Maximum and Minimum Bounds on Freezing-Melting Rates with Time-Dependent Boundary Conditions

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Analytical solutions to one-dimensional melting-freezing problems in which the densities of the two phases are constant, but different from each other, are limited to a few special cases, nearly all of which involve a constant wall temperature boundary condition. Much of this work is reviewed by Carslaw and Jaeger (*1*). Various approximative schemes have been employed. One of the more common is the pseudo-steady state assumption, which implies that the motion of the phase boundary is so slow that the diffusion process is essentially at steady state (*2*, *3*). Another approach uses a polynomial approximation for the temperature distribution, in a manner similar to the well-known Pohlhausen integral method for laminar boundary layers (*4*). Because of the inherent nonlinearity due to the moving boundary, no general solution for arbitrary boundary conditions exists. Zener (*2*) and also Kirkaldy (*3*) employed a dimensionless distance $\lambda = x/\delta$, where x is the distance from the wall, and δ is the thickness of the new phase, in discussing the pseudo-steady state approximation. The same variable is used here, but the authors now convert the differential equation and associated boundary conditions into integral equation form in order to establish upper and lower bounds for the rate of phase change with arbitrary monotonic wall temperature or wall flux.

STATEMENT OF THE PROBLEM

Consider a one-dimensional geometry in which the original phase (liquid or solid) at the fusion temperature is initially in contact with a flat plate, taken at $x = 0$. At time $t = 0$ a specified temperature T_w or heat flux F_o is applied at the plate, initiating the melting or freezing process. The thickness of the newly formed layer $\delta(t)$ is an unknown function which represents the desired solution. Since the original phase remains at the fusion temperature T_s, heat conduction in the new phase only has to be considered. The physical properties of this phase, including density, are assumed to be temperature independent. The heat equation for this phase may then be written:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \tag{1}$$

Suppose now the wall temperature is a monotonic, but otherwise arbitrary, function of time. For definiteness consider the melting process. The initial and boundary conditions are then

$$T(0, t) = T_w(t) \tag{2}$$

$$T(\delta, t) = T_s \tag{3}$$

$$-k \frac{\partial T}{\partial x}\bigg]_{x=\delta} = -\rho\Lambda \frac{d\delta}{dt} \tag{4}$$

The last equation expresses an energy conservation requirement at the phase boundary, which is stationary in λ space. It is therefore convenient to transform these equations to this space, giving*

$$p \frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial \lambda^2} + \frac{\lambda}{2}\dot{p}\frac{\partial U}{\partial \lambda} \tag{5}$$

where $\dot{p} = \frac{dp}{d\tau} = \frac{1}{\alpha}\frac{d\delta^2}{dt}$ is a dimensionless growth rate parameter, and $U = U(\lambda, \tau)$ is the dimensionless temperature of the new phase. The boundary conditions now become

$$U(0, \tau) = U_w(\tau) \tag{6}$$

$$U(1, \tau) = 1 \tag{7}$$

$$\frac{\partial U}{\partial \lambda}\bigg]_{\lambda=1} = -\frac{L}{2}\dot{p} \tag{8}$$

Equations (5) through (8) represent a concise description of the problem. In seeking bounds on the melting-freezing rates it is convenient to convert this set of equations to an integral equation. The details are given in the next section.

THE INTEGRAL REPRESENTATION

Integrating Equation (5) from $\lambda = 1$ to λ one obtains

$$p\frac{\partial}{\partial \tau}\int_1^\lambda U(\xi, \tau)\, d\xi = \frac{\partial U}{\partial \lambda} + \frac{L}{2}\dot{p} + \frac{\dot{p}}{2}\left\{\lambda U(\lambda, \tau) - 1 - \int_1^\lambda U(\xi, \tau)\, d\xi\right\} \tag{9}$$

Equations (6) through (8) have been employed, and the second term on the right in Equation (5) has been integrated by parts. Now integrate again from $\lambda = 1$ to λ and employ the identity

$$\int_1^\lambda d\xi \int_1^\xi U(\eta, \tau)\, d\eta = \int_1^\lambda (\lambda - \xi)\, U(\xi, \tau)\, d\xi \tag{10}$$

Thus

$$p\frac{\partial}{\partial \tau}\int_1^\lambda (\lambda - \xi)\, U(\xi, \tau)\, d\xi = U(\lambda, \tau) - 1 + \frac{L}{2}\dot{p}\,(\lambda - 1) + \frac{\dot{p}}{2}\left\{\int_1^\lambda \xi U(\xi, \tau)\, d\xi - \int_1^\lambda (\lambda - \xi)\, U(\xi, \tau)\, d\xi - (\lambda - 1)\right\} \tag{11}$$

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* This equation was previously derived by H. G. Landau, *Quart. Appl. Math.*, 8, 21, (1950), and in a different manner by G. Horvay, *J. Heat Transfer, Trans. Am. Soc. Mech. Engrs.*, 82C, 37 (1960).

The integrals on the right can be combined giving

$$p\frac{\partial}{\partial\tau}\int_1^\lambda (\lambda-\xi)\,U(\xi,\tau)\,d\xi = U(\lambda,\tau)-1+$$
$$\frac{\dot p}{2}(L-1)(\lambda-1)+\frac{\dot p}{2}\int_1^\lambda (2\xi-\lambda)\,U(\xi,\tau)\,d\xi \quad (12)$$

This is the required integral equation. Note that it contains within it the two boundary conditions at $\lambda = 1$. To make use of the boundary condition at $\lambda = 0$ one finds that Equation (12), evaluated at the wall, becomes after a slight rearrangement

$$\frac{d}{d\tau}\left\{p\left[\int_0^1 \xi U(\xi,\tau)\,d\xi+\frac{L-1}{2}\right]\right\} = U_w(\tau)-1 \quad (13)$$

Integrating Equation (13) with respect to τ and noting that $p(0) = 0$ one gets

$$p(\tau) = \frac{\int_0^\tau [U_w(\tau')-1]\,d\tau'}{\int_0^1 \xi U(\xi,\tau)\,d\xi+\frac{L-1}{2}} \quad (14)$$

For freezing L would be replaced by $-L$. This equation gives an expression for p directly in terms of an integral of the temperature profile and the boundary conditions at the plate. It has the usual advantage of integral formulations in that it is relatively insensitive to small variations in the kernel function from the exact solution.

To find upper and lower bounds for the melt thickness one proceeds to find bounds on the integral in the denominator of Equation (14). First note that $U(\xi,\tau) \geqq 1$. Hence

$$\frac{1}{2} < \int_0^1 \xi U(\xi,\tau)\,d\xi < U_{\max}\int_0^1 \xi\,d\xi = \frac{U_{\max}}{2} \quad (15)$$

where $U_{\max}$ is equal to the monotonic wall temperature. Employing these inequalities in Equation (14) one obtains

$$\frac{2}{U_w+L-1}\int_0^\tau (U_w-1)\,d\tau' \leqq p$$
$$\leqq \frac{2}{L}\int_0^\tau (U_w-1)\,d\tau' \quad (16)$$

Differentiating this expression one has

$$\frac{2(U_w-1)}{U_w+L-1} \leqq \dot p \leqq \frac{2}{L}(U_w-1) \quad (17)$$

It is easy to show that Equations (16) and (17) hold also for the freezing process, with the sign of L reversed. The equality sign on the right corresponds to the existence of a linear temperature profile. For moderate melting conditions such that $(U_w - 1)/L << 1$, Equation (16) gives close bounds for p. A better approximation is obtained by taking an average value of the denominators in the bounds:

$$p \sim \frac{2\int_0^\tau (U_w-1)\,d\tau'}{L+\frac{U_w-1}{2}} \quad (18)$$

For the constant wall temperature case this reduces to

$$\delta^2(\tau) \sim 4\,\beta^2{}_{\text{avg}}\tau \quad (19)$$

where

$$\beta^2{}_{\text{avg}} = \alpha\left[\frac{2\Lambda}{C_p(T_w-T_s)}+1\right]^{-1} \quad (20)$$

A simple numerical example will serve to illustrate the closeness of these bounds. Consider a semi-infinite block of ice, initially at the freezing temperature, whose surface is subjected to a step increase in temperature of 5°C. This problem has an exact solution (*1*), given by

$$\delta^2 = 4\beta^2\tau \quad (21)$$

where β satisfies

$$\beta e^{\beta^2}\,\mathrm{erf}\beta = \frac{C_p(T_w-T_s)}{\Lambda\sqrt{\pi}} \quad (22)$$

Hence the bounds in (16) give the correct time dependence. The proportionality constants for this case are: $\beta_{\min} = 0.1715$, $\beta_{\max} = 0.1768$, $\beta_{\text{avg}} = 0.174$, and $\beta = 0.175$. It is seen that the upper and lower bounds are within 3% of each other and that the approximate β_{avg}, calculated from Equation (20), is about 0.5% from the exact value.

ARBITRARY WALL HEAT FLUX

In this event Equation (2) is replaced by

$$-\left.\frac{\partial T}{\partial x}\right]_{x=0} = F_o(t) \quad (23)$$

In terms of the dimensionless variable λ this becomes:

$$-\left.\frac{\partial U}{\partial\lambda}\right]_{\lambda=0} = \frac{F_o\delta}{T_s} \quad (24)$$

Integrating the energy equation with respect to λ, and employing now Equation (24), one obtains, after an integration by parts

$$p\frac{\partial}{\partial\tau}\int_0^\lambda U(\xi,\tau)\,d\xi = \frac{\partial U}{\partial\lambda}+\frac{F_o(\tau)\,\delta(\tau)}{T_s}+$$
$$\frac{\dot p}{2}\left\{\lambda U(\lambda,\tau)-\int_0^\lambda U(\xi,\tau)\,d\xi\right\} \quad (25)$$

Setting $\lambda = 1$ in this expression one gets for melting

$$p\frac{d}{d\tau}\int_0^1 U(\xi,\tau)\,d\xi = -\frac{L}{2}\dot p+\frac{F_o(\tau)\,\delta(\tau)}{T_s}+$$
$$\frac{\dot p}{2}\left\{1-\int_0^1 U(\xi,\tau)\,d\xi\right\} \quad (26)$$

Noting that $\dot p = 2\delta\dot\delta$ one can manipulate this to give

$$\frac{d}{d\tau}\left\{\delta\left[\int_0^1 U(\xi,\tau)\,d\xi+L-1\right]\right\} = \frac{F_o(\tau)}{T_s} \quad (27)$$

Upon integrating one obtains

$$\delta(\tau) = \frac{\int_0^\tau \frac{F_o(\tau')}{T_s}\,d\tau'}{\int_0^1 U(\xi,\tau)\,d\xi+L-1} \quad (28)$$

This is the integral formulation in terms of the boundary condition at the plate. If the denominator is constant, corresponding to a constant wall temperature, and $\delta \sim \tau^{1/2}$, then $F_o \sim \tau^{-1/2}$, which is consistent with the exact solution (*1*). For monotonic, but otherwise arbitrary, wall flux it is somewhat more difficult to bound the integral in the denominator in Equation (28), since the wall temperature is not specified. Examination of Equation (5) shows that the curvature of the temperature profile is everywhere and at all $t > 0$ of the same sign. Thus for melting $\frac{\partial U}{\partial\tau} \geqq 0$ and $p\frac{\partial U}{\partial\lambda} \leqq 0$, so that $\frac{\partial^2 U}{\partial\lambda^2} \geqq 0$. It can be seen

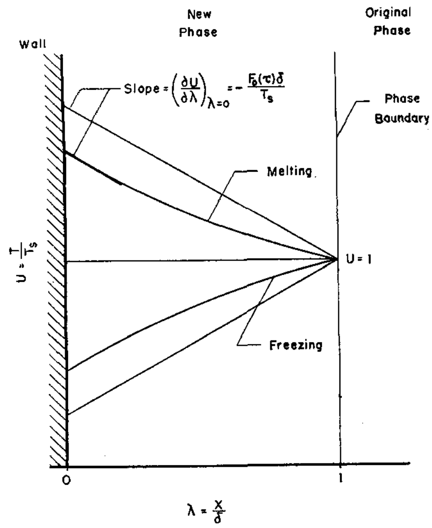

Fig. 1. Diagrammatic representation of upper and lower bounds to dimensionless temperature profile vs. dimensionless distance from the wall in melting or freezing with specified wall heat flux.

from Figure 1, which is drawn to illustrate upper and lower bounds for both melting and freezing, that for melting

$$U \leq \frac{F_o(\tau)\,(1-\lambda)\,\delta}{T_s} + 1 \tag{29}$$

where use has been made of Equation (24). One immediately obtains

$$0 \leq \int_0^1 U(\xi,\tau)d\xi - 1 \leq \frac{F_o(\tau)\delta}{2T_s} \tag{30}$$

When the right-hand inequalities are inserted into Equation (28), a quadratic inequality is obtained for the film thickness:

$$\frac{F_o\delta^2}{2T_s} + \delta L - \frac{1}{T_s}\int_0^\tau F_o(\tau')d\tau' \geq 0 \tag{31}$$

which yields

$$\frac{1}{LT_s}\int_0^\tau |F_o(\tau')|\,d\tau' \geq \delta \geq -\frac{LT_s}{|F_o|} + \frac{T_s}{|F_o|}\left[L^2 + \frac{2|F_o|}{T_s^2}\int_0^\tau |F_o(\tau')|\,d\tau'\right]^{1/2} \tag{32}$$

Written in this form the same formula applies to freezing. It is easily verified from the binomial theorem applied to the right-hand side of Equation (33) that the upper and lower limit approach each other if

$$L^2 >> \frac{2|F_o|}{T_s^2}\int_0^\tau |F_o(\tau')|\,d\tau' \tag{33}$$

In this event

$$\delta = \frac{1}{LT_s}\int_0^\tau |F_o(\tau')|\,d\tau' \tag{34}$$

or

$$\rho\Lambda\delta = k\int_0^t |F_o(\tau')|\,d\tau' \tag{35}$$

This is clearly an enthalpy balance in which only latent heat effects are important. More precisely one finds, on truncating the binomial expansion of the lower bound in Equation (32) at the third term, that

$$0 \geq \delta - \frac{c}{\Lambda}\int_0^\tau |F_o(\tau')|\,d\tau' \geq -\frac{c^3\,|F_o(\tau)|\left(\int_0^\tau F_o(\tau')\,d\tau'\right)^2}{2\,\Lambda^3} \tag{36}$$

CONSTANT FLUX CONDITION

When a metal slab melts or freezes by transfer of heat at its surface to a gas at a temperature very much different from the fusion temperature, the temperature driving force remains relatively constant, in view of the large difference in the metallic and gaseous thermal conductivities, so that a constant flux condition is a good approximation. Define now a dimensionless melt (or frost) thickness $\delta^* = \delta/\sqrt{\tau}$ and a dimensionless thermal boundary layer thickness $\eta = \frac{F_o\,c\sqrt{\tau}}{\Lambda}$. For this case inequality (32) may be written:

$$\eta \geq \delta^* \geq \frac{1}{\eta}[-1 + (1 + 2\eta^2)^{1/2}] = g(\eta) \tag{37}$$

For small η one has

$$g(\eta) = \eta - \frac{1}{2}\eta^3 + \frac{1}{2}\eta^5 - \ldots \tag{38}$$

Hence for small η from (37)

$$\delta^* = \eta + 0(\eta^3) \tag{39}$$

so that the approximation is quite good until η becomes comparable to unity. For small times an exact solution of this problem has been given by Evans II, Isaacson, and MacDonald (5), who expanded $\delta^* = \delta^*(\eta)$ in a Maclaurin series and found the first five coefficients by direct substitution:

$$\delta^* = \eta - \frac{1}{2}\eta^3 + \frac{5}{6}\eta^5 - \ldots \tag{40}$$

It is seen that the lower bound $g(\eta)$ is correct to $0(\eta^5)$.

This representation is useless for $\eta \geq 1$. For large η, $g(\eta) \sim \sqrt{2}$, so that the bounds diverge rapidly. However for $\eta = 1$ and 2, $g(\eta)/\eta$, which is the ratio of the upper to lower bounds, is 0.76 and 0.62, respectively. Hence the range of useful solutions has been extended to $\eta \sim 2$.

Finally some typical numerical examples are given. For a semi-infinite copper melt initially at the fusion temperature, losing heat with an overall heat transfer coefficient of 0.5 B.t.u./(hr.)(sq.ft.)(°F.) to the surroundings at ambient temperature, after 4 hr. $\eta = 0.98$ and the estimated thickness of solidified copper is 44 in. with a ± 12% error. As a second example consider a steel sheet subject to a flowing stream of very hot gas, such that a uniform heat flux of 10^5 B.t.u./(hr.)(sq.ft.)(°F.) is imposed at the surface. After 200 sec. $\eta = 0.68$, and the melt thickness is estimated to be 1.26 in. with a possible error of ± 8.6%.

It is seen from these examples that the present approximation is adequate for the time and length scales involved in the usual metallurgical and rocket applications. For larger scales, such as are involved in the cooling of geological or stellar masses, a higher-order approximation may be necessary.

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NOTATION

c = specific heat of new phase

$F_o(t) = -\left.\dfrac{dT}{dx}\right|_{x=0}$

k = thermal conductivity of new phase

$L = \Lambda/cT_s$

$p = \delta^2$

$\dot{p} = d\delta^2/d\tau$

t = time

T = absolute temperature of new phase

T_w = wall temperature

T_s = fusion temperature

$U = T/T_s$

$U_w = T_w/T_s$

x = distance from plate

Greek Letters

α = thermal diffusivity, $k/\rho c$

$\delta(t)$ = distance from plate to phase boundary

$\delta^*(\eta) = \delta/\sqrt{\tau}$ dimensionless melt (or frost) thickness

$\eta = \dfrac{C F_o \sqrt{\tau}}{\Lambda}$, dimensionless thermal boundary layer thickness

$\lambda = x/\delta$, dimensionless distance coordinate

Λ = latent heat of fusion

ρ = density of material in contact with plate

$\tau = \alpha t$

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Nuclear Radiation-Induced Cracking of *n*-Hexadecane

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A representative paraffin hydrocarbon in the gas oil range, *n*-hexadecane, has been irradiated in the Industrial Reactor Laboratories' 5 mw. nuclear research reactor. In the vapor phase radiation-induced cracking proceeded efficiently, and G values* for radiation conversion of *n*-hexadecane were 200 to 1,200 at temperatures near 750°F. Total conversions of *n*-hexadecane were less than 3 wt. % and were due only in part to the radiation effect. The distributions of products which were obtained were similar to those which result from thermal cracking of *n*-hexadecane. There were however significant increases in the yields of hydrogen, reductions in the yields of very light hydrocarbons and small yields of high molecular weight products. At temperatures above 850°F. extensive thermal cracking obscured the effects of radiation.

In liquid phase radiation-induced cracking at 750°F. conversions of *n*-hexadecane up to 15 wt. % have been obtained at liquid spaces velocities near 4 v./hr./v. In many exposures nearly one-half of this conversion was attributed to the direct utilization of radiation. The corresponding G values were 30 to 60. The products obtained have been accounted for by adding together the products which would be expected from a radiation-induced reaction producing primarily dimer, from radiation-initiated chain propagated cracking, and thermally initiated chain cracking. The product distribution from these reactions can be changed by variation of the cracking temperature and/or radiation dose.

Nuclear reactors built to produce electric power are now competitive in high fuel-cost areas of the United States. Nuclear reactor technology, under continuing development, may in the near future be applied to the design of reactors which will be used for chemical or petroleum processing. In addition kilocurie sources of Co-60 and Cs-137 are available, and techniques for their application are being developed.

Radiation processing will become of commercial interest when nuclear radiation energy can be employed more economically than other energy forms to sustain established processes. In addition radiation processing may be of commercial interest if unique and valuable products can be produced. Growth in nuclear radiation processing thus depends strongly upon the basic information obtained in research in radiation chemistry and upon development of the ability to use large nuclear radiation sources.

The radiation chemistry of hydrocarbons, studied extensively at ambient temperatures (*1, 2, 3, 4, 5*), has more recently been studied at elevated temperatures (*6, 7, 8*). Radiation-induced cracking in the vapor phase was emphasized at elevated temperatures, since it was anticipated that the radiation might effectively be utilized by initiating free-radical chain types of reactions. High radiation yields were reported at intermediate (*6*) and high temperatures (*8*). Although these high yields have been reported, thermal cracking tended to mask radiation effects at high temperatures, while at intermediate temperatures and short residence times conversions were low. It gen-

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* Molecules *n* hexadecane converted per 100 ev. of energy absorbed.