

CHAPTER 2

PROBLEMS WITH EXPLICIT SOLUTIONS

The formulation of Stefan Problems as models of basic phase-change processes was presented in §1.2. Under certain restrictions on the parameters and data such problems admit **explicit solutions in closed form**. These simplest possible, explicitly solvable Stefan problems form the backbone of our understanding of all phase-change models and serve as the only means of validating approximate and numerical solutions of more complicated problems.

Unfortunately, closed-form explicit solutions (all of which are of similarity type) may be found only under the following very restrictive conditions: 1-dimensional, semi-infinite geometry, uniform initial temperature, constant imposed temperature (at the boundary), and thermophysical properties constant in each phase.

Within these confines we present a succession of models of increasingly complicated phase-change processes.

We begin with the simplest possible models, the classical 1-phase Stefan problem (§2.1), and 2-phase Stefan Problem (§2.2), modeling the most basic aspects of a phase-change process (as discussed in §1.2). We present the Neumann similarity solution and familiarize the reader with some of the information it conveys.

Next (§2.3) we relax the assumption of constant density by allowing the densities of solid and liquid to be different (but each still a constant), thus bringing density change effects into the picture. We study the effect of volume expansion (no voids), and of shrinkage (causing formation of a void near the wall). In each case we formulate explicitly solvable thermal models (neglecting all mechanical effects) and examine the effect of density change on the Neumann solution. More precise models, which include mechanical effects but don't admit explicit solutions, are derived from first principles in the last subsection.

In §2.4 we introduce supercooling, thus relaxing the assumption that the phase-change occurs at the melt temperature T_m . We discuss the thermodynamics of phase-coexistence and derive the Laplace-Young, Clausius-Clapeyron and Gibbs-Thomson relations from first principles. The classical Mullins-Sekerka morphological stability analysis is also presented.

In §2.5 we discuss binary alloy solidification, coupling heat conduction and solute diffusion. We present the classical model of Rubinstein and its explicit solution, as well as various other models of freezing over an extended temperature range.

The introduction of each new physical phenomenon in the simplest possible setting (dictated by the desire to have explicit solutions available) helps us understand the phenomenon more easily and see its effects on the solution.

Similarity solutions in cylindrical and spherical geometries for special problems are the subject of §2.6. Finally, in §2.7 we present a contrived (artificial) multi-dimensional phase-change problem whose explicit solution may serve as benchmark for 2 or 3 dimensional numerical codes. Such a debugging tool becomes necessary because **no** explicitly solvable phase-change problem exists in 2 or 3 dimensions.

Each phase-change process involving *melting* has a counterpart involving *freezing*. For consistency throughout our discussions we will be treating the case of *melting*, unless we are specifically interested in a solidification process (as in §2.5). The parallel developments for freezing will be mostly left as exercises for the reader in the PROBLEMS, but the changes needed to turn the solution of the one to the other will be indicated in the text.

2.1. THE ONE-PHASE STEFAN PROBLEM

2.1.A Introduction

The simplest explicitly solvable phase-change problem is the 1-phase Stefan Problem (§1.2.F) with **constant** imposed temperature and constant thermophysical properties. Its solution is the classical Neumann similarity solution [CARSLAW-JAEGER], [RUBINSTEIN] involving the error function. As prototype example we treat the **melting** problem leaving the case of freezing for the reader to examine via the Problems.

The term “one-phase” refers to only one of the phases (liquid) being “active”, the other phase staying at the melt temperature T_m (§1.2.F). Thus the physical situation is the following:

PHYSICAL PROBLEM: Melting of a (semi-infinite) slab, $0 \leq x < \infty$, initially **solid** at the melt temperature, T_m , by imposing a **constant** temperature $T_L > T_m$ on the face $x = 0$. Thermophysical parameters: ρ , c_L , k_L , L , $\alpha_L = k_L / \rho c_L$, all constant.

The physical realization of this problem is an insulated pipe, filled with a PCM, and exposed at one face to a heat source, while its length is so great that the second face is not reached by the melting front during the life of the experiment (**Figure 2.1.1**). The experiment begins with the material initially solid and at its melt temperature. The nearby face temperature is raised as quickly as possible to the value T_L and maintained at that value for all time. This may be done by pumping a heat exchange fluid at temperature T_L at very high mass flow rate across the face. The mathematical model of this process leads, as in §1.2, to the following:

MATHEMATICAL PROBLEM (1-phase Stefan Problem for a slab melting from the left):

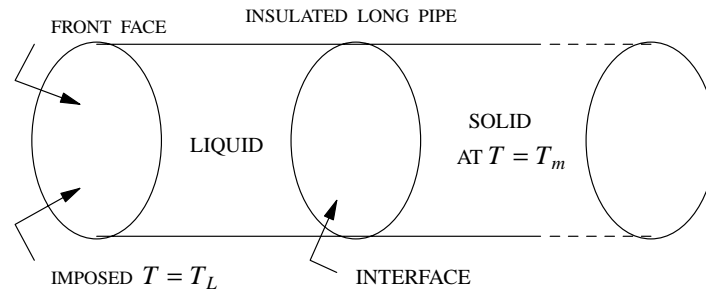


Figure 2.1.1. Physical realization of the One-Phase Stefan Problem.

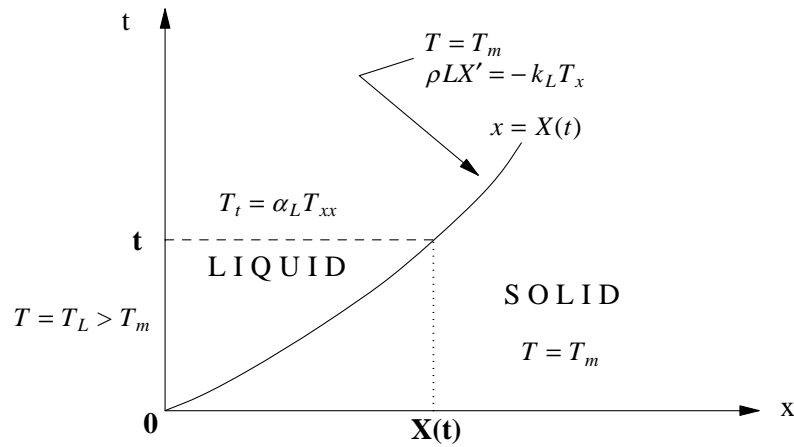


Figure 2.1.2. Space-time diagram for the One-Phase Stefan Problem.

Find $T(x, t)$ and $X(t)$ such that (**Figure 2.1.2**)

$$T_t = \alpha_L T_{xx}, \quad 0 < x < X(t), \quad t > 0 \text{ (liquid)} \quad (1)$$

$$T(X(t), t) = T_m, \quad t \geq 0 \quad (2a)$$

$$\rho L X'(t) = -k_L T_x(X(t), t), \quad t > 0 \quad (2b)$$

$$X(0) = 0, \quad \text{(material initially completely solid)} \quad (3)$$

$$T(0, t) = T_L > T_m, \quad t > 0 \quad (4)$$

The corresponding problem for a slab **freezing** from the left due to a temperature $T_S < T_m$ being imposed at $x = 0$ is formally obtained by replacing every subscript L by S and the latent heat L by $-L$ in (2b).

2.1.B The Neumann Solution

We introduce the similarity variable

$$\xi = \frac{x}{\sqrt{t}}, \quad (5)$$

and seek the solution in the form

$$T(x, t) = F(\xi), \quad (6)$$

with $F(\xi)$ an unknown function. Accordingly it is natural that we would seek the interface location $X(t)$ to be proportional to \sqrt{t} , searching therefore for a constant A for which

$$X(t) = A\sqrt{t}. \quad (7)$$

Substituting into (1) and integrating we obtain

$$F(\xi) = B \int_0^{\xi} e^{-\frac{s^2}{4\alpha_L}} ds + C = B\sqrt{\pi\alpha_L} \operatorname{erf}\left(\frac{\xi}{2\sqrt{\alpha_L}}\right) + C \quad (8)$$

for B, C constants, where

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-s^2} ds \quad (9)$$

denotes the **error function** [ABRAMOWITZ-STEGUN] (see §1.2, also (28-35) below). Conditions (4) and (2a) yield

$$C = T_L \text{ and } B = \frac{T_m - T_L}{\sqrt{\pi\alpha_L} \operatorname{erf}(A/2\sqrt{\alpha_L})} \quad (10)$$

Set

$$\lambda = \frac{A}{2\sqrt{\alpha_L}}, \quad \Delta T_L = T_L - T_m, \quad (11)$$

and

$$\mathbf{St}_L = \frac{c_L \Delta T_L}{L} = \mathbf{Stefan\ Number}. \quad (12)$$

Then the Stefan condition (2b) leads to an equation for λ :

$$\lambda e^{\lambda^2} \operatorname{erf}(\lambda) = \frac{k_L}{\rho L} \frac{\Delta T_L}{\sqrt{\pi\alpha_L}} = \frac{c_L \Delta T_L}{\sqrt{\pi} L} = \frac{\mathbf{St}_L}{\sqrt{\pi}}. \quad (13)$$

Hence it is more convenient to express the solution in terms of λ . From (5-7, 11),

$$X(t) = 2\lambda\sqrt{\alpha_L t}, \quad (14)$$

and from (5-8,10)

$$T(x, t) = T_L - \Delta T_L \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_L t}}\right)}{\operatorname{erf}(\lambda)}, \quad (15)$$

with λ a root of the transcendental equation

$$\lambda e^{\lambda^2} \operatorname{erf}(\lambda) = \mathbf{St}_L / \sqrt{\pi}. \quad (16)$$

It is easily shown (PROBLEM 2) that the quantity $f(\lambda) = \lambda e^{\lambda^2} \operatorname{erf} \lambda$ is a strictly increasing function of $\lambda \geq 0$, $f(0) = 0$, $\lim_{\lambda \rightarrow \infty} f(\lambda) = +\infty$, and therefore the graph of $y = f(\lambda)$ intersects any horizontal line $y = \mathbf{St}_L / \sqrt{\pi}$ exactly once. In other words, for each value of $\mathbf{St}_L > 0$, there exists a **unique** root, λ , of equation (16), **Figure 2.1.3**. Once λ is found by solving the transcendental equation (16), the solution of the Stefan Problem is given by (14-15). This is the classical **Neumann solution** to the Stefan Problem (after F. Neumann).

Note that the uniqueness of the root λ implies the uniqueness of the *similarity* solution, i.e. that (14-15) is the only solution of the form (6-7). Is this the *only possible* solution of (1-4)? The answer is Yes. The Stefan problem is a well-posed mathematical problem (§1.2.C, §4.5), so it admits only one solution. Uniqueness of the solution follows from the much more general uniqueness of a weak solution presented in §4.4.

2.1.C Dimensionless form

We observe in (16) that the value of the root λ and hence also the solution, depends on a *single dimensionless parameter*, the **Stefan Number**, defined in (12). This is better brought out by undimensionalizing the problem itself. We introduce the dimensionless length and time variables,

$$\zeta = \frac{x}{\hat{x}}, \quad Fo = \frac{\alpha_L}{\hat{x}^2} t = \mathbf{Fourier\ Number}, \quad (17)$$

where \hat{x} is any convenient length scale (note that there is no “natural” length in this problem), and the dimensionless interface and temperature

$$\Sigma(Fo) = \frac{X(t)}{\hat{x}}, \quad u(\zeta, Fo) = \frac{T(x, t) - T_m}{\Delta T_L}, \quad (18)$$

where $\Delta T_L = T_L - T_m$ as in (11). Then the Stefan Problem (1-4) takes the form (PROBLEM 6)

$$u_{Fo} = u_{\zeta\zeta}, \quad 0 < \zeta < \Sigma(Fo), \quad Fo > 0 \quad (19)$$

$$u(\Sigma(Fo), Fo) = 0, \quad Fo > 0 \quad (20)$$

$$\Sigma'(Fo) = -\mathbf{St}_L \cdot u_{\zeta}(\Sigma(Fo), Fo), \quad Fo > 0 \quad (21)$$

$$\Sigma(0) = 0 \quad (22)$$

$$u(0, Fo) = 1, \quad Fo > 0, \quad (23)$$

containing a *single parameter*, the Stefan number (12). For alternative dimensionless forms see §3.1.

The Neumann similarity solution of the dimensionless problem (19-23) is given by (PROBLEM 7)

$$\Sigma(Fo) = 2\lambda\sqrt{Fo}, \quad Fo \geq 0, \quad (24)$$

$$u(\zeta, Fo) = 1 - \frac{\operatorname{erf}\left(\frac{\zeta}{2\sqrt{Fo}}\right)}{\operatorname{erf}\lambda}, \quad 0 \leq \zeta \leq \Sigma(Fo), \quad Fo \geq 0, \quad (25)$$

with λ the root of the same transcendental equation

$$\lambda e^{\lambda^2} \operatorname{erf}\lambda = \frac{St_L}{\sqrt{\pi}}. \quad (26)$$

2.1.D The root λ versus the Stefan Number

As the only parameter present in the problem (19-23), the Stefan number St_L completely characterizes the melting process. We may think of it as representing the ratio of the “sensible heat”, $c_L \Delta T_L$ to the latent heat L . That this is indeed a correct interpretation will be shown in §2.2.G. Note that for a freezing process we define the Stefan number by

$$St_S = \frac{c_S(T_m - T_S)}{L}.$$

To gain perspective, let us compute St for some materials in typical phase-change processes.

EXAMPLE 1: Ice and Water. Ice and water are the solid and liquid phases of the same material (H_2O). Under ordinary conditions the temperature of ice is less than the value $T_m = 273.15 \text{ K}$ (0°C); upon warming, ice melts at this temperature with a latent heat $L = 333.4 \text{ kJ/kg}$, and water is found at temperatures above T_m . Its specific heat is $c_L = 4.1868 \text{ kJ/kg K}$. Due to the low value of the ratio c_L/L , the Stefan Number for melting of ice is typically no more than 1; e.g. with $T_L = 37^\circ\text{C}$ (body temperature), we have $St_L = 0.46$.

In freezing of water, the specific heat of ice varies strongly with temperature (see (1) §1.2), typically in the range of $1 \leq c_S \leq 2.09$, which results in even smaller Stefan numbers. For example, in a food freezing process, we may have $T_S = -20^\circ\text{C}$; taking $c_S = 2$ as representative value, we find $St_S = c_S(T_m - T_S)/L \approx 0.12$.

EXAMPLE 2: Copper. For copper $T_m = 1356.2 \text{ K}$ and $L = 204.9 \text{ kJ/kg}$. Suppose that copper, initially at the temperature 1470 K , cools down to T_m and solidifies; for liquid copper the average specific heat is $c_L = .51 \text{ kJ/kg K}$, hence we have $St = .28$. Suppose that the process includes cooling to room temperature; for this temperature range a representative value of the specific heat is $c_S = .45 \text{ kJ/kg K}$; thus the temperature drop ΔT in the Stefan number is approximately 1200 K and $St = 2.64$.

EXAMPLE 3: Melting of a Paraffin Wax. Paraffin waxes have high latent heat. A typical paraffin wax is N- Octadecane for which $\bar{c} = 2.16$ kJ/kg K, $L = 243$ kJ/kg and the melting temperature $T_m = 301.2$ K. Over a range of temperature $\Delta T = 100$ K, $St = .89$. Like water, paraffin waxes generally have low Stefan numbers associated with their melting and solidification.

EXAMPLE 4: Melting of Silicon-Dioxide from Room Temperature. Silica (silicon dioxide) is a material with a high specific heat. In fact, over a range of temperatures from room temperature to its melting point at $T_m = 1996$ K the average specific heat is $\bar{c} = 1.12$ kJ/kg K, while its latent heat is $L = 158.3$ kJ/kg. Hence for a melting process from room temperature (298 K), $St = 12$.

These examples point to the following rule of thumb. For certain families of non-metallic solids such as waxes, St is small; hence, the bulk of heat stored or released from them is latent heat. For metals St is of the order 1-10 and so the effect of sensible heat is at least as large as that of latent heat. For other materials such as silicates St may be very large; the sensible heat will then dominate the heat transfer process. Of course St depends on the temperature drop ΔT experienced by the material during the heat transfer process (PROBLEM 14).

In general, the size of St will determine the suitability of a particular method for analyzing a given heat transfer process. For large St the process will essentially be one of pure conduction to which a variety of existing techniques are applicable. For small St the conduction heat transfer process will be dominated by the phase change.

Given a melting or freezing process, hence a Stefan number St , the transcendental equation

$$\lambda e^{\lambda^2} \operatorname{erf} \lambda = St/\sqrt{\pi} \quad (26)$$

is easily solvable by the Newton-Raphson iterative method [PRESS et al] using as initial “guess” the value $\sqrt{St/2}$. The latter is the approximate solution to (26) when $St \approx 0$, as we shall show in §2.1.F. **Figure 2.1.3** displays the values of the root λ for each St in the range $0 \leq St \leq 5$, found by the Newton-Raphson method.

For the convenience of the reader and easy reference we list here the basic properties of the **error function** [ABRAMOWITZ-STEGLUN]

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-s^2} ds \quad (27)$$

$$\operatorname{erf}(0) = 0, \quad \operatorname{erf}(\infty) = 1, \quad (28)$$

$$\operatorname{erf}(-z) = -\operatorname{erf}(z) \quad (29)$$

$$\frac{d}{dz} \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} e^{-z^2} > 0, \quad (30)$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \left(z - \frac{z^3}{3 \cdot 1!} + \frac{z^5}{5 \cdot 2!} - \frac{z^7}{7 \cdot 3!} + \dots \right), \quad (31)$$

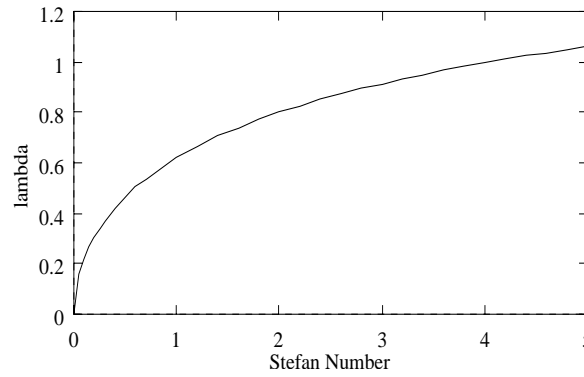


Figure 2.1.3. The root λ of (26) vs the Stefan Number.

$$\operatorname{erf}(z) \approx 1 - \frac{e^{-z^2}}{z\sqrt{\pi}} \left(1 - \frac{1}{2z^2} + \dots\right) \quad \text{as } z \rightarrow \infty, \quad (32)$$

$$\text{complementary error function:} \quad \operatorname{erfc}(z) = 1 - \operatorname{erf}(z). \quad (33)$$

Extensive tables of values appear in [ABRAMOWITZ-STEGUN], but many Fortran libraries contain $\operatorname{erf}(z)$. A useful analytical approximation to the error function is given by the following relation:

$$\operatorname{erf} z = \begin{cases} 1.128z, & 0 \leq z \leq 0.15 \\ -0.0198 + z(1.2911 - 0.4262z), & 0.15 \leq z \leq 1.5 \\ 0.8814 + 0.0584z, & 1.5 \leq z \leq 2 \\ 1, & 2 \leq z \end{cases} \quad (34)$$

In the same spirit, an effective approximation to the root λ of (26) is given by the expression

$$\lambda \approx 0.706\sqrt{St} \{1 - 0.21(0.5642 \cdot St)^{0.93-0.15St}\}. \quad (35)$$

This relation has less than a 1% relative error for $0 < St < 0.83$, a relative error below 5% for $0.83 < St < 4.28$ and below 10% for $St < 4.86$.

2.1.E Example: Melting a slab of ice

A slab of ice is 10 cm thick. It is initially solid and at its melt temperature of 0°C . One face of the slab is insulated while from the initial moment $t = 0$ of our experiment, the other will be set at the warm temperature of 25°C and maintained at this value for all time. We have placed three thermocouples in the slab, at depths of 1 cm, 3 cm and 5 cm. We wish to know the time of melt of the portions up to each thermocouple location, as well as the melting time for the entire slab. We wish also to learn about the appearance of the time-temperature measurements

provided by the thermocouples, as well as the appearance of the temperature distribution as a function of position. The information that we seek is provided by the relations (14) (for the melt front), and (15) (for the temperature distribution). Before we hasten to compute, however, let us consider what we need to know and what we are ignoring in our idealized melting model.

Firstly, this problem is not just a “textbook” question, but one that appears in various forms in a variety of applications. Three analogous cases that come to mind are the thawing of food, the freezing or melting of the ground under a highway, and the freezing of ground around an earth-based heat exchanger for a heat pump. Even if the basic geometry of the process is not slab-like, the slab geometry may be a good approximation to it. Thus for a large portion of the melting process of a rectangular region, the corners do not affect the process very much and it may be considered as if uncoupled melting or freezing processes are taking place at each face. Similarly unless the pipe radius is very small the freezing or melting around a pipe is roughly speaking, slab-like.

The words “roughly speaking” as used above are meaningful. While one may strive for unlimited accuracy (and indeed, in the absence of that goal, a “rule of thumb approach” will be questionable), nevertheless heat transfer process simulation carries with it the burden of many sources of inaccuracy. These include the lack of accurate thermophysical parameter values [TOULOUKIAN], the simplifications needed to apply the tools of mathematics to the goal of simulation, and the simplifications needed to carry out experiments. The latter may arise, for example, from the changes of density of a material under a change of phase, etc. (see PROBLEMS 11-13). Besides, rough, first-cut approximations are informative, and, possibly, sufficient in some circumstances.

In our example we are ignoring the thermal effects of the change of density, which is reasonable for small temperature gradients and small volumes. For the only effect of a density change is to replace less dense ice by denser water, thus in effect “pulling” the material towards the heating face. This action would induce convection in the liquid region (which is negligible due to the smallness of the region involved), while the solid remains at the melt temperature for all time. The mechanical effect of this action would, of course, be to buckle the container (if it is tightly sealed) at the far end, (.1 m), an effect with which we are not concerned ! In any case, density change effects will be discussed in §2.3.

The assumption of the initial temperature being at the melting point is difficult to attain in practice but may be “nearly” reached. As we will see in §2.2, the estimate of the melt-depth that we will obtain will be greater than that obtained when the initial subcooling is indeed taken into account (see §2.2).

Since our process is only “one-phase”, we only need the relevant properties of water which are: melt temperature = $T_m = 0^\circ C$, density = $\rho = 1 \text{ g/cm}^3$, specific heat = $c_L = 4.1868 \text{ J/g}^\circ C$, conductivity = $k_L = 0.564 \times 10^{-2} \text{ J/cm s}^\circ C$, thermal diffusivity = $\alpha_L = k_L / \rho c_L = 1.347 \times 10^{-3} \text{ cm}^2/\text{s}$, latent heat = $L = 333.4 \text{ J/g}$. We then compute the Stefan number St and obtain the melt front history $X(t)$ and the temperature distribution $T(x, t)$ from (14-16).

The temperature drop for our process is $\Delta T_L = T_L - T_m = 25^\circ\text{C}$, and thus the Stefan number is $St = c_L \Delta T_L / L = 0.314$. Using the Newton-Raphson method of PROBLEM 9 we find the root λ of (16) to be $\lambda = 0.3777$. A much simpler method for solving the transcendental equation is to use relation (35), giving us the value $\lambda = 0.3776$. If you are really “in a hurry” to obtain a “back of the envelope” estimate, the value of $\sqrt{St/2}$ is 0.3962 (see §2.1.F) with a relative error of 4.9%, which is well within the needs of a reasonable “sizing” estimate.

From (14), the time needed for the melting front to reach a given depth X is

$$t_{melt} = X^2 / (4 \lambda^2 \alpha_L) . \quad (36)$$

Let t_{melt}^1 , t_{melt}^2 , t_{melt}^3 and t_{melt}^4 be the times needed for the melt front $X(t)$ to reach the thermocouples at depths $X = 1, 3, 5$ centimeters, and the right hand face at 10 centimeters, respectively. Substitution into (36) yields

$$\begin{aligned} t_{melt}^1 &= 1301.44 \text{ sec} = 0.36 \text{ hr} \\ t_{melt}^2 &= 11713 \text{ sec} = 3.25 \text{ hr} \\ t_{melt}^3 &= 32536 \text{ sec} = 9.04 \text{ hr} \\ t_{melt}^4 &= 130144 \text{ sec} = 36.15 \text{ hr} \end{aligned}$$

In **Figure 2.1.4** we see the simulated thermocouple readings at the three depths where they were assumed placed. Note that the curves are all convex downward, and heading asymptotically to the wall value of 25°C . **Figure 2.1.5** is interesting. It shows temperature distributions in the liquid at the times t_{melt}^1 , t_{melt}^2 and t_{melt}^3 , that to all intents and purposes are linear in the spatial variable. This is a particular case of the general “rule of thumb” that for small values of the Stefan number St , the temperature in the phase change process is at any time essentially at its steady state, (quasistationary, see (38) and §3.1) because of the quickness of the response of temperature relative to the movement of the phase change front. In **Figure 2.1.6** we see the moving front as a function of time.

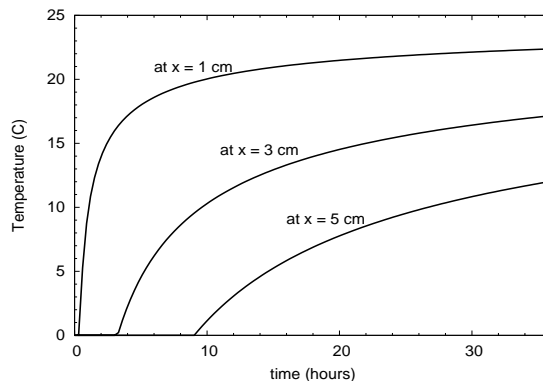


Figure 2.1.4. Melting of ice: temperature histories at three depths.

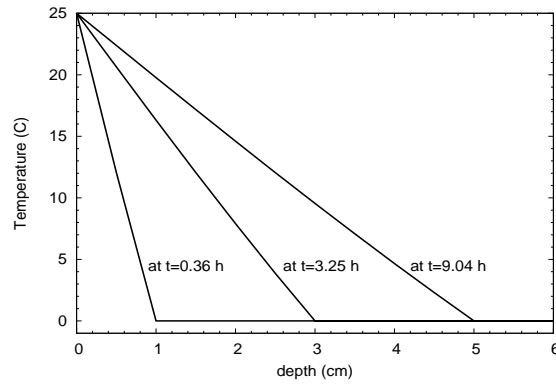


Figure 2.1.5. Melting of ice: temperature profiles at three times.

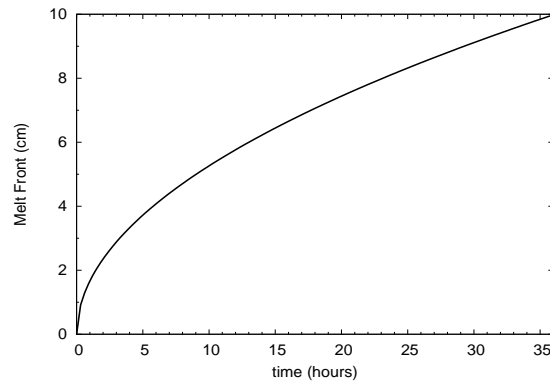


Figure 2.1.6. Melting of ice: interface location.

2.1.F The case of small Stefan Number

For many materials of interest the specific heat is considerably smaller than the latent heat so that the Stefan number for processes with moderate ΔT is of the order 10^{-1} or less. Consider equation (26). For $St \approx 0$, λ must also be small, and by (31) $\lambda e^{\lambda^2} \operatorname{erf} \lambda \approx \lambda \cdot \frac{2}{\sqrt{\pi}} \lambda$; hence (26) is approximately $\frac{2}{\sqrt{\pi}} \lambda^2 = \frac{St}{\sqrt{\pi}}$, or

$$\lambda \approx \sqrt{\frac{St}{2}} \quad \text{for } St \approx 0. \quad (37)$$

It also follows that for $0 \leq x \leq X(t) = 2\lambda\sqrt{\alpha_L t}$ the quantity $\frac{x}{2\sqrt{\alpha t}} \leq \lambda \ll 1$, whence, by (31),

$$\frac{\operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_L t}}\right)}{\operatorname{erf} \lambda} \approx \frac{\frac{2}{\sqrt{\pi}} \frac{x}{2\sqrt{\alpha_L t}}}{\frac{2}{\sqrt{\pi}} \lambda} = \frac{x}{X(t)},$$

and the Neumann temperature (15) becomes

$$T(x, t) \approx T_L - \Delta T_L \frac{x}{X(t)}, \quad 0 \leq x \leq X(t), \quad t \geq 0. \quad (38)$$

For each $t > 0$ this is linear in x , i.e. the temperature profile at each time is a straight line joining the point $(x = 0, T = T_L)$ with $(x = X(t), T = T_m)$. This is the reason for the linear profile in **Figure 2.1.5**.

Note that (38) satisfies the steady-state equation $T_{xx} = 0$, while the Neumann temperature satisfies $T_{xx} = \frac{1}{\alpha_L} T_t$. It is an approximate solution to (1-4), valid when $St_L \approx 0$ and it is called the *quasistationary approximation*, the subject of **§3.1, 3.2**.

PROBLEMS

PROBLEM 1. (a) Formulate the 1-phase Stefan problem for a slab initially liquid at T_m , freezing from the left due to an imposed constant temperature $T_S < T_m$ at $x = 0$.

(b) Verify that the freezing problem results formally by replacing every subscript L by S and L by $-L$ in (1-4).

PROBLEM 2. Show that $f(\lambda) = \lambda e^{\lambda^2} \operatorname{erf} \lambda$, $\lambda > 0$, is strictly increasing [$f'(\lambda) > 0$ for any $\lambda > 0$].

PROBLEM 3. Verify the Neumann solution, i.e. that (14-16) satisfy (1-4).

PROBLEM 4. For the case of freezing, in **PROBLEM 1**,

(a) Seek the similarity solution in the form: $X(t) = 2\lambda\sqrt{\alpha_S t}$, $T(x, t) = F(\xi)$, $\xi = x/\sqrt{t}$, and show that, with λ satisfying $\lambda e^{\lambda^2} \operatorname{erf} \lambda = St_S/\sqrt{\pi}$,

$$T(x, t) = T_S + [T_m - T_S] \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) / \operatorname{erf} \lambda, \quad 0 \leq x \leq X(t), \quad t \geq 0,$$

(b) Verify that the solution for freezing results formally from the solution for melting by the formal substitutions mentioned in **PROBLEM 1** (b). Note in particular, that the equation for λ is the same.

PROBLEM 5. Show that (5) is the only possible similarity variable for the heat equation (1) of the form $\xi = x^\gamma t^\delta$.

PROBLEM 6. Derive the dimensionless form (19-23) of the 1-phase Stefan Problem (1-4) for the variables (17-18).

PROBLEM 7. (a) Seek the similarity solution of (19-23) in the form

$$\Sigma(Fo) = 2\lambda\sqrt{Fo}, \quad u(\zeta, Fo) = F(\xi), \quad \xi = \frac{\zeta}{\sqrt{Fo}},$$

and show that this leads to (24-26).

(b) By direct change of variables, obtain the solution in physical variables (14-15) from the dimensionless solution (24-25).

PROBLEM 8. Repeat PROBLEMS 6,7 for the freezing case (see PROBLEMS 1,4).

PROBLEM 9. Write and implement a numerical scheme for solving (26) based on the Newton-Raphson method

$$\lambda_{n+1} = \lambda_n - \frac{f(\lambda_n)}{f'(\lambda_n)}, \quad \lambda_0 = \sqrt{St/2},$$

where $f(\lambda) = \lambda e^{\lambda^2} \operatorname{erf} \lambda - \frac{St}{\sqrt{\pi}}$, and produce a table of values of the root λ for $0 < St < 5$, $St = .01, .02, \dots$.

PROBLEM 10. Freezing of water: Repeat the work of §2.1.E for the freezing of water initially at its melting point and subject to a face temperature of -25°C . In this range, the properties of ice may be taken as: $\rho_S = 0.91 \text{ g/cm}^3$, $c_S \approx 2 \text{ J/g K}$, $k_S \approx .023 \text{ J/cm s K}$, hence $\alpha_S = .0125 \text{ cm}^2/\text{s}$. You may use the approximation (35) for the root of equation (26), and the approximation of (34) in the evaluation of the temperature function.

PROBLEM 11. A box has been constructed to house an experiment in melting and freezing of materials. The experiments are to be “one-dimensional”, in the sense that all but one of the box’s faces are insulated; the non-insulated face is Aluminum through which Copper tubes carrying a cooling/heating fluid pass. What problems can arise from the change of density of the material that takes place when it melts or freezes? How would you deal with these problems? What difficulties would arise in your modeling efforts as a result of your handling of these problems.

PROBLEM 12. In the course of doing the experiments of the last PROBLEM you encounter a material which in its liquid phase dissolves large amounts of air. What may happen to your experiment?

PROBLEM 13. In the course of performing a melting experiment and recording the temperature values read by a thermocouple held along a thin wire across the box of PROBLEM 11, you find that the temperature value “jumped” through a short temperature range discontinuously. The range begins at the melt temperature, the density of the solid is greater than that of the liquid, and the thermocouple and recording equipment are in order. What could have caused the jump?.

PROBLEM 14. Let us stretch our imagination to the following (physically) imaginary case: A slab of ice at the melt temperature is to be melted via an imposed face temperature of 36000°C . How much will melt in 10 minutes? Explain your result.

2.2. THE TWO-PHASE PROBLEM ON A SEMI-INFINITE SLAB

In §2.1 we examined the explicit solution to the one-phase problem on a semi-infinite slab corresponding to a uniform initial temperature T_m and an initially solid phase (for a melting problem), or liquid phase (for a freezing problem). A more realistic scenario is one in which the initial state of the PCM, say for a melting process, is solid, but its initial temperature is some value T_S below T_m . This is the case discussed in §1.2 and the subject of this section. For the problem to be *explicitly* solvable, it is necessary to assume that the slab is semi-infinite. While this would seem to rule out its utility for problems on a finite slab, the slow heat conduction and phase change process found in most actual melting, freezing and casting processes make the semi-infinite case a reasonable approximation to that of the finite interval case (see §2.2.C). The assumptions listed in §1.2.B are assumed to hold.

2.2.A Problem statement and solution

As prototype 2-phase process we consider the following

PHYSICAL PROBLEM: Melting of a semi-infinite slab, $0 \leq x < \infty$, initially **solid** at a **uniform** temperature $T_S \leq T_m$, by imposing a **constant** temperature $T_L > T_m$ on the face $x = 0$. Thermophysical parameters: ρ , c_L , c_S , k_L , k_S , L , $\alpha_L = k_L/\rho c_L$, $\alpha_S = k_S/\rho c_S$, all constant (see §1.2).

The mathematical model of this process, derived in §1.2 is the following:

Two-phase Stefan Problem (for a semi-infinite slab melting from the left):

Find a temperature distribution $T(x, t)$ and an interface function $X(t)$ satisfying the following conditions (**Figure 2.2.1**):

Heat equation in melt region

$$T_t = \alpha_L T_{xx}, \quad 0 < x < X(t), \quad t > 0, \quad (1a)$$

Heat equation in solid region

$$T_t = \alpha_S T_{xx}, \quad X(t) < x, \quad t > 0, \quad (1b)$$

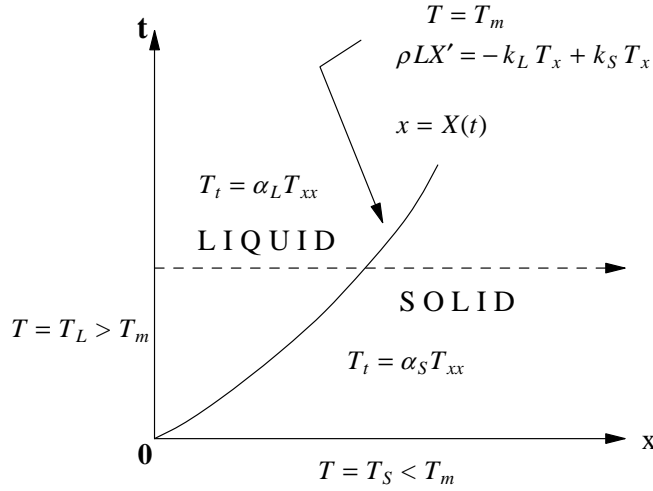


Figure 2.2.1. Space-time diagram for the Two-Phase Stefan Problem.

Interface temperature

$$T(X(t), t) = T_m, \quad t > 0, \quad (1c)$$

Stefan condition

$$\rho L X'(t) = -k_L T_x(X(t)^-, t) + k_S T_x(X(t)^+, t), \quad t > 0, \quad (1d)$$

Initial conditions

$$T(x, 0) = T_S < T_m, \quad x > 0, \quad X(0) = 0, \quad (1e)$$

Boundary conditions

$$T(0, t) = T_L > T_m, \quad \lim_{x \rightarrow \infty} T(x, t) = T_S, \quad t > 0. \quad (1f)$$

Recall (§1.2) that the right-hand side of the Stefan condition (1d) is the flux jump $q_L - q_S$ at the interface $x = X(t)$. The notation $T_x(X(t)^\mp, t)$ serves to remind us that these are *limiting* values of $T_x(x, t)$ as $x \rightarrow X(t)^\mp$ (from the left (liquid) and from the right (solid)).

Because of the structure of the problem we can again find a solution in terms of the similarity variable $\xi = x/\sqrt{t}$. Guided by the 1-phase case, we seek the solution in the form $X(t) = 2\lambda\sqrt{\alpha_L t}$, $T(x, t) = F_L(\xi)$ in the liquid and $T(x, t) = F_S(\xi)$ in the solid, with λ an unknown constant and F_L, F_S unknown functions of the similarity variable ξ . Using the procedure of §2.1.B, we obtain (PROBLEM 2) the

Neumann solution of the 2-phase Stefan Problem (1):

Interface location

$$X(t) = 2\lambda\sqrt{\alpha_L t}, \quad t > 0 \quad (2a)$$

Temperature in the liquid region $0 < x < X(t)$, $t > 0$:

$$T(x, t) = T_L - (T_L - T_m) \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_L t}}\right)}{\operatorname{erf} \lambda}, \quad (2b)$$

Temperature in the solid region $x > X(t)$, $t > 0$:

$$T(x, t) = T_S + (T_m - T_S) \frac{\operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right)}{\operatorname{erfc}(\lambda\sqrt{\alpha_L/\alpha_S})}. \quad (2c)$$

Here λ is the solution to the transcendental equation

$$\frac{\mathbf{St}_L}{\exp(\lambda^2) \operatorname{erf}(\lambda)} - \frac{\mathbf{St}_S}{\nu \exp(\nu^2 \lambda^2) \operatorname{erfc}(\nu \lambda)} = \lambda\sqrt{\pi}, \quad (2d)$$

with

$$\mathbf{St}_L = \frac{c_L(T_L - T_m)}{L}, \quad \mathbf{St}_S = \frac{c_S(T_m - T_S)}{L}, \quad \nu = \sqrt{\frac{\alpha_L}{\alpha_S}}. \quad (3)$$

By PROBLEM 5, the transcendental equation (2d) has exactly one root $\lambda > 0$, and therefore the similarity solution (2) is unique for each $\mathbf{St}_L > 0$, $\mathbf{St}_S \geq 0$, $\nu > 0$. The fact that this is the *only* solution follows from the general uniqueness theory (see §4.4) or it may be proved directly [RUBINSTEIN].

Note that when $T_S = T_m$, we have $\mathbf{St}_S = 0$ and (2) reduces to the similarity solution of the 1-phase problem (§2.1.B), as expected. The presence of the term containing \mathbf{St}_S in (2d) simply reduces the magnitude of the root and therefore, for any $\mathbf{St}_S > 0$, we have

$$\lambda_{2-phase} < \lambda_{1-phase}. \quad (4)$$

This of course is expected for it says merely that the presence of initial subcooling in the solid will slow down the melting process (given by $X(t) = 2\lambda\sqrt{\alpha_L t}$), since some heat must go to raising the temperature of the solid to T_m before it can melt.

The Neumann solution for the case of freezing (PROBLEM 1) may be formally obtained from (2) by simply interchanging the subscripts L and S and replacing the latent heat L by $-L$ (PROBLEM 7).

2.2.B Dimensionless form

The 2-phase problem in physical variables, (1), contains nine parameters, namely, ρ , c_L , c_S , k_L , k_S , L , T_m , T_L , T_S . Undimensionalization reduces the number to four, the minimum necessary to specify the problem. Indeed, set (see (3))

$$\mathbf{St}_L = \frac{c_L(T_L - T_m)}{L}, \quad \mathbf{St}_S = \frac{c_S(T_m - T_S)}{L}, \quad \nu = \sqrt{\frac{\alpha_L}{\alpha_S}}, \quad (5)$$

and with \hat{x} being any convenient length (no *natural* length scale is present here),

introduce the dimensionless variables : $\zeta = x / \hat{x}$, $Fo = \alpha_L t / \hat{x}^2$, and

$$\Sigma(Fo) = \frac{X(t)}{\hat{x}}, \quad u^L(\zeta, Fo) = \frac{T(x, t) - T_m}{T_L - T_m}, \quad u^S(\zeta, Fo) = \frac{T(x, t) - T_m}{T_m - T_S}. \quad (6)$$

Then, problem (1) takes the form (PROBLEM 8)

$$u_{Fo}^L = u_{\zeta\zeta}^L, \quad 0 < \zeta < \Sigma(Fo), \quad Fo > 0 \text{ (liquid)}, \quad (7a)$$

$$v^2 u_{Fo}^S = u_{\zeta\zeta}^S, \quad \Sigma(Fo) < \zeta < \infty, \quad Fo > 0 \text{ (solid)}, \quad (7b)$$

$$u^L(\Sigma(Fo), Fo) = u^S(\Sigma(Fo), Fo) = 0, \quad Fo > 0, \quad (7c)$$

$$\Sigma'(Fo) = -St_L \cdot u_{\zeta}^L + (St_S / v^2) \cdot u_{\zeta}^S, \quad \zeta = \Sigma(Fo), \quad Fo > 0, \quad (7d)$$

$$u^S(\zeta, 0) = -1, \quad 0 < \zeta < \infty, \quad \Sigma(0) = 0 \quad (7e)$$

$$u^L(0, Fo) = +1, \quad \lim_{\zeta \rightarrow \infty} u^S(\zeta, Fo) = -1, \quad Fo > 0, \quad (7f)$$

which contains only the three parameters defined in (5).

Its similarity solution is easily found to be (PROBLEM 10)

$$\Sigma(Fo) = 2\lambda\sqrt{Fo} \quad (8a)$$

$$u^L(\zeta, Fo) = +1 - \frac{\operatorname{erf}\left(\frac{\zeta}{2\sqrt{Fo}}\right)}{\operatorname{erf} \lambda}, \quad 0 \leq \zeta \leq \Sigma(Fo), \quad Fo > 0, \text{ (liquid)} \quad (8b)$$

$$u^S(\zeta, Fo) = -1 + \frac{\operatorname{erfc}\left(v \frac{\zeta}{2\sqrt{Fo}}\right)}{\operatorname{erfc}(v\lambda)}, \quad \Sigma(Fo) \leq \zeta, \quad Fo > 0, \text{ (solid)} \quad (8c)$$

with λ the unique root of the (already dimensionless) equation (2d).

2.2.C Approximations to the root λ

We know from §2.1.F that in the 1-phase case, $St_L \approx 0$ implies $\lambda_{1-phase} \approx \sqrt{St_L/2}$. Since, by (4), $\lambda_{2-phase} < \lambda_{1-phase}$ always holds, $St_L \approx 0$ implies $\lambda_{2-phase} \approx 0$. To the lowest order, equation (2d) is approximately $St_L/(2\lambda^2) - St_S/(v\lambda\sqrt{\pi}) = 1$, whence

$$\lambda_{2-phase} \approx \frac{1}{2} \left[-\frac{St_S}{v\sqrt{\pi}} + \sqrt{2St_L + \left(\frac{St_S}{v\sqrt{\pi}}\right)^2} \right] \text{ for } St_L \approx 0. \quad (9a)$$

If, in addition, $St_S \gg St_L \approx 0$, this simplifies to

$$\lambda_{2-phase} \approx \frac{v\sqrt{\pi}}{2} \frac{St_L}{St_S}. \quad (9b)$$

An approximation, analogous to (35) §2.1, applicable to a narrow but useful range of situations is the following:

$$\lambda_{2-phase} \approx 0.706\sqrt{St} \{1 - [0.21 + U(0.51 - 0.169 St)] \cdot (0.5642 St)^B\} \quad (9c)$$

which is valid when $\alpha_L = \alpha_S$ for $St + 0.8U \leq 2$, where $St := St_L$, $U = (T_m - T_S)/(T_L - T_m)$, and $B = \frac{0.93}{1 + 0.69 U^{0.7}} - 0.15 St$. Its error is less than 10% and usually less than 3-5%.

Highly accurate values may be found numerically, using, for example, Brent's method [PRESS et al] or even plain bisection. Note that most FORTRAN libraries already contain the error function.

Some materials have extremely small latent heat of melting. Considering $L = 0$ as an approximation to such a case, (2d) reduces to

$$\frac{c_L(T_L - T_m)}{e^{\lambda^2} \operatorname{erf} \lambda} = \frac{c_S(T_m - T_S)}{v e^{v^2 \lambda^2} \operatorname{erfc}(v\lambda)} \quad (9d)$$

Note that then by (1d), there will be no flux jump at the interface, only the specific heat and conductivity may have jumps. The interface will simply be the isotherm $T = T_m$.

2.2.D Approximating the finite slab case

It is of interest and useful to know when we may consider a finite slab, $0 \leq x \leq l$, as being semi-infinite. Clearly, if the back face, $x = l$, is anything but insulated then there is an active boundary condition there which influences the temperature throughout the slab immediately (§1.2) and no semi-infinite approximation is possible. With $q(l, t) = 0$, the question is up to what time will the Neumann solution approximately satisfy this boundary condition? In other words, given $\varepsilon > 0$, we want the time up to which

$$q(l, t) = -k_S T_x(l, t) = \frac{k_S \Delta T_S}{\sqrt{\pi \alpha_S t} e^{l^2/4\alpha_S t} \operatorname{erfc}(v\lambda)} < \varepsilon, \quad (10)$$

$\Delta T_S = T_m - T_S$. Using $e^{l^2/4\alpha_S t} > l^2/4\alpha_S t$, (10) will certainly hold up to time t^* given by

$$t < t^* := \varepsilon^2 \left(\frac{\pi}{\alpha_S} \right) \left(\frac{l^2 \operatorname{erfc}(v\lambda)}{4k_S \Delta T_S} \right)^2. \quad (11)$$

EXAMPLE 1 : In melting a slab of ice of thickness $l = 1 \text{ m}$, initially at $T_S = -10^\circ\text{C}$, via $T_L = 25^\circ\text{C}$ at $x = 0$, an estimate of the time up to which the Neumann solution flux at $x = l$ remains less than $\varepsilon = 10^{-3} \text{ kJ/m}^2 \text{ s}$ is $t^* \approx 20 \times 10^{-6} \text{ seconds}$! (PROBLEM 13).

An alternative to keeping the flux at $x = l$ small is to ask for how long does the (solid) flux at $x = l$, $q_S(l, t)$, stay a small percentage of the incoming flux, $q_L(0, t)$, namely

$$\left| \frac{q_S(l, t)}{q_L(0, t)} \right| \leq \varepsilon. \quad (12)$$

We find that this will happen up to time (PROBLEM 12)

$$t \leq t^{**} := \frac{l^2}{4\alpha_S \ln \frac{A}{\varepsilon}} \quad \text{with} \quad A = v \frac{k_S \Delta T_S}{k_L \Delta T_L} \frac{\operatorname{erf} \lambda}{\operatorname{erfc}(v\lambda)}, \quad (13a)$$

which may be roughly estimated, using $\operatorname{erf} \lambda > \frac{2}{\sqrt{\pi}} (\lambda - \frac{\lambda^3}{3})$, $\operatorname{erfc}(v\lambda) < 1$, by

$$t \leq \frac{l^2}{4\alpha_S \ln \frac{B}{\varepsilon}}, \quad B = v \frac{k_S \Delta T_S}{k_L \Delta T_L} \frac{2}{\sqrt{\pi}} (\lambda - \frac{\lambda^3}{3}). \quad (13b)$$

EXAMPLE 2: For the situation of EXAMPLE 1, we have $B \approx 0.94$, so (12) will hold with $\varepsilon = 1\%$ at least up to time $t^{**} \approx 186$ s, and with $\varepsilon = 10^{-6}$ up to 61 seconds (PROBLEM 13). Yet another possibility is described in PROBLEM 15.

In order to use the Neumann solution as a debugging tool for a numerical simulation of phase-change in a finite slab, we do not have to rely to such approximations. Instead, one may impose at the back face $x = l$ the Neumann temperature itself. This neutralizes the effect of the back face and direct comparison of the computed temperatures and front location with the Neumann solution is meaningful. The same could be done experimentally if one had the means to exactly control the time varying back-face temperature, which is difficult to achieve.

2.2.E Energy content and Stefan numbers

In the 2-phase Stefan Problem of §2.2.A, at any $t > 0$, the interval $[0, X(t))$ is occupied by liquid and $[X(t), \infty)$ by solid. The total energy (heat) in the system consists of the sensible heat of the solid and of the liquid and the latent heat of liquid. Taking T_S as the (reference) temperature of zero energy (in order to have zero energy at $x = \infty$), we have (per unit crosssectional area)

$$\text{sensible heat of liquid: } E_L^{\text{sens}}(t) = \int_0^{X(t)} \rho c_S [T_m - T_S] dx + \int_0^{X(t)} \rho c_L [T(x, t) - T_m] dx, \quad (14a)$$

$$\text{sensible heat of solid: } E_S^{\text{sens}}(t) = \int_{X(t)}^{\infty} \rho c_S [T(x, t) - T_S] dx, \quad (14b)$$

$$\text{Latent heat of liquid: } E^{lat}(t) = \rho L X(t). \quad (14c)$$

For the Neumann solution, (2), these turn out to be (PROBLEM 18)

$$E_L^{sens}(t) = \rho L \mathbf{St}_S X(t) + \rho L \mathbf{St}_L X(t) \frac{1 - e^{-\lambda^2}}{\sqrt{\pi} \lambda \operatorname{erf} \lambda}, \quad (15a)$$

$$E_S^{sens}(t) = \rho L \mathbf{St}_S X(t) \left[\frac{1}{\sqrt{\pi} \nu \lambda e^{(\nu\lambda)^2} \operatorname{erfc}(\nu\lambda)} - 1 \right]. \quad (15b)$$

At time $t = 0$, the system was solid at T_S , so had energy zero (by our choice of T_S as the reference temperature); the only heat that came in up to time $t > 0$ is (PROBLEM 19)

$$Q(t) := \int_0^t q(0, s) ds = \int_0^t -k_L T_x(0, s) ds = \frac{\rho L \mathbf{St}_L X(t)}{\sqrt{\pi} \lambda \operatorname{erf} \lambda}. \quad (16)$$

One may easily verify the heat balance (PROBLEM 20)

$$E_L^{sens} + E_S^{sens} + E^{lat} = Q. \quad (17)$$

It is interesting to note that the ratios of sensible to latent heats are constants (independent of time). Indeed, from (15) and (2d), we find, for example,

$$\frac{E_L^{sens}(t)}{E^{lat}(t)} = \mathbf{St}_S + \mathbf{St}_L \frac{1 - e^{-\lambda^2}}{\sqrt{\pi} \lambda \operatorname{erf} \lambda}, \quad (18a)$$

$$\frac{E_L^{sens} + E_S^{sens}}{E^{lat}} = \frac{\mathbf{St}_L}{\sqrt{\pi} \lambda \operatorname{erf} \lambda} - 1. \quad (18b)$$

When $\mathbf{St}_L \approx 0$, the right-hand side of (18a) is $\approx \mathbf{St}_S + \frac{\mathbf{St}_L}{2}$, (PROBLEM 22), and therefore *in the 1-phase case (i.e. $\mathbf{St}_S = 0$)*, the Stefan number represents twice the ratio of sensible to latent heat (PROBLEM 23).

The above relationships may be used as simple checks on the validity of computer codes as well as in finding the heat stored in the system, see §2.2.G.

2.2.F Shape of melting and cooling curves

Placing a thermocouple at a location x^* , an experimenter records the temperature of that location over time. Plotting these temperatures against time produces a *melting or cooling curve*, $T = T^*(t)$. This is the most precisely and easily measurable quantity in a phase-change experiment, so it is important to know what to expect. The theoretical melting curve, corresponding to the experimental one, is the curve $T = T(x^*, t)$, with x^* the fixed thermocouple location. We are interested in its shape and qualitative features.

As it is easier to work in dimensionless variables, we set

$$\zeta^* = \frac{x^*}{\hat{x}} \quad \text{and} \quad \tau^* = \left(\frac{\zeta^*}{2\lambda} \right)^2 = \text{melt time of } \zeta^*, \quad (19)$$

and examine the Neumann solution (8), of our melting problem (1). For notational convenience we denote dimensionless time (Fourier Number) by τ .

During $0 \leq \tau \leq \tau^*$, the point $\zeta = \zeta^*$ is solid with temperature, (8c),

$$u(\zeta^*, \tau) = -1 + \frac{\operatorname{erfc}\left(v \frac{\zeta^*}{2\sqrt{\tau}}\right)}{\operatorname{erfc}(v\lambda)}, \quad 0 \leq \tau \leq \tau^*, \quad (20)$$

where λ is the root of (2d). Computing $u_\tau(\zeta^*, \tau)$ and $u_{\tau\tau}(\zeta^*, \tau)$, we see that (PROBLEM 24) $u_\tau(\zeta^*, \tau) > 0$, hence $u(\zeta^*, \tau)$ is increasing for $0 \leq \tau \leq \tau^*$, and

$$u_{\tau\tau}(\zeta^*, \tau) \geq 0 \quad \text{for} \quad \tau \leq \hat{\tau} = \frac{v^2 \zeta^{*2}}{6}, \quad (21)$$

hence $u(\zeta^*, \tau)$ is a convex curve up to $\tau \leq \hat{\tau}$. Thus, we have two possibilities. If $\hat{\tau} > \tau^*$, i.e. if $v\lambda > \sqrt{3/2}$, then the melting curve stays convex during $0 \leq \tau \leq \tau^*$, **Figure 2.2.2(a)**. Otherwise, it changes its concavity at $\tau = \hat{\tau} < \tau^*$, **Figure 2.2.2(b)**.

After ζ^* melts, its temperature follows (8b). Again, we see that (PROBLEM 25) $u_\tau(\zeta^*, \tau) > 0$ and

$$u_{\tau\tau}(\zeta^*, \tau) \leq 0 \quad \text{for} \quad \tau \geq \hat{\tau} := \frac{\zeta^{*2}}{6}. \quad (22)$$

Hence, if $\hat{\tau} < \tau^*$, i.e. if $\lambda < \sqrt{3/2}$, then by (22) the melting curve is concave forever, **Figure 2.2.3(a)**. Otherwise, $u(\zeta^*, \tau)$ is convex during $\tau^* \leq \tau \leq \hat{\tau}$ and concave thereafter, **Figure 2.2.3(b)**.

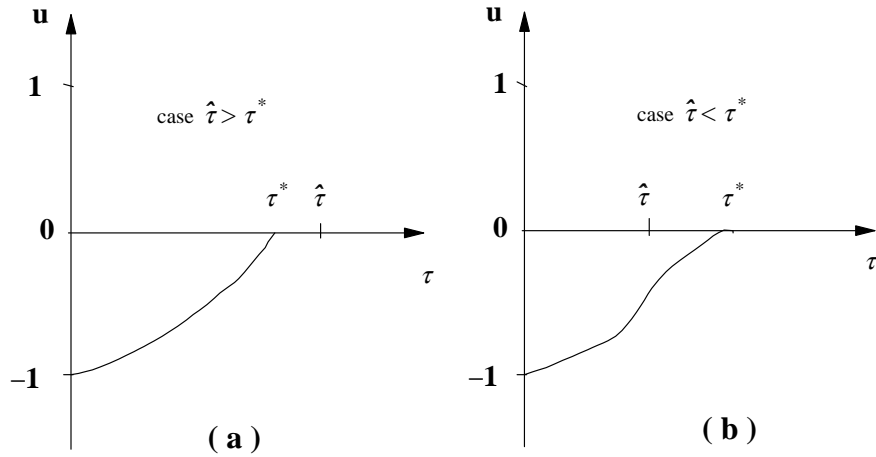


Figure 2.2.2. Shape of melting curve before ζ^* melts.

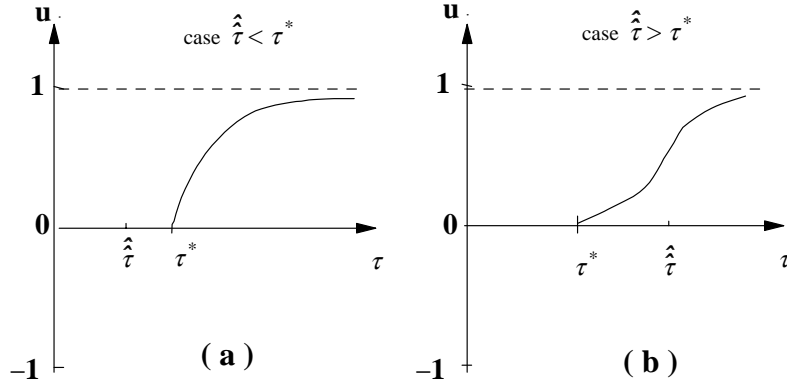


Figure 2.2.3. Shape of melting curve after ζ^* melts.

It follows that the overall melting curve will consist of an appropriate combination of convex and concave time-histories. Clearly, cooling curves are similar in shape but, of course, decreasing.

EXAMPLE 3 : Melting of ice, initially at $T_S = -10^\circ\text{C}$, via $T_L = 25^\circ\text{C}$ at $x = 0$. With parameter values given in §2.1.E and PROBLEM 10 §2.1 the dimensionless constants are: $St_L = 0.314$, $St_S = 0.06$, $\nu = 0.02137$, and the corresponding root is $\lambda = 0.09178$. Let us imagine a thermocouple at location $\zeta^* = 0.2$. Then, from (19, 21-22) we find $\tau^* = 1.187$, $\hat{\tau} = 3 \times 10^{-6}$, $\hat{\tau} = 0.0067$. Since $\hat{\tau} \ll \tau^*$, the melting curve at $\zeta^* = 0.2$ would change concavity but at a very early time.

When an actual experiment or a computer simulation exhibit qualitatively different melting curves than expected from the above, then one must question the simplifying features of the model used (constant thermophysical properties, neglecting various effects, like supercooling or convection, etc).

On the other hand, if the expected behavior occurs then such curves may be used to check the accuracy of parameter values. For example, the jump in the slope of a melting curve at the melt time is a measurable quantity (with a differential thermal analyzer). For the Neumann solution this jump is, (from PROBLEMS 24-25)

$$\llbracket u_\tau(\zeta^*, \tau^*) \rrbracket_{solid}^{liquid} = \frac{\lambda}{\sqrt{\pi} \tau^*} \left[\frac{e^{-\lambda^2}}{\text{erf } \lambda} - \frac{\nu e^{-\nu^2 \lambda^2}}{\text{erfc}(\nu \lambda)} \right]. \quad (23)$$

For $St_L \approx 0$ and $St_S > St_L$ we know that $\lambda \approx \frac{\nu \sqrt{\pi}}{2} \frac{St_L}{St_S}$ (see (9b)) and, expanding erf to first order in λ , (23) yields

$$\llbracket u_\tau(\zeta^*, \tau^*) \rrbracket_{solid}^{liquid} \approx \frac{1}{2\tau^*} \left[1 - \frac{1}{\frac{k_S}{k_L} \frac{\Delta T_S}{\Delta T_L} - 1} \right], \quad (24)$$

with $\Delta T_S = T_m - T_S$, $\Delta T_L = T_L - T_m$. By measuring the left-hand side, (24) could be used to check the correctness of data values for the ratio of conductivities k_S/k_L .

2.2.G An example

For many years effective means have been sought for storing heat as the latent heat of melting of a material. The prime source of such energy is solar, which is intermittent, and whose energy, derived during sunlit periods, is needed at other times. A material under intense study as a candidate for such a role is Glauber's salt (sodium sulfate decahydrate). Its thermal properties are as follows:

$\rho = 1460 \text{ kg/m}^3$, $T_m = 32^\circ\text{C}$, $L = 251.21 \text{ kJ/kg}$, $c_L = 3.31$, $c_S = 1.76$ ($\text{kJ/kg}^\circ\text{C}$), $k_L = 0.59 \times 10^{-3}$, $k_S = 2.16 \times 10^{-3}$ ($\text{kJ/m s}^\circ\text{C}$) whence $\alpha_L = 1.22 \times 10^{-7}$, $\alpha_S = 8.4 \times 10^{-7}$ (m^2/s).

Let the face of a long can of Glauber's salt be exposed to a warm temperature $T_L = 90^\circ\text{C}$. Initially it is solid at the temperature $T_S = 25^\circ\text{C}$. We wish to describe the resulting melting process. Here we have $St_L = 0.76422$, $St_S = 0.049$, $\nu = 0.3811$, and solving (2d) numerically, $\lambda = 0.520815$. Hence, the location of the phase change front at any time is $X(t) = 3.64 \times 10^{-4}\sqrt{t}$ meters.

In **Figure 2.2.4** we see the temperature profiles at three times. We note that the temperature is very nearly linear in space with a jump in slope at the interface $x = X(t)$. The variation of the temperature in time at three depths in the material is shown in **Figure 2.2.5**. Again we see a jump in the slope at the time when the phase change takes place. We note the extreme flatness of the curves as we move to greater depth, something that is typical of actual processes. A simple calculation shows that for any x we have $T_t(x, 0) = 0$ so, all melting curves start with zero slope; since $(\nu\lambda)^2 < 3/2$ here (§2.2.F), there is a concavity change before the melt time, as in **Figure 2.2.2(b)**, but due to scaling this effect cannot be seen in **Figure 2.2.5**.

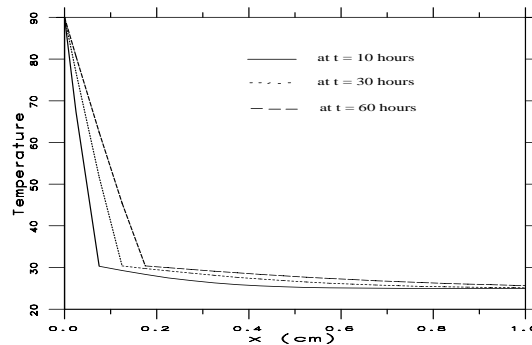


Figure 2.2.4. Temperature profiles at three times.

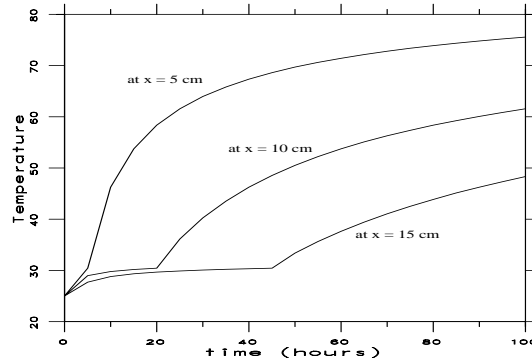


Figure 2.2.5. Temperature histories at three points.

At this point we have “modeled” the process, meaning that the temperature (given by (2b,c) is related in a known way to the thermal properties and the initial and boundary temperature. Of primary interest in heat storage is the “heat inventory” at any time. For example, after 1 hour the melt-depth is $X(3600s) = 0.0218 m$, and the amount of heat that has entered the system is (from (16)) $Q(3600s) = 12306 kJ/m^2$. Of this amount, $E^{lat} = \rho LX = 7995.5 kJ/m^2$ is stored as latent heat and the rest, $4310.5 kJ/m^2$, as sensible heat (of which, $E_L^{sens} = 3308$ in the liquid and only $E_S^{sens} = 1002.5$ in the semi-infinite solid, by (15)).

PROBLEMS

PROBLEM 1. State precisely the 2-phase Stefan Problem for **freezing** from the left with initial temperature $T_L > T_m$ and imposed temperature $T_S < T_m$ at $x = 0$. Compare with (1).

PROBLEM 2. Derive (2) by following the procedure of §2.1.B.

PROBLEM 3. Verify that (2) solves (1).

PROBLEM 4. The function $g(x) := e^{x^2} \operatorname{erfc}(x)$ is *decreasing* while the function $h(x) := x e^{x^2} \operatorname{erfc}(x)$ is *increasing*, for $x > 0$. These functions arise in the similarity solutions in §2.2, 2.3 and 2.4. Their monotonicity properties may be proved as follows: (a) Set $\phi(x) := e^{-x^2} g'(x) = 2x \operatorname{erfc} x - \frac{2}{\sqrt{\pi}} e^{-x^2}$, $x > 0$. Show that $\phi(0) < 0$, $\phi(x) \rightarrow 0$ as $x \rightarrow \infty$ and $\phi'(x) > 0$ for $x > 0$. Conclude that $\phi(x) < 0$, whence $g'(x) = e^{x^2} \phi(x) < 0$, for $x > 0$. (b) Set $\psi(x) := e^{-x^2} h'(x)$, $x > 0$. Show that $\psi(0) = 1$, $\psi(x) \rightarrow 0$ as $x \rightarrow \infty$

and $\psi'(x) = 2e^{-x^2}g'(x) < 0$ (from part (a)). Conclude that $\psi(x) > 0$, so also $h'(x) = \psi(x)e^{x^2}(x) > 0$ for $x > 0$.

PROBLEM 5. To prove that, for any $St_L > 0$, $St_S \geq 0$, $\nu > 0$ equation (2d) has a unique root $\lambda > 0$, set $f(\lambda)$ equal to the left-hand side of (2d), $\lambda > 0$. Use (28-33) of §2.1 and the previous PROBLEM to show that

- (a) $f(0) = +\infty$, $f(\infty) = -\infty$; conclude that the equation $f(\lambda) = \lambda\sqrt{\pi}$ has at least one (positive) solution.
 (b) $f(\lambda)$ is strictly decreasing for $\lambda > 0$; conclude that $f(\lambda) = \lambda\sqrt{\pi}$ has exactly one (positive) solution.

PROBLEM 6. Seek an alternative form of the similarity solution by setting $X(t) = 2\lambda\sqrt{\alpha_S t}$ with $T(x, t)$ as before. Compare with (2).

PROBLEM 7. Derive the Neumann solution for the freezing case described in PROBLEM 1.

PROBLEM 8. Derive the dimensionless form (7).

PROBLEM 9. Corresponding to the alternative choice suggested in PROBLEM 6, one may choose as Fourier number (dimensionless time) $Fo = \alpha_S t / \bar{x}^2$. Derive the dimensionless form of (1) with this choice of Fo . Compare with PROBLEM 8.

PROBLEM 10. Seek the similarity solution of (7) in the form $\Sigma = 2\lambda\sqrt{Fo}$, $u(\zeta, Fo) = F(\xi)$, $\xi = \zeta / \sqrt{Fo}$, to obtain (8).

PROBLEM 11. Prove that equation (9d) has unique solution. Using other sources find a material for which a phase change with an ignorable latent heat is of interest and for which the relation is relevant.

PROBLEM 12. Derive (13).

PROBLEM 13. In the situation of Example 1, §2.2.D, estimate the time up to which the Neumann solution will be a reasonable approximation to this finite-slab problem, according to the criterion (10) with $\varepsilon = 10^{-3}$, and according to criterion (12) with $\varepsilon = 1\%$.

PROBLEM 14. Repeat PROBLEM 13 with the same ε , but using the approximation (9c) for λ and the first term of (32) §2.1 for $\operatorname{erfc}(\nu\lambda)$.

PROBLEM 15. As another alternative in §2.2.D, consider the problem of §2.2.C for the condition that the temperature at the right hand side of a finite slab be closer to the initial temperature T_S than some prescribed tolerance ε . Derive an estimate similar to (10) for the condition that $|T(l, t) - T_S| < \varepsilon$.

PROBLEM 16. Apply the results of (10), of (12), and of PROBLEM 15 to the case of Glauber's salt of §2.2.G for $l = 0.5m$. Feel free to use the approximation (34) §2.1 for the error function.

PROBLEM 17. Integral of the error function. By interchanging the order of integration show that

$$\int_0^X \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_L t}}\right) dx = \frac{2}{\sqrt{\pi}} \int_0^X \int_0^{\frac{x}{2\sqrt{\alpha_L t}}} e^{-s^2} ds dx = X \operatorname{erf} \lambda - \frac{2}{\sqrt{\pi}} (1 - e^{-\lambda^2}) \sqrt{\alpha_L t},$$

$$\int_X^\infty \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_S t}}\right) dx = \frac{2}{\sqrt{\pi}} \int_X^\infty \int_{\frac{x}{2\sqrt{\alpha_S t}}}^\infty e^{-s^2} ds dx = \frac{2\sqrt{\alpha_S t}}{\sqrt{\pi}} e^{-(v\lambda)^2} - X \operatorname{erfc}(v\lambda).$$

PROBLEM 18. Using the previous PROBLEM, derive relations (15).

PROBLEM 19. Derive relation (16).

PROBLEM 20. Verify the heat balance (17).

PROBLEM 21. Derive relations (18).

PROBLEM 22. Show that when $\lambda \approx 0$, the last term in (18a) to lowest order is $St_L/2$.

PROBLEM 23. In the 1-phase case, approximate the temperature by the average of T_m and T_L to show that the ratio of sensible to latent heat is half the Stefan number, in agreement with the result of PROBLEM 18.

PROBLEM 24. Compute the time derivatives $u_\tau(\zeta^*, \tau)$, $u_{\tau\tau}(\zeta^*, \tau)$ of (20) and verify (21).

PROBLEM 25. Compute the time derivatives $u_\tau(\zeta^*, \tau)$, $u_{\tau\tau}(\zeta^*, \tau)$ of (8b) and verify (22).

PROBLEM 26. Verify the work in the Example of §2.2.F.

PROBLEM 27. Derive relation (23) and its approximation (24).

PROBLEM 28. Check the work in §2.2.G.