only quasi-static evolutions in absence of gravity are considered, the density and surface tension values of the melt are irrelevant, i.e. no weight, no inertia, no convection (the surface tension value modifies the internal pressure in the melt but not its shape). Since the solid-liquid interface is assumed planar (Martínez and Cröll, 1992), the only two material parameters in the model are the relative change in density from solid to liquid, $\Delta\rho/\rho$ (silicon shows an anomalous contraction of 8% in volume upon melting, similarly to water that contracts 9% when ice melts), and the growth angle, ϕ (the receding angle between the liquid slope and the solid slope when the crystal grows), that for silicon is 11° (13° for germanium).

The linear analysis of the interface shapes of liquid bridges between circular supports and nearly-cylindrical shapes is well documented in Meseguer et al. (1996), and it can be used to predict the molten shape when the initial solid bar of constant radius R_0 melts in a length L_0 . The axisymmetric liquid interface $R_F(Z)$ spanning a length L_0 has the shape (cylindrical, if not for the density change on melting):

$$F(z) = 1 + \frac{\Delta\rho}{\rho} \frac{\Lambda}{2} \frac{\cos(z) - \cos(\Lambda)}{\sin(\Lambda) - \Lambda \cos(\Lambda)}, \quad (1)$$

where $\Delta\rho/\rho=-0.08$ for silicon and sizes have been scaled with the initial rod radius, i.e. $F=R_F/R_0$, $\Lambda=L_0/(2R_0)$ and $z=Z/R_0$. The melt is considered in weightlessness.

But the aim is to predict the sequence of shapes $R_F(Z,t)$ spanning a length L_0 from $Z_1(t)$ to $Z_1(t)+L_0$ during the float zoning. In order to go on using the linear analysis of the interface shapes as in Meseguer et al. (1996), a time-varying non-dimensionalisation is introduced in the following way. Let $R_1(t)=R_F(Z_1,t)$ and $R_2(t)=R_F(Z_2,t)$ be the radii at the ends (say 1 for the left and 2 for the right) of the molten zone at an instant t . We introduce the non-dimensional variables:

$$F \equiv \frac{R_F}{\frac{R_1 + R_2}{2}}, \quad z \equiv \frac{Z - \frac{Z_1 + Z_2}{2}}{\frac{R_1 + R_2}{2}}, \quad \Lambda \equiv \frac{Z_2 - Z_1}{R_1 + R_2}, \quad h \equiv \frac{R_2 - R_1}{R_1 + R_2}, \quad v \equiv \frac{V_F}{\pi \left(\frac{R_1 + R_2}{2} \right)^2 (Z_2 - Z_1)} - 1, \quad (2)$$

where now the melt shape $F(z,t)$ extends from $z=-\Lambda$ to $z=\Lambda$ in the new coordinates centred midway in the melt, Λ is the slenderness of the molten zone (aspect ratio), h measures the inequality in radial sizes at the two ends, and v measures the excess volume relative to the cylindrical one with the mean radius (V_F is the molten volume in dimensional units). The target then is to find the functions $h(t)$ and $v(t)$ due to the growing process, since the shape $F(z,t)$, in the linear approximation is just (Meseguer et al. 1996):

$$F(z) = 1 + v \frac{\Lambda}{2} \frac{\cos(z) - \cos(\Lambda)}{\sin(\Lambda) - \Lambda \cos(\Lambda)} + h \frac{\sin(z)}{\sin(\Lambda)}, \quad -\Lambda \leq z \leq \Lambda. \quad (3)$$

valid for $v \ll 1$ (small departures from the cylindrical volume) and $h \ll 1$ (small relative difference in end radii). Neglected non-linear effects would be of order v^2 , vh or h^2 .

The evolution of the floating zone is modelled as follows. The seed or growing front (let say the left end, subscript 1) progresses in such a manner as to maintain the so called growth angle, ϕ , constant, that in this linear analysis means (Figure 1):

$$\frac{dR_1}{dZ_1} = \left. \frac{dF}{dz} \right|_{z=-\Lambda} - \phi, \quad (4)$$

where the melt spans from $z=-\Lambda$ to $+\Lambda$ in the adapted coordinates. Substitution of Eq. (3) in Eq. (4) gives:

$$\frac{dR_1}{dZ_1} = v \frac{\Lambda}{2} \frac{\sin(\Lambda)}{\sin(\Lambda) - \Lambda \cos(\Lambda)} + h \frac{\cos(\Lambda)}{\sin(\Lambda)} - \phi. \quad (5)$$

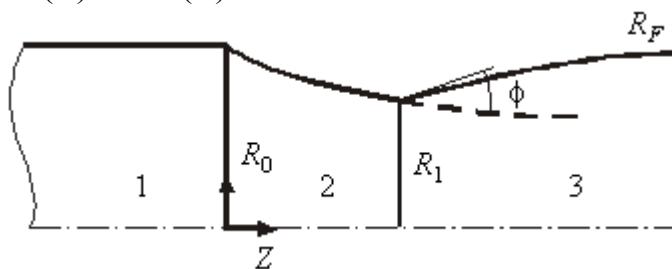


Fig. 1. Detail of growth angle geometry: 1) seed; 2) grown crystal; 3) melt.

The feeding front radius doesn't change during the process. The volume of liquid in the molten zone, V_F , assuming planar solid-liquid interfaces (what was demonstrated a good approximation in Martínez and Eyer (1986)), changes in spite of the molten length being kept constant, if the end radii are not equal in size. That is:

$$\frac{dV_F}{dZ_1} = \pi (R_2^2 - R_1^2) \left(1 + \frac{\Delta\rho}{\rho} \right), \quad (6)$$

where the last parenthesis in Eq. (6) stands for the different in density of the two infinitesimal solid slices (the left one leaving and the right one entering) exchanged by the liquid volume in a time dt while the left-hand end advances dZ_1 .

LINEAR SOLUTION

The solution to be found, in non-dimensional variables, is $h(\zeta)$ and $v(\zeta)$; i.e. how the growing radius (relative to the initial one) and the excess volume (relative to the cylindrical one) evolve with the axial position of the growing front, ζ , made dimensionless with the initial radius, i.e.:

$$\zeta \equiv \frac{Z_1}{R_0}. \quad (7)$$

If $h(\zeta)$ and $v(\zeta)$ were known, and taking into account that $R_2=R_0$ all the time, one gets from the definitions in Eqs. (2) and retaining only linear terms:

$$R_1 = R_0(1-2h), \quad V_F = 2\pi R_0^3 \Lambda_0(1+v-2h), \quad \Lambda = \Lambda_0(1+h), \quad (8)$$

which, upon substitution in Eq. (5) and Eq. (6) yield respectively:

$$-2 \frac{dh}{d\zeta} = v \frac{\Lambda_0}{2} \frac{\sin(\Lambda_0)}{\sin(\Lambda_0) - \Lambda_0 \cos(\Lambda_0)} + h \frac{\cos(\Lambda_0)}{\sin(\Lambda_0)} - \phi, \quad (9)$$

$$2\pi R_0^2 \Lambda_0 \left(\frac{dv}{d\zeta} - 2 \frac{dh}{d\zeta} \right) = \pi \left(R_0^2 - R_0^2(1-4h) \right) \left(1 + \frac{\Delta\rho}{\rho} \right), \quad (10)$$

The last equation more properly arranged stands:

$$\frac{dv}{d\zeta} = 2 \frac{dh}{d\zeta} + \frac{2h}{\Lambda_0} \left(1 + \frac{\Delta\rho}{\rho} \right). \quad (11)$$

Thus, we finally have the linear system, in matrix form:

$$\begin{bmatrix} \frac{dh}{d\zeta} \\ \frac{dv}{d\zeta} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} h \\ v \end{bmatrix} + \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}, \quad (12)$$

with

$$a_{11} = \frac{-\cos(\Lambda_0)}{2\sin(\Lambda_0)}, \quad a_{12} = \frac{-\Lambda_0}{4} \frac{\sin(\Lambda_0)}{\sin(\Lambda_0) - \Lambda_0 \cos(\Lambda_0)}, \quad a_{21} = 2a_{11} + \frac{2}{\Lambda_0} \left(1 + \frac{\Delta\rho}{\rho} \right), \quad a_{22} = 2a_{12}, \quad (13)$$

$$b_1 = \frac{\phi}{2}, \quad b_2 = \phi, \quad (14)$$

that, completed with the appropriate initial conditions, i.e. $h(0)=0$ (equal ends before processing) and $v(0)=\Delta\rho/\rho=-0.08$ (volume contraction for melting silicon), gives the solution sought in a linear differential form. The later can easily be integrated in terms of its eigenvectors, giving rise to exponential complex functions with the real part indicating exponential growth or decay of the functions. Here it is

not even necessary to integrate the system to gain valuable insight to the problem of the stability of the crystal growth, as commented below.

RESULTS

The autonomous linear system corresponding to Eq. (12), once the material is fixed (e.g. silicon) has only one parameter, the slenderness of the molten bridge Λ_0 . For small Λ_0 the crystal growing first necks and then recovers the initial radius after a small overshooting. For a certain Λ_0 that cancels the real part of the eigenvalues in Eq. (12) ($\Lambda_0=2.25$ for silicon), the system oscillates in a limit cycle (the crystal grown alternatively necks and bulges). For larger Λ_0 the floating zone process becomes unstable by unbounded necking (until the molten bridge disrupts by mechanical instability). This behaviour is seen in the phase diagram for Eq. (12), shown in Figure 2, obtained by direct integration of Eq. (12). All growth processes start from the point ($h=0, v=-0.08$) and progress as indicated by the arrow. Additionally the steady solutions to Eq. (12) (cancelling the derivatives) show that, for $\Lambda_0 < 2.25$, the stable attractor is the point ($h=0, v=2\phi[1/\Lambda_0-1/\tan(\Lambda_0)]$), e.g. (0, 0.4) for $\Lambda_0=2$, as can be seen in Figure 2.

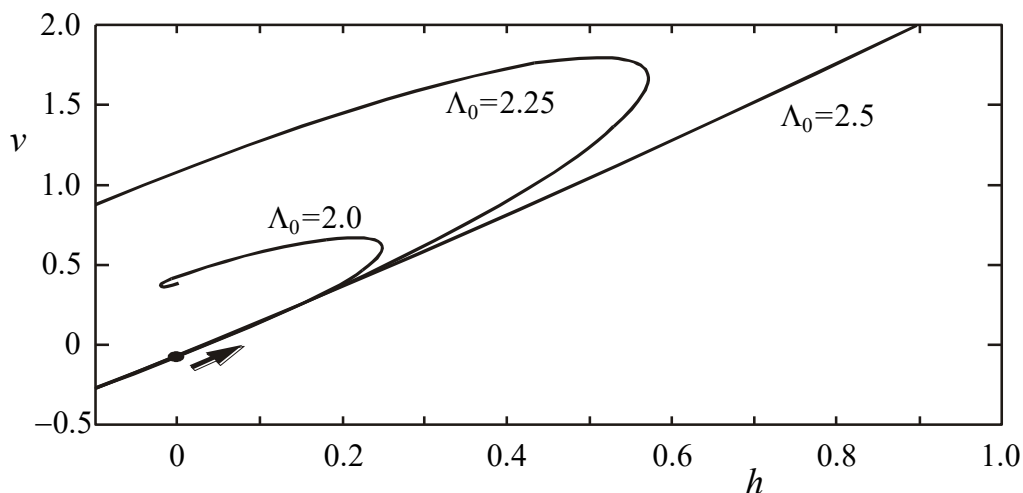


Fig. 2. Analytical results for the floating zone process of silicon crystal growth for three initial lengths of the melt (Λ_0 , kept constant), showing the excess volume, v (relative to that of a cylinder) versus the relative difference in radii at both ends of the liquid, h , as the zoning progress (starting at $h=0$ and $v=-0.08$, black point) in the direction of the arrow.

These analytical results compare very well qualitatively to the non-linear numerical simulation developed in Martínez, Meseguer and Perales (2001) that is shown below (Figures 3 to 5) to place the analytical results in a better context.

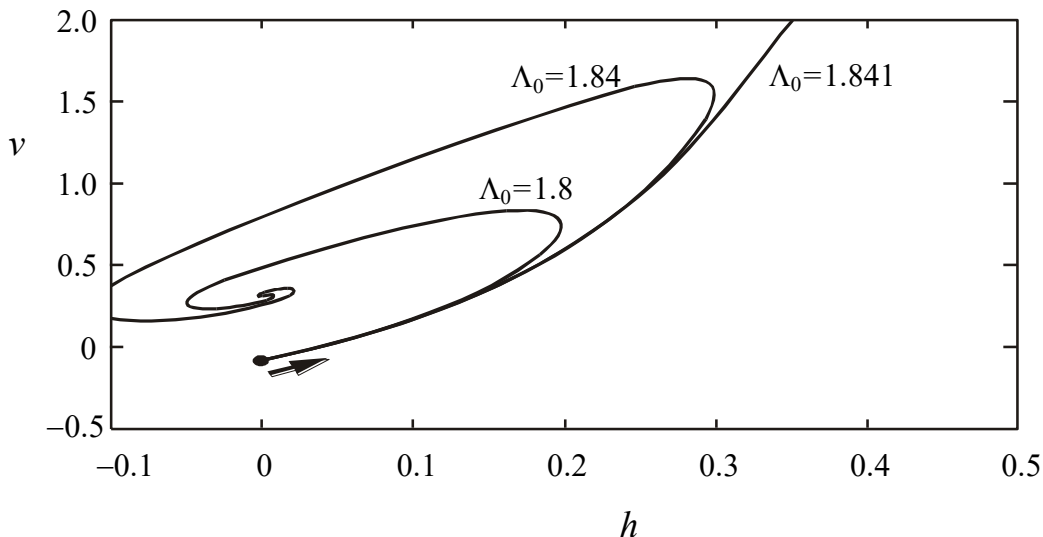


Fig. 3. Same as Figure 2 but corresponding to the non-linear numerical simulation. Note that although the start and end points are the same as in the linear analytical solution shown in Figure 2, there is not limit cycle here and the bounds on the radial deformation are nearly halved here.

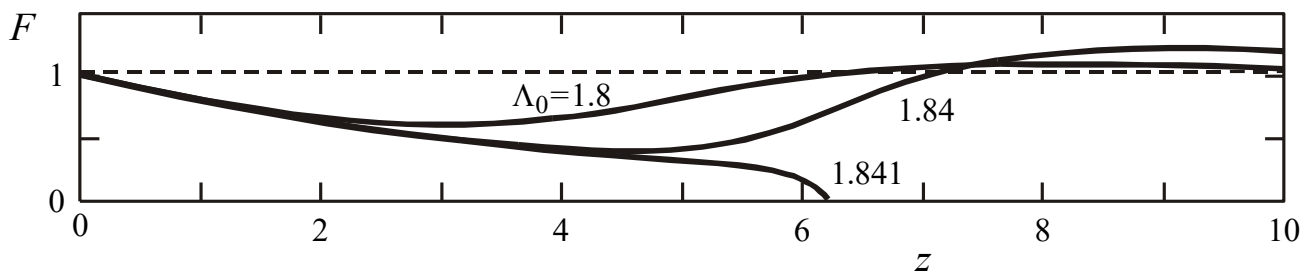


Fig. 4. Grown crystal shape for silicon floating zone processing, obtained by non-linear numerical simulation. Non-dimensional radius, F , vs. non-dimensional axial coordinate, z , for three initial lengths of the melt, Λ_0 (i.e. the aspect ratio, kept constant).

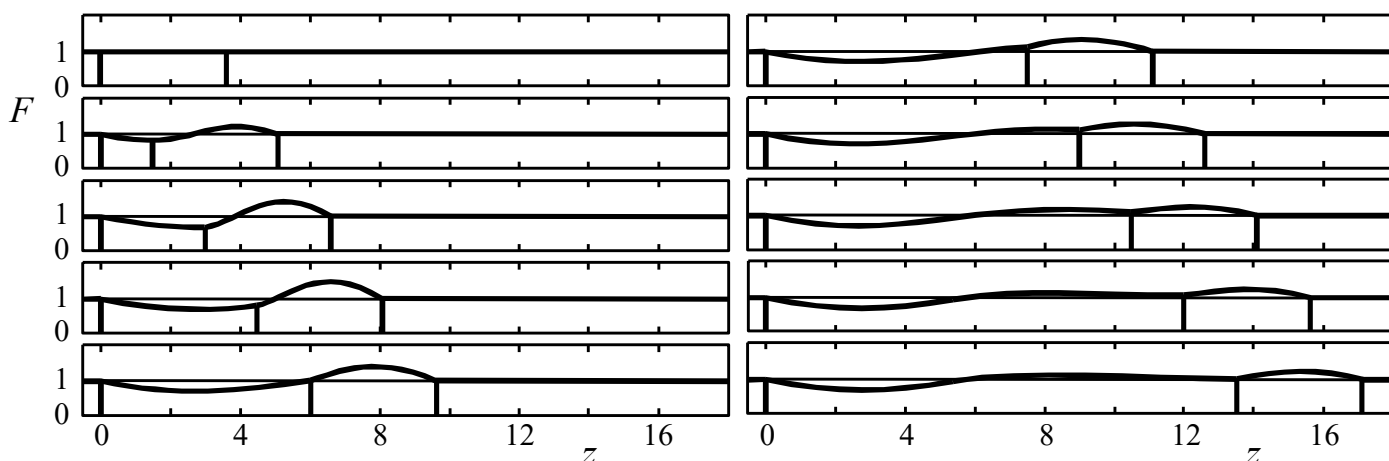


Fig. 5. Sequence of shapes during the floating zone processing of a silicon rod, obtained by non-linear numerical simulation: 1, crystal; 2, melt; 3, feed rod. The length of the molten bridge is $\Lambda_0=1.8$ assumed maintained constant by a suitable heating law.

ACKNOWLEDGMENTS

The authors acknowledge the support of the Spanish Ministerio de Ciencia y Tecnología (MCYT).
Analytical modelling of floating zone crystal growth

REFERENCES

- Cröll, A., Kaiser, T., Schweizer, M., Danilewsky, A.N., Lauer, S., Tegetmeier, A., Benz, K.W., Floating-zone and floating-solution-zone growth of GaSb under microgravity. *J. Crystal Growth* **191**, pp. 365-376, 1998.
- Martínez, I. and Cröll, A., Liquid bridges and floating zones, in Materials and Fluid Sciences in Microgravity, ESA SP-333, pp. 135-142, 1992.
- Martínez, I. and Eyer, A., Liquid bridge analysis of silicon crystal growth experiments under microgravity *J. Cryst. Growth* **75**, pp. 535-544, 1986.
- Martínez, I., Meseguer, J. and Perales, J. M., Simulation of non-axisymmetric floating zone crystal growth under microgravity, *Microgravity Sci. Technol* (submitted), 2001.
- Meseguer, J., Bezdenejnykh, N.A. and Rodriguez-de-Francisco, P., On the use of liquid bridges as accelerometers, *Microgravity Sci. Technol.* **9**, pp. 62-69, 1996.
- Meseguer, J, Perales, J.M., Martínez, I., Bezdenejnykh, N.A. and Sanz, A., Hydrostatic instabilities in floating zone crystal growth process, *Current Topics in Cryst. Growth Res.* **5**, pp. 27-42, 1999.