THE STABILITY OF THE MOVING BOUNDARY IN SPHERICAL AND PLANAR GEOMETRIES AND ITS RELATION TO NUCLEATION AND GROWTH

Rahul Basu[1]

[1]Sambhram Institute of Technology, VTU
MS Palya, Jalahalli (E)
Bangalore 560097, Ka,India

Keywords: Nucleation[1], Stability[2], Moving Boundary Problem[3]

Abstract

Coupled heat and mass diffusion equations are set up and solved for various Stefan numbers. A stability criterion is developed for the moving interface. The general MBP is of importance in many fields, particularly in directional solidification. The analysis is applied to the homogenous nucleation and growth of a spherical particle. Traditional analyses have relied on energy balances between surface and volumetric energy. An exact solution is analyzed for appropriate boundary conditions here. The present derivation presents unpublished analyses using perturbation and consideration of the unknown moving boundary of the nucleating particle. Only certain solutions for the MBP are known and it is difficult to find solutions for the general case due to the extreme non-linear nature of the problem because of discontinuous material properties across the liquid and solid regions, and the unknown position of the liquid solid phase boundary. These concepts are applied to nucleation and phase field theory for homogenous nucleation with application to amorphous alloy formation.

1.Introduction

The problem of solidification and melting is of interest in such diverse areas as geology, metallurgy, food processing and cryosurgery. Carslaw and Jaeger (1) claim only certain solutions known for certain geometries. Some of the earlier works on the interface boundary are by Mullins Sekerka (2), and Pedroso Domoto (3). The problem was first tackled by Stefan (4) in the analysis if the melting of polar ice in the late 1800's. The classic work of Mullins Sekerka (2) dealt with a perturbation analysis of the moving phase interface. In this paper a stability criterion is derived for the moving interface in the convective case, with appropriate linearization. The nucleating phase is treated as having a moving boundary, and stability analyzed as an MBP. Some experimental data is applied and ball park figures for amorphous film formation are analysed using ideas of phase field theory and laser thermal fluctuations. Other configurations like needles, whiskers, lamellae can also be studied by appropriate coordinate transformations.

2 Solidification of a spherical body

The solutions to the equations within and outside the nucleating phase have to satisfy certain conditions for stability, and are listed in Paterson (5). The usual analysis of nucleation relies on thermodynamics and a balance of surface and volumetric free energy, giving a 'Critical Nucleus" size or radius which depends on the surface energy, (Surface tension) and the Gibbs Free energy (Volumetric based). It does not describe the subsequent growth of the stable nucleus with time. The phase field theory of nucleation has formulations which include fluctuations as homogenous nucleation (6), exponents depending on geometry and dof's., nucleation or diffusion controlled growth across the interface, and KJMA analysis (7) , (8). Perturbation Stability of the nucleus has also had a large group of adherents starting with the seminal papers of Mullins and Sekerka, (2). The Moving Boundary analysis for the Sphere is adapted to describe this phenomenon which may by contrast appear deceptively simple. The solutions in the two regions (nucleating solid and matrix) are:

$$\theta_1 = A[(K_1 t)^{0.5} /r \exp (-r^2/K_1 t) - \pi/2 \operatorname{erfc} [r/2 (K_1 t)^{0.5}] - B \qquad 1$$

(similarly for region 2).
Applying boundary conditions, $,_1\theta = \Theta$ when $t = 0$, $R = 0$ and $_1\theta = -B$
$C = q/4\pi k_2 (K_2)^{0.5}$
$B = ,\Theta$ where melting temperature is zero and initial temperature is $- .\Theta$
The equation for α is obtained from the interfacial energy balance

$$q/4\pi \exp(-\alpha^2/4K_2) - k_1\alpha\Theta /[1- \alpha/2(\pi/K_1 t)^{0.5} \exp(\alpha^2/K_1) \operatorname{erfc}(\alpha/2(K_1)^{0.5}] = L\rho\alpha^3/2 \qquad 2$$

Setting particular values for the physical parameters, solutions can be obtained by solving this transcendental equation. Results are in Figures 1 and 2.

2.1 Adiabatic Boundary (Insulated wall)

Consider now the case of the boundary conditions where an adiabatic condition is imposed at the origin. By transforming to a rectilinear case, it is seen that this is equivalent to the problem of an insulated wall with a freeze front moving away or to it. Physically this would correspond to a nucleus forming on an insulated wall. Homogenous nucleation has been difficult to prove but it is likened to nucleation on walls of a capsule or substrate, (8). In terms of the above analysis, it can be arrived at by putting the constant C in the general solution to be zero,

$$\text{since } d\theta_1/dr = C (K_1 t)/r^2 \exp(- r^2/4K_1 t), \qquad 3$$

and if the flux at $r = 0$ is zero the constant C should be identically 0. Furthermore, from the initial condition , at $t = 0$ and $r =$ infinity, the temperature is $-\Theta$;
Hence the first term in the thermal balance equation which depended on C drops out, and one is left with

$$-k_1\alpha\Theta/[1-\alpha/2(\pi/K1)^{0.5} \exp(\alpha^2/4K_1) \operatorname{erfc}(\alpha/2(K_1)^{0.5}] = L\rho\alpha^3/2 \qquad 4$$

The solution of this equation occurs at 0.0108, which is less than the previous case. A similar problem has been analyzed by McCue (9) , where the problem is set up as follows

$$du/dt = 1/r^2\, d/dr(r^2\, du/dr) \quad R < r < 1 \qquad 5$$

$dv/dt = K/r^2 \, d/dr (r^2 \, dv/dr) \quad 0 < r < R$ 6

where the variables have been scaled s.t R is the interface, u=v =0 at the interface (r=R)
B.C. u = -1 on r=1,U =0 on r =R, dv/dr =0 on r=0,V=0 on R
*I.C. v =V at t =0,R =1 at t=0 (*u describes the solid and v the liquid phase temperatures.The problem describes inward solidification of a liquid sphere). It is claimed this has no solution.

2.2 SPHERICAL DIRICHLET BOUNDARY CONDITIONS

For the Dirichlet problem, (eg. The freezing of molten liquid), the boundary conditions are
$\theta_2(\infty, t) = 0$ at t = infinity
Initial temperature Θ,
Final temperature $\theta_2(\infty, t=\text{infinity}) = 0$
Setting up the equations and putting the interface temperature as 0, the interfacial conditions give exactly the same balance equation as the one already obtained for the "adiabatic" case. Specifically, the solutions are in each region,

Liquid $\theta_1 = (\theta_m + \theta_0)[\text{spherf}(x)/\text{spherf}(\alpha)] - \theta_0$ 7

Solid $\theta_2 = \theta_m[\text{spherf}(x)/\text{spherf}(\alpha)]$ 8

When the m.p. temperature is taken as zero as in the earlier cases. The thermal balance equations are the same for the two instances (Dirichlet and zero heat source and /or adiabatic). Although the thermal profiles may be non identical, the results show that they are different only up to an additive or multiplicative constant varying with the initial temperature.

2.3 HEAT SINK OR SOURCE AT ORIGIN. For the case of the heat sink or source at the origin, the solution given in Paterson (5) is easily fitted to the boundary conditions. The general solution can be expressed as

$u = A + B\left(t^{0.5}/r \exp(-r^2/4t) - (\pi/2)^{0.5} \text{erfc}(r/2(t)^{0.5})\right)$ 9

Applying u = -1 at t =0, gives A = -1
Whereas u = 0 on r = R (interface), gives an expression for B in terms of spherf(λ), specifically, B = 1/spherf(λ)
Examining dv/dr = 0 on r =0.

The general solution for v= $C + D[\text{spherf}(r/(Kt)^{0.5})]$ 10

$dv/dr = -D (Kt)^{0.5}/r^2 \exp(-r^2/Kt))$ 11

At r =0, the expression is 0 if D =0.
Thus the solution for v given the stated B.C. is v = C =V (at t =0, and for all t) ,
If v =0 on r =R, this condition is incompatible with the stated condition v =Vat t =0, because the analytical solution for v(r,t) is a constant. Hence either v =0 or v=V, so only v =0 can be chosen

to be consistent with the temperature (reduced) at the phase interface., i.e. the mp stays constant in the molten region as dT/dx =0 at x =0, (and hence no flux of heat).
Thus v=0, (equal to the melting point everywhere in the liquid).
Hence the problem stated has a solution

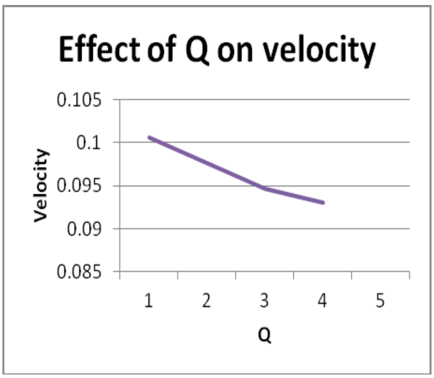
$u = -1 + B (\text{spherf}(r/2 t^{0.5})), B = 1/\text{spherf} (\lambda)$
$R < r < 1$ 12
$v = 0 , \ 0 < r < R$
Where R = 1 at t =0. v =V at t =0 and v = 0 at r =R cannot be simultaneously satisfied by the same expression for v which is a constant (This has relevance for the case of nucleation on an insulated wall or container as for instance a thermos flask).

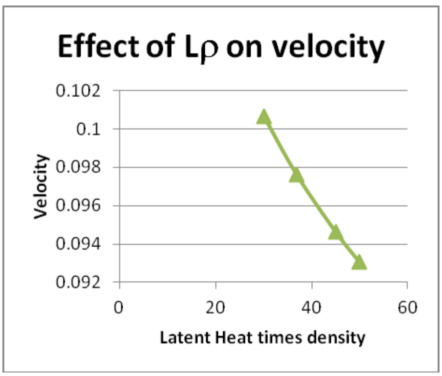
3 Results for parameter variation for the sphere.

The predominant effect arises from the variation of the velocity parameter in the thermal balance equation, given in eqn[2]. Although transcendental terms occur, the main effect is from the power term on the r.h.s of eqn[2], the terms on the LHS are exponentials and for small α are small and can be replaced by 1 . An approximate eqn for eqn [2] for small α can be expressed as

$$q/4\pi - K_1\alpha\, \Theta/(1-\alpha/2\, (\pi/4)^{0.5}) = L\, \rho\, \alpha^{3}/2 \qquad 13$$

For the spherical case if q is neglected (self ablation) this equation is a cubic in α . In the cylindrical case, the power is one less on the RHS.





.

Figure1 Q vs Velocity of freezing **Figure 2 Lρ/2 versus velocity of freezing**

3.1 SUBLIMATION OR ABLATION OF A SPHERE

The problem of sublimation is of significance when the nucleus forms in a rarefied atmosphere or vacuum without an intermediate liquid phase. Mathematically it can be described by using he appropriate parameters in the thermal balance equation given in Paterson, (5).

The parameters for the vapour are: ρ =1.694 Kg/m^3 at 1 bar, diffusivity 2.338 x 10^{-5} m^2/s, conductivity varying from .016 to .0248 W/m/K, L =540 cal/gm. With the same values for the heat source, the reaction is driven by the heat of sublimation which is 540+73.6 =613.6 cal/gm, and a simulation by WOLFRAM gives: $x \approx 0.0846932830339482\ldots$ For the adiabatic case, the solution is much less since the motion of the interface depends on the latent heat of the solid-liquid+liquid-vapour=solid vapour.

Solution is given as $\{x \to -0.000122892\}$

The velocity is about three orders of magnitude less, and is seen to move in the opposite direction to normal freezing buildup, as is to be expected for ablation or sublimation. Table 1 gives further values

4 NUCLEATION WITH COUPLED HEAT AND MASS TRANSFER

In case of coupled mass and heat transfer, application is made to nucleation with both mass and thermal diffusion across the interface. Take the rectilinear case without loss of generality. Following the development in Luikov (12), the thermal equation with the mass coupled terms are given after non dimensionalisation by:

$T'' + \eta/2\ T' + (\varepsilon L/\rho c_p)\ dc/dt$ 14

Relating the concentration derivative to the thermal gradient by $C' = T'/g$. 15

T' is related again to T by the convection relation $dT/dx = h/k\ T$, 16

with appropriate modifications for the non dimensionalisation and derivatives relating d/dx to d/dη.Eventually the linearised coupled diffusion equation is obtained where the effect of c' is replaced by using the concentration-thermal gradient:

For the liquid phase: $[\boldsymbol{D}^2 + \eta/2\boldsymbol{D}]\ \theta = 0$ 17

For the solid phase with the remelt term:

$[\boldsymbol{D}^2 + \eta/2\boldsymbol{D} + (\varepsilon L/\theta m c_p)\ Bi/2g]\ \theta = 0$ 18

Introducing a small parameter $\mu = g/(\varepsilon\ Ste)$

$\mu\theta'' + Fo\ \mu/2\ \theta' + Bi/2 = 0$ 19

(Note: the convective boundary condition is incorporated via the Bi parameter)

4.1 PERTURBATION SOLUTIONS:

Mullins Sekerka (2) look at perturbation from the effect of variation of the phase boundary on the concentration. This is a micro view, whereas in the present approach the effect of boundary parameters on the diffusive field is looked at in the larger picture. Eqn (19) has the following solutions:

Inner solution

$\mu\theta'' + F_0\, \mu/2\, \theta' = 0$ 20

$\theta'' + F_0 /2\, \theta' = 0,$ 21

which is easily solved in terms of exponentials.

Outer solution

$F_0\, \mu/2\, \theta' + Bi/2 = 0,$ 22

taking $F_0\, \mu$ as the small parameter, the solutions are obtained as a polynomial series. Additionally, if Fo is very small,

$\mu\theta'' + Bi/2 = 0,$ 23

With the stated boundary conditions, an exact solution can be obtained as follows for the Dirichlet, Convective scenarios: General solution exp (Y) η

$Y = [- Fo\, \mu/2 \; + - sqrt((Fo\, \mu/2)^2 \; - 4\, \mu\, Bi/2)]/2\mu$ 24

Pedroso Domoto (3), did not consider coupled mass and thermal effects, while Soward(18) developed a unified solution for cylinders and spheres.

4.2 EFFECT OF BOUNDARY CONDITIONS on STABILITY:

Regardless of the boundary conditions, the characteristic of the differential equation is unchanged and depends only on the Fourier, Stefan and Biot numbers, the stability of the solution being unaffected by the pre multiplying and additive constants to the solution. Other approaches to the study of ablation use low temperature sublimation models to visualize the effects of high temperature ablation in space, (12- 14). Ablation is also being used in cryosurgery to produce low temperatures behind ablating surface tissues, (14). Some researchers use ablation to analyze ice cores, (15) while other applications are seen in laser ablation of space debris (16). An application of the method of finding the transcendental root of the thermal balance equation [5] is extended to the case of the sublimation of ice from a sphere.

Two cases are possible

a) sublimation from the surface of the sphere

b) deposition from vapour to solid (accretion) on the sphere

The second possibility is physically possible as formation of snow crystals and hoar frost directly from vapour. The pressure effect is not included in the equations, and hence the results are obtained assuming the pressure remains constant. By transforming the problem to rectilinear coordinates it is seen that this sign change in L merely shifts a sublimating surface from one direction to the other. Here, it depends on the sign of the terms in eqn[4]. Focusing on the case of self sublimation (ice-vapour), heat source strength q is set to zero, and using the appropriate values for ice and vapour, the results are given in Table 1.

Applications for the methods described above have been suggested for the formation of nano composites with micro spheres embedded in a matrix , Wu (17), while the problem of exact solution of spherical phase change remains unsolved, Soward, McCue, Stewartson (18,19, 20). Soward (18) has given a perturbation expression which is applicable to either the cylindrical or spherical cases by changing the exponent of the terms in the series. For the problem with an insulated boundary, it needs to be asserted that a variable error function solution is physically and mathematically inconsistent with the constant derivative boundary conditions. With laser heating of the surface, the oscillations are normally damped very quickly within the boundary layer depending on the Fourier number which is the coefficient of the first order term in the inner solution (eqn 20). The stability analysis done earlier in the paper shows that oscillations may be sustained in the heated layer if the discriminant is negative. The discriminant is given by $\sqrt{[(Fo\,\mu/2)^2 - 4\,\mu\,Bi/2]}$. If μ is small, it can be neglected and the discriminant approximates to $(-2\,\mu\,Bi)^{1/2}$ which is the imposed oscillation on the attenuation curve as it leads to a cosine or sine component to the exponential damping for the main Fo μ term. The critical value for the discriminant is found to be $\mu = 8\,Bi/(Fo)^2$ .Substitution of typical values for F_0 and Bi with μ give an attenuation factor varying with these numbers. For typical values of the order of 1 to 0.1, the main parameter of effect would be the small parameter μ which varies inversely as the Stefan number. Hence the laser frequency would be amplified by this factor in the film, and if typical laser frequencies of 10^{-6} to 10^{-9} are encountered, then the subsurface frequencies get amplified by this factor depending mainly on the inverse Stefan number, possibly as high as 10^2. Typical values for surface and bulk nucleation frequencies in silicate glass are 10^7/s, 10^{10}/s (21). Following the general idea of the phase field and homogenous nucleation one may expect nucleation sites to occur at the fluctuations of the phase concentration. Thus, if the imposed heating frequency is of the same value or a harmonic, but of an opposite phase, the net result is a cancelling out, whereby nuclei do not have the chance to form at the uneven concentration points. By tuning the parameters of the source and material, one can get frequencies of pulse heating in this range and thus prevent nucleation from occurring, leading to amorphous structures. A recent paper shows how a glassy structure was obtained by laser heating a Pt foil (22). The amorphous structure was an unexpected result but quite possibly a result of rapid quenching. Since a thin foil is involved, self quenching is not an option, neither is convective heat transfer in ambient conditions, so there must have been some other factor at work, which could be something of the type discussed above (attenuation of the incoming frequency by the overall bulk thermodynamic parameters). Approximately, the Stefan number for Pt is $\Delta T/1000$, hence if ΔT is small due to convection, then μ is sufficiently high to attenuate the fluctuations to interfere with nucleation and one gets amorphous solid foil.

5.CONCLUSION:

An approximate and exact solution for the spherical moving boundary problem has been developed. Fluid flow convection has been neglected, however heat convection at the boundary has been incorporated in the linearised model. Numerical calculations show the self sublimation and self accretion velocities for the sphere differ by an order of magnitude, given the same boundary conditions. The perturbation analysis reveals a singularity at the origin; however, the spherical error function gives solutions that adapt to various boundary conditions. The boundary conditions for the adiabatic case, (no heat flux at the boundary) are equivalent to the Dirichlet as far as the moving phase velocity is concerned. The convective case can be reduced to the rectilinear case for certain adjustment in the constants. Solutions have been computed for the self freezing and ablation case of the sphere. Phase field concepts show that a possible explanation for observed amorphous film formation in Pt foil could be the neutralizing disturbing frequency imposed by laser fluctuations(22).

References

[1] H S Carslaw & J C Jaeger, *Conduction of Heat in Solids*, 2nd Ed., Clarendon Press, (Oxford, 1959)
[2]. W.W.Mullins & R..F. Sekerka "Morphological stability of a particle growing by diffusion and heat flow".*J. Appl. Phys*, 34, 323-329,(1963)
[3]. R.L. Pedroso and G.A.Domoto , "Perturbation solutions for spherical solidication of saturated liquids ", *J Heat Transfer*, 95, 42-46,(1973)
[4]. **J**. **Stefan**, "Ueber die Theorie der Eisbildung, insbesondere ueber die Eisbildung im Polarmeere.", *Ann. Phys. Chem.*, N. S. 42, 269 (1891).
[5].S. Paterson, "Propagation of a boundary of fusion",*Glasgow Math Assn Proc*., 1, 42-47,(1952)
[6] L Granaszyl T Puzsten, T Borszonyi, "Phase field Theory of Nucleation and polycrystalline pattern formation", in "*Handbook of Rheoretical and computational nano technology*", V9, pp535-572, Am. Sci. Publ., Cal. 2006
[7] J.T. Serra, S. Venkatraman, M,. Stoica etal,, " Non-isothermal kinetic analysis of the crystallization of metallic glasses using the Master Curve method", *Materials 2011*, 4, 2231-2243, doi10.3390/ma412231/www.mpi.com/journal/materials
[8] S.E.Swanson, " Relation of nucleation and crystal growth rate to the development of granitic textures", *Am.Mineral*. v62, p966-978, 1977
[9]. S W McCue, B Wu, J M Hill, "Classical two-phase Stefan problem for spheres", *Proc Roy Soc* (A),464 2055-76,(2008)
[10]. H S Carslaw & J C Jaeger, *Conduction of Heat in Solids*, 2nd Ed., Clarendon Press, (Oxford, 1959) , 276
[11] A.V. Luikov," Systems of differential equations of heat and mass transfer in capillary porous bodies", *Int J Heat Mass Transfer*, 18, 1-14, (1975)
[12]. S.G.Arless, F.L.Milder, M.Abboudi, D.Wittenberger, S.Carroll " Method of simultaneously freezing and heating tissue for ablation", *USPatent* 8287526 B2, Oct 16 2012
[13]. C.S. Combs, N T Clemens, A M Danehy, ""Development of Naphthalene PLIF for visualizing ablation products from a Space capsule shield", *doi 10.2514/6.2014-1152*
[14.] C.S. Combs, N T Clemens, P M Danehy, "Visualization of Capsule Reentry Vehicle Heat Shield Ablation using Naphthalene PLIF," in *17th Intl Symp. Of laser techniques in Fluid mechanics*, Lisbon Portugal, 7-1- July 2014.
[15]. H Reinhardt, M Kriews, H Miller etal, "Laser Ablation Inductively Coupled Plasma Mass Spectrometry: A New Tool for Trace Element Analysis in Ice Cores", .*Fresenius J Anal Chem* 370, 629-639,(2001)
[16]. D A Liedahl, S B Libby, A Rubenchik, "Momentum transfer by laser ablation of irregularly shaped space debris", *Arxiv.org:1004.0390.pdf*
[17]B.Wu, Mathematical modeling of nanoparticle melting or freezing http://ro.uow.edu.au/theses/787
[18] A .M. Soward, "A unified approach to Stefan's problem for spheres and cylinders", *Proc Roy Soc* A, 373,131-147,(1980)

[19] SW McCue , JR King , D S Riley, "Extinction behavior for two-dimensional inward-solidification problems", *Proc Roy Soc* (A), 459, 977-999,(2003)
[20]. K Stewartson and RT Waechter , " On Stefan's problem for spheres" . *Proc Roy Soc* Lond A,348 ,415-426,(1976)
[21] V.M. Fokin and E.D. Zanotto, "Surface and volume nucleation and growth in TiO2–cordierite glasses ",*J. Non-Cryst. Solids* **246**, 115 (1999).
[22] Xraysweb.lbl.gov/bl1222/research_Application/PtAmblasermelt.pptPt foil

Nomenclature

A,B,C,D,E constants
D differenial operator
a(t),R(t) interface position with time
g thermal concentration gradient
c concentration
K diffusivity
k conductivity
L latent heat of transformation (melting or vaporization)
Q heat sink/source strength
r radius
s, r coordinates in rectilinear and cylindrical, or spherical coordinates
t time
u,v , U,V temperatures
α eigenvalue for position of interface
μ (g/ Stefan parameter)
ε remelt, porosity term
ρ Density
ν nucleation frequency
θ non dimensional temperature
Θ non dim. initial temperature
η Fourier number (non dimenionalised time/ distance)
Fo =Fourier number
Bi =Biot number Ste= Stefan number (latent heat/sensible heat)
erf error function, spherf spherical error function(see ref 5)
grad gradient function, Ei exponential integral function

KJMA: Kolmogorov,Johnson, Mehl Avrami

Table 1 Self Sublimation velocity vs latent heat density

Lρ/2	Interface Velocity	Lρ/2	Interface Velocity
-250	-.006365	250	-.0001508
-306.8	-.005758	306.8	-.0001229
-400	-.00506	400	-.00009427
-450	-.0047713	450	-.0000838
-500	-.00453	500	-.000075425

Water: k_2 =0.00144 Cal/cm sec K, K_2 = 0.00144 cm^2/sec, Ice: k_1 = 0.0053 Cal/cm.sec.K, K_1 = 0.0155 cm^2/sec, Lρ=73.6, q= 2.38 cal/cm.sec