

# MATHEMATICAL MODELING OF MELTING AND FREEZING PROCESSES

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# CHAPTER 1

## PROBLEM FORMULATION

The purpose of simulation is to gain understanding of the process being simulated. Building understanding is complex, involving iterative use of experiment and observation on the “physical plane” and model building and analysis on the “conceptual plane.” The act of formulating a mathematical model tests our understanding of the physical process. Do we know what is important, and what may be ignored? Do we believe that we know the underlying relationships between the entities making up our process well enough to formulate them in mathematical terms?

This book is concerned with simulating the processes of melting and freezing on a macroscopic scale. Very few processes are more familiar to us than these. Yet our interest in them, motivated by processes of increasing complexity, has grown steadily in recent years, while our intuition is increasingly tested. On the one hand we know that it will take half a day to defrost a piece of meat. On the other hand, we have not the slightest intuition about the performance of a material used to store solar energy as the latent heat of melting as it cycles through repeated freeze/thaw cycles. The growing use of Silicon brings us into intimate contact with processes involving freezing of supercooled liquid; alloy processing in space leads us to surface-tension driven convection; laser induced melting brings us to the edge (and perhaps beyond it) of credibility of the heat equation, our fundamental tool for heat transfer modeling on a macroscopic scale. Time scales have broadened. When Stefan formulated the classical phase change model, the credible time scale for processes of interest could be measured in days to several years. In recent years the authors have dealt with problems whose time scales are measured in pico-seconds, and with problems whose time scales are literally 20,000,000 years. Thus our need to know has expanded, and with it, our intuition about even simple processes has waned. To build our intuition we need experiment and observation on the one hand, and better simulation tools on the other.

In this chapter we formulate the classical Stefan-type model of melting and freezing. Historically this problem has been regarded as lying on the border between tractable and intractable problems. It is nonlinear, and its principal difficulty lies in the fact that one of its unknowns is the region in which it is to be solved. For this reason it is called a “moving boundary problem.” Our intuition tells us that for most reasonable phase change processes energy conservation prevails. This is manifested in two ways: the heat equation, its differential expression, holds within liquid or solid, and a “jump” condition expressing energy conservation, prevails along the curves separating solid from liquid. Are there such curves? Sometimes we really do see “nice” curves separating solid from liquid, and sometimes instead, we see “fuzzy” or even “fat” regions in place of

sharp curves. The classical formulation is based on an underlying assumption, which we will later discard, that the front is indeed of zero thickness.

The chapter is divided into three sections. The first presents an overview of the physical ideas relevant to phase-change processes. In the second we introduce the precise mathematical formulation of the basic physical facts leading to the “Stefan Problem”, the prototype of all phase-change models and a central subject of this book. In the third section we discuss some of the complications and difficulties encountered in more realistic phase-change processes.

## 1.1. AN OVERVIEW OF THE PHENOMENA INVOLVED IN A PHASE-CHANGE

Several mechanisms are at work when a solid melts or a liquid solidifies. Such a change of phase involves heat (and often also mass) transfer, possible supercooling, absorption or release of latent heat, changes in thermophysical properties, surface effects, etc. We shall briefly discuss these in *rough* qualitative terms in order to orient the reader and introduce the terminology.

It is important to note that although the focus of our discussions is **solidification and melting**, the *principles, ideas, and many of the results* apply as well to other first-order phase transitions, including certain solid-to-solid transitions, vapor condensation and evaporation (gas-liquid transition), sublimation (gas-solid transition), or even certain magnetization phenomena. A clear qualitative picture of first-order phase transitions is presented in [CALLEN], [PIPPARD], [WALDRAM].

Both solid and liquid phases are characterized by the presence of cohesive forces keeping atoms in close proximity. In a **solid** the molecules vibrate around fixed equilibrium positions, while in a **liquid** they may “skip” between these positions. The macroscopic manifestation of this vibrational energy is what we call **heat** or **thermal energy**, the measure of which is **temperature**. Clearly atoms in the liquid phase are more energetic (hotter) than those in the solid phase, all other things being equal. Thus before a solid can melt it must acquire a certain amount of energy to overcome the binding forces that maintain its solid structure. This energy is referred to as the **latent heat**  $L$  (heat of fusion) of the material and represents the difference in thermal energy (enthalpy) levels between liquid and solid states, all other things being equal. Of course, solidification of liquid requires the removal of this latent heat and the structuring of atoms into more stable lattice positions. In either case there is a major re-arrangement of the entropy of the material, a characteristic of first-order phase transitions.

There are three possible modes of heat transfer in a material: **conduction**, **convection** and **radiation**. Conduction is the transfer of kinetic energy between atoms by any of a number of ways, including collision of neighboring atoms and

the movement of electrons; there is no flow or mass transfer of the material. This is how heat is transferred in an opaque solid. In a liquid heat can also be transferred by the flow of particles, i.e. by convection. Radiation is the only mode of energy transfer that can occur in a vacuum (it requires no participating medium). Thermal radiation, emitted by the surface of a heated solid, is radiation of wave-length roughly in the range 0.1 to 10 microns ( $\mu m$ ). An excellent source on the fundamentals of heat transfer modes is [BIRD et al], see also [WHITAKER].

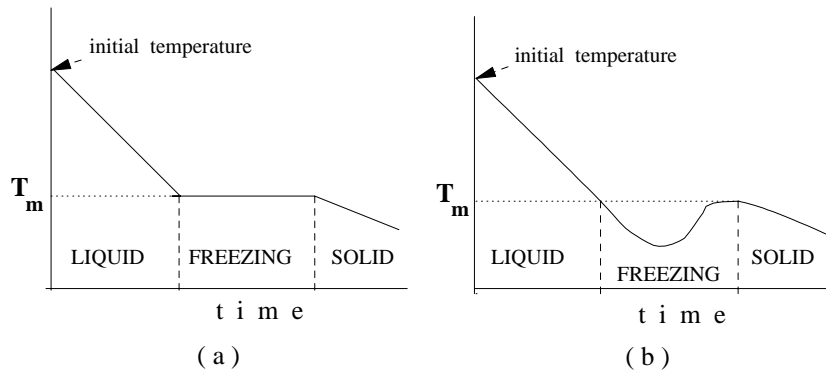
The transition from one phase to the other, that is, the absorption or release of the latent heat, occurs at some temperature at which the stability of one phase breaks down in favor of the other according to the available energy. This **phase-change**, or **melt temperature**  $T_m$  depends on pressure. Under fixed pressure,  $T_m$  may be a particular fixed value characteristic of the material (for example, 0°C for pure water freezing under atmospheric pressure), or a function of other thermodynamic variables (for example, of glycol concentration in an anti-freeze mixture).

Most solids are crystalline, meaning that their particles (atoms, molecules, or ions) are arranged in a repetitive lattice structure extending over significant distances in atomic terms. In this context atoms may be regarded as spheres of diameter 2 to 6 Angstroms (1 Angstrom =  $10^{-10}$  meters). Since formation of a crystal may require the movement of atoms into the solid lattice structure, it may well happen that the temperature of the material is reduced below  $T_m$  without formation of solid. Thus **supercooled liquid**, that is, liquid at temperatures below  $T_m$ , may appear; such a state is thermodynamically *metastable* [CALLEN], [TURNBULL] (see §2.4). We note that melting requires no such structuring, possibly explaining why “superheating” is rarely observed [CHRISTIAN]. To see the possible effect of supercooling (also called *undercooling* sometimes), typical cooling curves for both normal freezing and supercooling are shown schematically in **Figure 1.1.1**. These curves are meant to show the temperature of a sample of material as a function of time, as heat is extracted from the sample at a constant rate. Note that for the supercooling curve of **Figure 1.1.1(b)**, the temperature rapidly rises back to the melt temperature  $T_m$  when crystallization does take place. This can occur only if the latent heat released upon freezing is sufficient to raise the temperature to  $T_m$ , i.e., the liquid was not cooled too much. Liquid cooled to a temperature so low that the latent heat is not sufficient to raise its temperature to  $T_m$ , is referred to as being **hypercooled**.

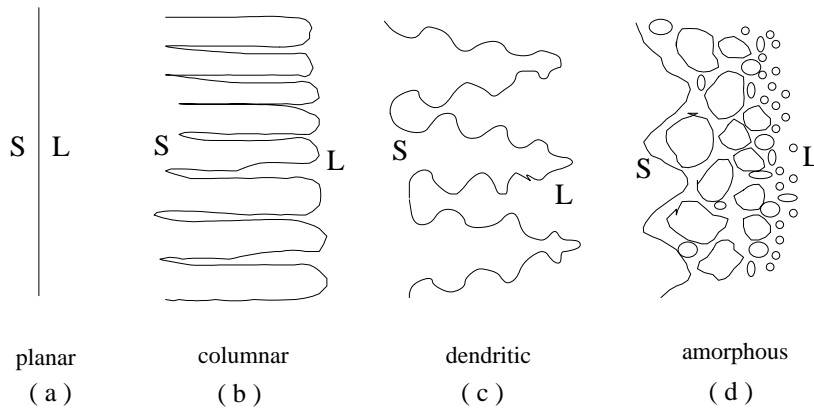
The phase-transition region where solid and liquid coexist is called the **interface**. Its thickness may vary from a few Angstroms to a few centimeters, and its microstructure may be very complex, depending on several factors (the material itself, the rate of cooling, the temperature gradient in the liquid, surface tension, etc.). For most pure materials solidifying under ordinary freezing conditions at a fixed  $T_m$  the interface appears (locally) planar and of negligible thickness. Thus it may be thought of as a “sharp front,” a surface separating solid from liquid at temperature  $T_m$ . In other cases, typically resulting from supercooling, the phase-

transition region may have apparent thickness and is referred to as a “mushy zone”; its microstructure may now appear to be dendritic or columnar (shown schematically in **Figure 1.1.2**). The local freezing temperature at a curved solid surface facing the liquid becomes depressed by an amount depending on the solid-liquid surface tension and the local curvature. This so-called **Gibbs-Thomson effect** is small for the overall freezing process, but crucial for the resulting microstructure of the interface [PORTER-EASTERLING], [KURZ-FISHER], [GURTIN] (see §2.4).

Most thermophysical properties of a material (usually varying smoothly with temperature) undergo more or less sudden changes at  $T_m$ . For example the heat capacity of aluminum changes by 11% at its melt temperature (of 659°C), but that of silicon changes by only 0.3% (at 1083°C). Such **discontinuities in thermophysical properties** complicate the mathematical problems because they



**Figure 1.1.1.** Cooling curves for (a) normal freezing and (b) with supercooling.



**Figure 1.1.2.** Common interfacial morphologies (schematic).

induce discontinuities in the coefficients of differential equations. However the most fundamental and pronounced effects are due to changes in density.

Typical **density changes** upon freezing or melting are in the range of 5% to 10% but can be as high as 30%. For most materials the solid is denser than the liquid, resulting in possible formation of voids in freezing or breaking of the container in melting (§2.3). On the other hand water expands on freezing, resulting in broken pipes on cold days and ice floating instead of filling the bottom of the oceans. The density variation with temperature induces flow by natural convection in the presence of gravity, rapidly equalizing the temperature in the liquid and greatly affecting heat transfer. In microgravity there is no natural convection but “Marangoni” convection [MYSHKIS et al], due to surface tension (capillary) effects, may arise instead and dominate heat transfer. All these effects may complicate a phase-change process beyond our ability to analyze effectively.

The explanation of why and how the phenomena mentioned above occur is the subject of physical theories, some still under development. Discussions may be found in the relevant literature [CALLEN], [CHALMERS], [FLEMINGS], [KURZ-FISHER], [LANDAU-LIFSHITZ], [PORTER-EASTERLING], [ROSENBERGER], [TILLER], [TURNBULL], [WALDRAM].

The subject of this book is the mathematical modeling and analysis of phase change processes at the **macroscopic** level. The purpose of mathematical modeling is to quantify the process in order to be able to predict (and ultimately control) the evolution of the temperature field in the material, the amount of energy used and stored, the interface location and thickness, and any other quantity of interest. Thus the equations and conditions that express the physics of the process must be formulated subject to certain accepted approximations; these result from the simplifying assumptions made in order to obtain a manageable problem. We will attempt to state such assumptions as clearly as possible so that the reader will be aware of the limitations of the resulting model.

When referring to a material that undergoes a phase change we will often use the abbreviation “PCM” to represent the term “Phase Change Material.”

## PROBLEMS

**PROBLEM 1.** It is asserted that if the density of ice were greater than that of water then life on earth would be impossible. Why?

**PROBLEM 2.** Ice-making is a major industrial activity. It is said that the person developing a method for pumping supercooled liquid without it freezing would become “rich and famous.” Why?

**PROBLEM 3.** In your experience is it more common or less common to observe sharp freezing fronts. Give an example.

**PROBLEM 4.** It was very cold yesterday and yet the snow on the roof partly melted. Where could the heat have come from?

**PROBLEM 5.** Suppose that you are flying in a plane at a very high altitude and you can fire a water droplet into the cold exterior air. Describe what you think will happen to it.

**PROBLEM 6.** Describe the appearance of the curve corresponding to that of **Figure 1.1.1(b)** for the case of superheating of a solid.

## 1.2. FORMULATION OF THE STEFAN PROBLEM

### 1.2.A Introduction

We begin by formulating the mathematical model of a simple melting or freezing process incorporating only the most basic of the phenomena mentioned in §1.1. This model is known as the **Classical Stefan Problem** and constitutes the foundation on which progressively more complex models can be built by incorporating some of the effects initially left out. The characteristic of phase-change problems is that, in addition to the temperature field, the **location** of the interface is unknown. Problems of this kind arise in fields such as molecular diffusion, friction and lubrication, combustion, inviscid flow, slow viscous flow, flow in porous media, and even optimal decision theory. Overviews of the origins of such problems, referred to as “moving boundary problems” or “free boundary problems” may be found in [RUBINSTEIN] and in [ELLIOTT-OCKENDON], [CARSLAW-JAEGER] and [CRANK]; see also the conference proceedings [OCKENDON-HODGKINS], [WILSON-SOLOMON-BOGGS], [FASANO-PRIMICERIO, 1983], [BOSSAVIT-DAMLAMIAN-FREMOND], [HOFFMANN-SPREKELS], [CHADAM-RASMUSSEN] on moving boundary problems.

We start with a discussion of the physical assumptions leading to the Stefan Problem. Then we introduce the basic concepts and equations of heat conduction, boundary conditions, and interface conditions, ending up with the precise mathematical formulation of the Classical Stefan Problem.

### 1.2.B Assumptions

It is crucial to have a clear picture of exactly which phenomena are taken into account and which are not, because a model can at best be as good as its underlying physical assumptions. To make the assumptions as clear as possible we present, in **Table 1.1**, a summary of the physical factors involved in a phase change and the simplifying assumptions that will lead us to the classical Stefan Problem.

Our phase change process involves a PCM (phase change material) with constant density  $\rho$ , latent heat  $L$ , melt temperature  $T_m$ , phase-wise constant specific heats  $c_L, c_S$ , and thermal conductivities,  $k_L, k_S$ . Heat is transferred only isotropically (see below) by conduction, through both the solid and the liquid; the phases



**Table 1.1**

<i>Physical Factors Involved in Phase change Processes</i>	<i>Simplifying Assumptions for the Stefan Problem</i>	<i>Remarks on the Assumptions</i>
1. Heat and mass transfer by conduction, convection, radiation with possible gravitational, elastic, chemical, and electro-magnetic effects.	Heat transfer isotropically by conduction only, all other effects assumed negligible.	Most common case. Very reasonable for pure materials, small container, moderate temperature gradients.
2. Release or absorption of latent heat	Latent heat is constant; it is released or absorbed at the phase-change temperature.	Very reasonable and consistent with the rest of the assumptions.
3. Variation of phase-change temperature	Phase-change temperature is a fixed known temperature, a property of the material.	Most common case, consistent with other assumptions.
4. Nucleation difficulties, supercooling effects	Assume not present.	Reasonable in many situations.
5. Interface thickness and structure	Assume locally planar and sharp (a surface separating the phases) at the phase-change temperature.	Reasonable for many pure materials (no internal heating present).
6. Surface tension and curvature effects at the interface	Assume insignificant.	Reasonable and consistent with other assumptions.
7. Variation of thermo-physical properties	Assume constant in each phase, for simplicity ( $c_L \neq c_S$ , $k_L \neq k_S$ ).	An assumption of convenience only. Reasonable for most materials under moderate temperature range variations. The significant aspect is their discontinuity across the interface, which is allowed.
8. Density changes	Assume constant ( $\rho_L = \rho_S$ ).	Necessary assumption to avoid movement of material. Possibly the most unreasonable of the assumptions.

are separated by a sharp interface of zero thickness, an isotherm at temperature  $T_m$ , where the latent heat is absorbed or released.

This situation arises very often in applications with the result that the Stefan Problem is by far the most frequently applied model of a phase change process.

An additional assumption of mathematical nature often goes unmentioned. In deriving the model it will be assumed that all the functions representing physical quantities are as smooth as required by the equations in which they appear. Of course this has to be assumed a-priori in order to proceed with the formulation of the mathematical model, but has to be justified a-posteriori by proving that the resulting mathematical problem does indeed admit such smooth solutions. It turns out that this may not always be the case, making “weak solution” reformulations necessary (see §4.4).

**EXAMPLE.** The specific heat (in  $\text{kJ/kg K}$ ) of ice/water is well approximated by the relation

$$c = \begin{cases} 7.16 \times 10^{-3} T + .138, & T \leq 273 \text{ K (ice)} \\ 4.1868, & T \geq 273 \text{ K (water)}. \end{cases} \quad (1)$$

Similarly the thermal conductivity (in  $\text{kJ/m s K}$ ) is given by

$$k = \begin{cases} 2.24 \times 10^{-3} + 5.975 \times 10^{-6}(273 - T)^{1.156}, & T \leq 273 \text{ K} \\ 1.017 \times 10^{-4} + 1.695 \times 10^{-6} T, & T \geq 273 \text{ K} \end{cases} \quad (2)$$

Note that at the melt temperature  $T_m = 273 \text{ K}$ ,  $c_S = 2.0927$  is only about half of  $c_L = 4.1868$ , while  $k_S = 2.24 \times 10^{-3}$  is about four times larger than  $k_L = 0.5644 \times 10^{-3}$ .

### 1.2.C Heat Conduction

The fundamental quantities involved in conduction of heat through a material are: **temperature**, **heat** (thermal energy) and **heat flux**.

The **temperature** is a macroscopic measure of perpetual molecular movement. Its meaning and measurement are subjects of Thermodynamics [CALLEN], [REYNOLDS], [WALDRAM], and Heat Transfer [ECKERT-DRAKE], [McADAMS]. It is measured in degrees Kelvin (K), Celsius ( $^{\circ}\text{C}$ ) or Fahrenheit ( $^{\circ}\text{F}$ ).

The **heat** absorbed by a material under constant pressure is a thermodynamic quantity called the **enthalpy**. We shall denote the enthalpy (thermal energy) per unit mass by  $e$  and per unit volume by  $E$ , measuring the former in  $\text{kJ/kg}$ , and the latter in  $\text{kJ/m}^3$ . For a pure material heated under *constant pressure*, when there are *no* volume changes, the enthalpy represents the *total energy* ( see §2.3 ), and the heat absorbed is related to the temperature rise by

$$de = c dT . \quad (3)$$

The quantity

$$c(T) = \frac{de}{dT},$$

is the **specific heat** (heat capacity per unit mass) ( $\text{kJ}/\text{kg}^\circ\text{C}$ ) under constant pressure and represents the heat needed to raise the temperature of 1 kg of the material by  $1^\circ\text{C}$ . It is a property of the material, always positive, varies slowly with temperature, and is usually higher for the liquid phase than for the solid phase. Thus for example, the specific heat of water as given in (1) above can be taken as  $4.1868 \text{ kJ}/\text{kg}^\circ\text{C}$ , while that of ice at  $0^\circ\text{C}$  ( $273 \text{ K}$ ) is  $2.0927 \text{ kJ}/\text{kg}^\circ\text{C}$ . The heat accompanying a temperature rise is referred to as **sensible heat**, in contrast with the **latent heat of phase change**, absorbed or released at constant temperature (the melt temperature). In the context of a phase change process the most convenient reference temperature, relative to which temperature changes are measured, is the **phase-change** temperature of the material,  $T_m$  (provided it is constant). From (3) the sensible heat in a unit mass of material at temperature  $T$  is then given by

$$\text{sensible heat} = \int_{T_m}^T c(\bar{T}) d\bar{T}, \quad (4)$$

with  $c = c_L$  if the material is liquid ( $T > T_m$ ) and  $c = c_S$  if it is solid ( $T < T_m$ ). At  $T = T_m$  the material may be either liquid or solid. What distinguishes the two is the energy (enthalpy); liquid at  $T_m$  contains the latent heat  $L$  per unit mass, whereas solid at  $T_m$  has no latent heat. Hence, if we fix the energy scale by choosing  $e = 0$  for solid at  $T = T_m$ , the enthalpy is given by

$$e = \begin{cases} e^L(T) := L + \int_{T_m}^T c_L(\bar{T}) d\bar{T}, & \text{for } T > T_m \quad (\text{liquid}) \\ e^S(T) := \int_{T_m}^T c_S(\bar{T}) d\bar{T}, & \text{for } T < T_m \quad (\text{solid}) \end{cases} \quad (5)$$

Therefore the phases are characterized by *either* temperature *or* enthalpy as

$$\begin{aligned} \text{solid} & \iff T < T_m \iff e < 0, \\ \text{liquid} & \iff T > T_m \iff e > L, \end{aligned} \quad (6)$$

At  $T = T_m$  the enthalpy undergoes a jump of magnitude  $L$ . If  $e = 0$  the material is solid while for  $e = L$  it is liquid. Any region where

$$T = T_m \quad \text{and} \quad 0 < e < L \quad (7)$$

is referred to as a **mushy zone**. According to our Assumption 5 (§1.2.B) this region has zero thickness (a surface) and therefore the enthalpy jump across it is

$$\llbracket e \rrbracket_{solid}^{liquid} := e^L(T_m) - e^S(T_m) = L. \quad (8)$$

When the specific heats  $c_S, c_L$  are constants, (5) reduces to

$$e = \begin{cases} e^L(T) := L + c_L[T - T_m], & T \geq T_m & (liquid), \\ e^S(T) := c_S[T - T_m], & T \leq T_m & (solid), \end{cases} \quad (9)$$

the graph of which is shown in **Figure 1.2.1(a)**, and of its inverse in **Figure 1.2.1(b)**. For water/ice, (1) may be used to relate  $T$  directly to  $e$ ; when graphed we obtain the curve of **Figure 1.2.2**.

The amount of heat crossing a unit area per unit time is called the **heat flux**, denoted by  $\vec{q}$ , and measured in  $\text{kJ}/\text{s m}^2 = \text{kW}/\text{m}^2$ . The heat flux is a vector pointing in the direction of heat flow, and given by

$$\text{Fourier's Law:} \quad \vec{q} = -\underline{k} \nabla T \quad (10)$$

where the tensor  $\underline{k}$  is the **thermal conductivity** of the material, measured in  $\text{kJ}/\text{m s }^\circ\text{C}$  or  $\text{kW}/\text{m K}$ . In general it is a tensor with positive components varying with temperature. We shall assume **isotropic conduction**, i.e., that  $\underline{k}$  is a scalar  $k > 0$ . Typically, its value for the solid is higher than for the liquid. For water/ice, for example, we see from (2) that  $k_S$  is substantially greater than  $k_L$ . Regarding the isotropicity assumption, we note that in reality, even for ice frozen off a flat surface, there is a direction dependence of conductivity.

In circular cylindrical coordinates  $(r, \theta, z)$ ,

$$x = r \cos \theta, \quad y = r \sin \theta, \quad z = z, \quad (11a)$$

Fourier's law for an isotropic medium takes the form

$$\vec{q} = -k(T_r, \frac{1}{r}T_\theta, T_z), \quad (11b)$$

while in spherical coordinates  $(r, \phi, \theta)$

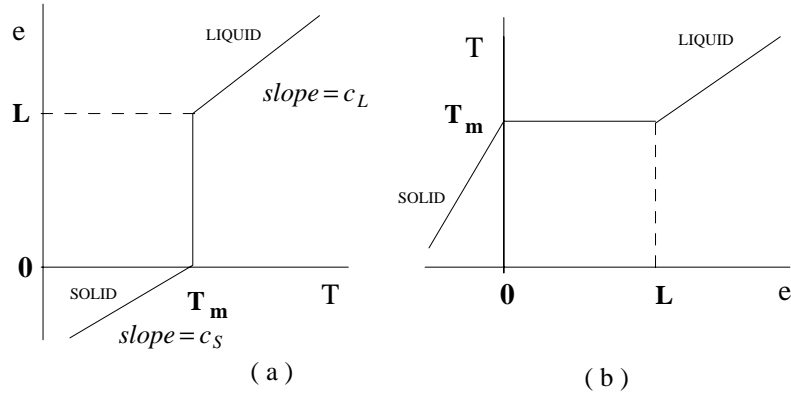
$$x = r \cos \theta \sin \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \phi, \quad (12a)$$

it takes the form

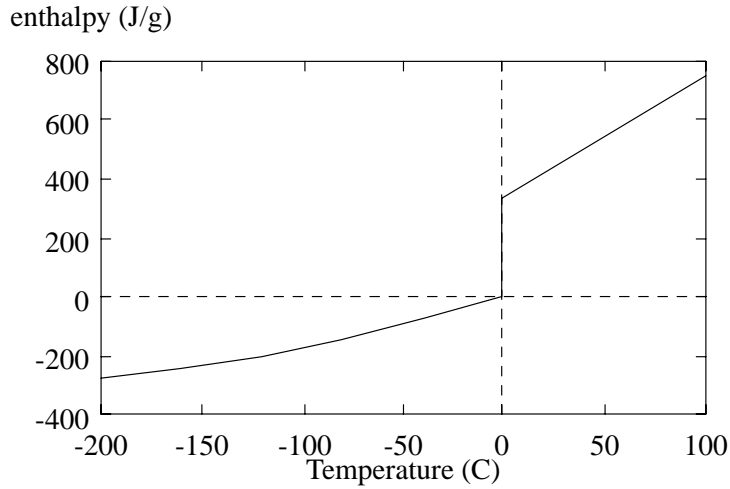
$$\vec{q} = -k(T_r, \frac{1}{r}T_\phi, \frac{1}{r \sin \phi}T_\theta). \quad (12b)$$

In one space dimension Fourier's law is expressed by

$$q = -k T_x \quad (13a)$$



**Figure 1.2.1.** Typical state relation,  $e = e(T)$ , and its inverse,  $T = T(e)$ , (with constant  $c_L, c_S$ ).



**Figure 1.2.2.** State relation,  $e = e(T)$ , for ice-water.

for the cartesian coordinate  $x$ , and by

$$q = -k T_r \tag{13b}$$

for the  $r$  direction in both the circular cylindrical and spherical systems.

The **heat flow rate** across a surface of area  $A$  and unit normal  $\vec{n}$  is given by

$$(\vec{q} \cdot \vec{n}) A = -k \nabla T \cdot \vec{n} A, \tag{14}$$

and represents the heat crossing the area  $A$  in the direction normal to the surface per unit time. Thus the radial heat flow rate through the surface of a circular

cylinder of radius  $r$  and height  $z$  is  $(-k T_r) 2\pi r z$ , and that through the surface of a sphere of radius  $r$  is  $(-k T_r) 4\pi r^2$ .

The fundamental law of conductive heat transfer is the

$$\text{Energy Conservation Law:} \quad (\rho e)_t + \operatorname{div} \vec{q} = F, \quad (15)$$

where  $F$  ( $\text{kJ}/\text{m}^3 \text{s}$ ) is a volumetric heat source ( $> 0$ ) or sink ( $< 0$ ). This is the differential form (the subscript  $t$  denotes partial derivative with respect to time) of the **First Law of Thermodynamics** (applied to the enthalpy, since this represents the total energy here, see §2.3.F):

$$\text{heat increase} = \text{heat in} - \text{heat out},$$

or, in terms of rates:

$$\frac{d}{dt} \iiint_V \rho e \, dV = \iiint_V F \, dV - \iint_S \vec{q} \cdot \vec{n} \, dS, \quad (16)$$

where  $V$  is a volume,  $S$  its surface and  $\vec{n}$  the *outward* unit normal to  $S$ . Since, by the Divergence Theorem, the surface integral equals  $\iiint_V \operatorname{div} \vec{q} \, dV$  and the volume is arbitrary, (15) is equivalent to (16). Expressing  $e$  and  $\vec{q}$  in terms of temperature via (3) and (10) we obtain the general

$$\text{Heat Conduction Equation:} \quad \rho c T_t = \operatorname{div}(k \nabla T) + F \quad (17)$$

expressing local conservation of heat conducted isotropically through the material according to Fourier's law. This is a partial differential equation obeyed by  $T(\vec{x}, t)$ , the temperature at location  $\vec{x}$  at time  $t$ . It holds at each point  $\vec{x}$  of the region occupied by a material of density  $\rho$ , specific heat  $c$ , and conductivity  $k$ .

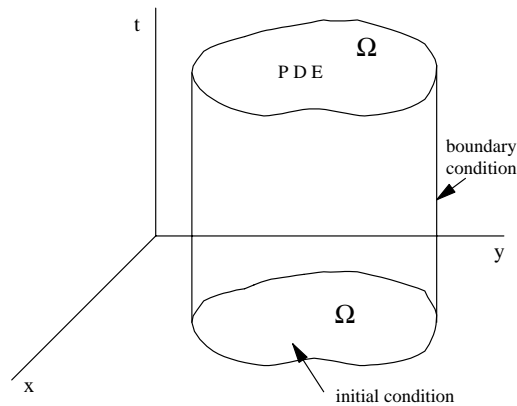
We recall the concept of **well-posedness**.

**DEFINITION.** A mathematical problem is said to be **well-posed** if it admits a unique solution that depends continuously on the data (small changes in the data result in small changes in the solution).

The well-posedness concept mimics the corresponding requirements on the physical problem being modeled. For most "standard" physical processes we expect a unique solution that will not "jump" in response to slight changes in input data.

A well-posed problem for equation (17) in a spatial domain  $\Omega$  and for positive time  $t > 0$  (**Figure 1.2.3**) requires the following information:

- (a) partial differential equation (17), valid for  $\vec{x}$  in  $\Omega$ ,  $t > 0$ ,
- (b) initial condition  $T(\vec{x}, 0) = T_{\text{init}}(\vec{x})$ ,  $\vec{x}$  in  $\Omega$ ,
- (c) boundary conditions (specify  $T$ , or its normal derivative, or a combination of both, see §1.2.D), at every point of the boundary,  $\partial\Omega$ , of  $\Omega$  for  $t > 0$ .



**Figure 1.2.3.** Space-time region for the Heat Conduction Equation.

Here  $T_{init}$  is a known initial temperature distribution.

The **boundary conditions** that most often arise in heat transfer are discussed in §1.2.D. Different types of boundary conditions may be imposed on different parts of the boundary, but **some** condition is needed on **each** part.

When the thermal conductivity  $k$  can be considered constant, then it is convenient to introduce the

$$\text{Thermal Diffusivity:} \quad \alpha = \frac{k}{\rho c} \quad (m^2/s), \quad (18)$$

and write (17) in the form known as the

$$\text{Heat Equation:} \quad T_t = \alpha \nabla^2 T + f, \quad (19)$$

which is now a **linear** parabolic equation, (see (23)).

In one-space dimension, when no internal sources are present, the Fourier Law, general Heat Conduction Equation, and Heat Equation take the forms

$$q = -k T_x, \quad (20)$$

$$\rho c T_t = (k T_x)_x, \quad (21)$$

$$T_t = \alpha T_{xx}. \quad (22)$$

Let us briefly recall the place the heat equation occupies among the “standard” partial differential equations. The classical second order partial differential equations of mathematical physics [COURANT-HILBERT], [CHESTER] [DUCHATEAU-ZACHMANN], [ZACHMANOGLU-THOE], [STRAUSS], are epitomized by the

$$\text{Laplace equation:} \quad 0 = \text{div}(\nabla u), \quad (23a)$$

the

$$\text{wave equation:} \quad u_{tt} = \operatorname{div}(\nabla u), \quad (23b)$$

and the

$$\text{heat equation:} \quad u_t = \operatorname{div}(\nabla u), \quad (23c)$$

where, for each, the right hand side contains derivatives only with respect to the spatial variables.

The Laplace equation is said to be of **elliptic** type, a class of equations for which time as such plays no role. Elliptic equations characterize steady state behavior of a system. To be well-posed a problem involving an elliptic equation in a region  $\Omega$  requires data around the entire boundary of the region, and will tell us what is happening in the interior.

**EXAMPLE 1.** A well-posed problem for the Laplace equation

$$\frac{1}{r} (ru_r)_r + \frac{1}{r^2} u_{\theta\theta} = 0 \quad (24a)$$

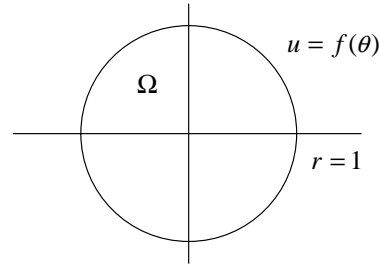
on the unit disk  $\Omega$  of the  $x, y$  plane in polar coordinates, is to seek a solution  $u$  to the equation within  $\Omega$  which on the boundary  $r = 1$  of  $\Omega$  is equal to a given function  $f(\theta)$  (**Figure 1.2.4**). It is easily seen by separation of variables that if  $f(\theta)$  can be expanded in a Fourier series

$$f(\theta) = \sum_{n=0}^{\infty} \alpha_n \cos(n\theta) + \beta_n \sin(n\theta), \quad (24b)$$

then the unique solution to this problem is (PROBLEM 10)

$$u(r, \theta) = \sum_{n=0}^{\infty} r^n [\alpha_n \cos(n\theta) + \beta_n \sin(n\theta)] . \quad (24c)$$

where  $\alpha_n$  and  $\beta_n$  are the Fourier coefficients of  $f(\theta)$ .



**Figure 1.2.4.** Region for Laplace's equation (24a).



The Wave Equation is said to be of **hyperbolic** type, and corresponds to time-dependent movement of a body due to conditions at its boundary. Solutions to the equation are functions  $u(\vec{x}, t)$  defined on the set of points  $(\vec{x}, t)$  where  $\vec{x}$  varies in some spatial domain  $\Omega$  and  $t$  varies on some interval  $0 \leq t \leq t_{\max}$ . Well-posedness requires the assignment of a condition everywhere on the boundary of  $\Omega$  throughout the time interval, together with an appropriate initial condition. Since this equation represents the second derivative  $u_{tt}$  in terms of spatial information, comparison with the case for ordinary differential equations implies that throughout  $\Omega$  an initial distribution of both  $u$  and  $u_t$  is needed for well-posedness.

**EXAMPLE 2.** A well posed problem for the wave equation in one space dimension for  $\Omega$  the interval  $0 \leq x \leq \pi$  is (**Figure 1.2.5**)

$$u_{tt} = u_{xx}, \quad 0 < x < \pi, \quad t > 0, \quad (25a)$$

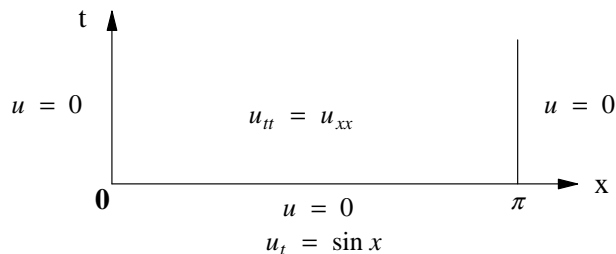
$$u(0, t) = 0, \quad t > 0 \quad (\text{boundary condition at } x = 0), \quad (25b)$$

$$u(\pi, t) = 0, \quad t > 0 \quad (\text{boundary condition at } x = \pi), \quad (25c)$$

$$u(x, 0) = 0, \quad 0 \leq x \leq \pi \quad (\text{initial condition}), \quad (25d)$$

$$u_t(x, 0) = \sin x, \quad 0 \leq x \leq \pi \quad (\text{initial condition}). \quad (25e)$$

The unique solution to this problem is  $u(x, t) = \sin t \sin x$ , (PROBLEM 11).



**Figure 1.2.5.** Region for the wave equation problem (25).

The heat equation is said to be of **parabolic** type. Now the time derivative appears only to first order. As with the wave equation a condition is still needed everywhere on the boundary of  $\Omega$ , but only one initial condition, the specification of the value of  $u(\vec{x}, t)$  for all  $\vec{x}$  in  $\Omega$  at the initial time  $t = 0$  is required (see below).

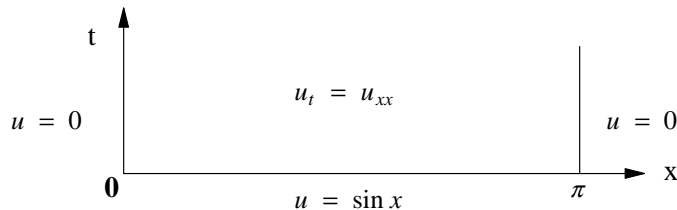
**EXAMPLE 3.** A well-posed problem for the one-dimensional heat equation on the interval  $0 \leq x \leq \pi$  is (**Figure 1.2.6**)

$$u_t = u_{xx}, \quad 0 < x < \pi, \quad t > 0 \quad (26a)$$

$$u(0, t) = 0, \quad t > 0 \quad (\text{boundary condition at } x = 0), \quad (26b)$$

$$u(\pi, t) = 0, \quad t > 0 \quad (\text{boundary condition at } x = \pi), \quad (26c)$$

$$u(x, 0) = \sin x, \quad 0 < x < \pi \quad (\text{initial condition}). \quad (26d)$$



**Figure 1.2.6.** Region for the heat equation problem (26).

The unique solution to this problem is  $u(x, t) = e^{-t} \sin x$ , (PROBLEM 12).

The wave equation and the heat equation differ in two fundamental aspects. The first is that while time is “reversible” for the wave equation, meaning that exchanging  $t$  with  $-t$  will not effect the behavior of the solution, it is not so for the heat equation. Indeed, “backward” problems involving the determination of an earlier thermal state from “final” data, are in general not well-posed. The second difference is that signals moving according to the wave equation have a finite speed, while for the heat equation signals are propagated at infinite speed. (see below).

**EXAMPLE 4.** Heat conduction in a semi-infinite slab:

Assume the slab  $0 \leq x < \infty$  is initially at a uniform temperature  $T_0$  and a temperature  $T_L$  is imposed at the face  $x = 0$ . Thus, we seek  $T(x, t)$  such that

$$T_t = \alpha T_{xx}, \quad 0 < x < \infty, \quad t > 0 \quad (27a)$$

$$T(x, 0) = T_0, \quad 0 < x < \infty \quad (27b)$$

$$T(0, t) = T_L, \quad \lim_{x \rightarrow \infty} T(x, t) = T_0, \quad t > 0. \quad (27c)$$

This is also a well-posed problem with solution (PROBLEM 14)

$$T(x, t) = T_L - (T_L - T_0) \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha t}}\right), \quad (28)$$

where the **error function** is given by [ABRAMOWITZ-STEGUN], §2.1,

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-s^2} ds. \quad (29)$$

The solution is discontinuous at  $x = 0, t = 0$ , but infinitely smooth for any  $t > 0$ . We see that heat conduction is a *smoothing* process, a property of parabolic equations not shared by hyperbolic ones (and a reason why “backward” parabolic problems are ill-posed, generally).

Note that as long as the face  $x = 0$  is held also at temperature  $T_0$ , the whole slab remains at  $T_0$ . The moment the face temperature is changed to a different temperature,  $T_L$ , say higher than  $T_0$ , the temperature at *every* point of the *entire*

slab also rises *immediately*, according to (28). Hence, the disturbance at  $x = 0$  is felt immediately everywhere! In this sense, the thermal signal travels with *infinite* speed, also a property of parabolic equations not shared by hyperbolic ones, as mentioned earlier. Clearly this contradicts our experience and suggests that the heat equation (actually Fourier's law) may be a poor model for heat conduction. Why is it then universally used as such? The reason is that this unphysical behavior is more "theoretical" than "practical": The error function increases to 1 extremely rapidly ( e.g.  $\text{erf}(5) \approx 1 - .15 \times 10^{-11}$  ) and therefore, for moderate  $T_L - T_0$ ,  $T(x, t)$  is *detectably* different from  $T_0$  *only* for points  $x$  very close to  $x = 0$  ( say,  $x < 10\sqrt{\alpha t}$  ); the rest of the slab will essentially be at  $T_0$ , as far as any measuring device can detect, in accord with experience.

Notice, however, that for *very large* temperature gradients (e.g. very large  $T_L - T_0$ ) this will not be the case and then the validity of Fourier's law does become questionable even from the "practical" point of view. Such situations arise in various applications, involving very intense local heating/cooling, e.g. laser annealing, and there have been various attempts at examining alternatives leading to "hyperbolic heat transfer" and "hyperbolic Stefan Problems", [OZICIK], [SOLOMON et al,1985], [SHOWALTER-WALKINGTON], [FRIEDMAN-HU], [LI].

### 1.2.D Boundary Conditions

In addition to knowing the initial temperature distribution, the thermal conditions on *every* exterior surface of the body must be known at all times. This requirement is not only physically obvious, but also mathematically necessary in order to have a well-posed mathematical problem for the parabolic equation (17).

Surface heating or cooling can be achieved by the following methods, each one inducing a boundary condition appropriate for equation (17).

#### I. Imposed temperature:

$$T(\vec{x}, t) = T_{\text{boundary}}(\vec{x}, t) \quad \text{for} \quad \vec{x} \in \partial\Omega, \quad t > 0, \quad (30)$$

i.e., the temperature at each boundary point is specified. This amounts to assuming perfect contact between the surface and a heat source of known temperature.

#### II. Imposed Flux:

$$-k \frac{\partial T}{\partial \vec{n}_{in}}(\vec{x}, t) = q_{\text{boundary}}(\vec{x}, t) \quad \text{for} \quad \vec{x} \in \partial\Omega, \quad t > 0, \quad (31)$$

where  $\vec{n}_{in}(\vec{x})$  is the inward normal to  $\partial\Omega$  at  $\vec{x} \in \partial\Omega$ , and  $\frac{\partial T}{\partial \vec{n}_{in}} = \nabla T \cdot \vec{n}_{in}$  denotes the directional derivative. This means we know the amount of heat entering the surface per unit area per unit time. Of course, what we really know is the amount of heat delivered to the surface by, say, a heater lamp, but not how much actually gets

inside unless there is perfect contact and no reflective losses. If the **absorptivity**  $a$  of the surface is known, then the right-hand side will be  $a \cdot q_{boundary}(\vec{x}, t)$ . In particular, (perfect) thermal insulation is expressed by

$$-k \frac{\partial T}{\partial \vec{n}_{in}} = 0. \quad (32)$$

### III. Convective Flux:

$$-k \frac{\partial T}{\partial \vec{n}_{in}}(\vec{x}, t) = h[T_{\infty}(\vec{x}, t) - T(\vec{x}, t)] \quad \text{for } \vec{x} \in \partial\Omega, \quad t > 0, \quad (33)$$

that is, the incoming flux is proportional to the temperature difference between the surface of the material and an imposed ambient temperature  $T_{\infty}$  (Newton's law of cooling). This is the most realistic means of heat input, achieved by pumping a heat transfer fluid (such as water or air) of known (and regulated) temperature  $T_{\infty}$  over a container wall. The wall creates in fact a thin boundary layer and is modeled effectively by an experimentally determined convective **heat transfer coefficient**,  $h$ . The units of  $h$  are  $\text{kJ}/\text{m}^2\text{s}^{\circ}\text{C}$ , and it depends on the material, geometry, and roughness of the wall, as well as the velocity and properties of the heat transfer fluid. Determination of heat transfer coefficients occupies a sizable part of the science of Heat Transfer, and there exist formulas for effective heat transfer coefficients under a myriad of physical situations (see [McADAMS], [CHAPMAN]).

### IV. Radiative Flux:

$$-k \frac{\partial T}{\partial \vec{n}_{in}}(\vec{x}, t) = \hat{h}[T_{\infty}(\vec{x}, t)^4 - T(\vec{x}, t)^4] \quad \text{for } \vec{x} \in \partial\Omega, \quad t > 0. \quad (34)$$

A hot body radiates heat with a flux which, according to Stefan's Fourth Power Law, is proportional to the difference of the fourth powers of the temperatures of the surfaces exchanging heat. The actual situation is very complicated, but (34) is often a satisfactory approximation [BIRD et al, Chap. 14]. The radiative heat transfer coefficient  $\hat{h}$  depends on the emissivities of the participating media, the geometry of walls and gaps, etc. Frequently radiative flux exists in conjunction with convective and/or conductive fluxes in which case the total incoming flux is their sum. Note that

$$T_{\infty}^4 - T^4 = (T_{\infty}^2 + T^2)(T_{\infty} + T) \cdot [T_{\infty} - T],$$

so that by absorbing  $(T_{\infty}^2 + T^2)(T_{\infty} + T)$  into the heat transfer coefficient the radiative boundary condition can be written as a convective boundary condition but with  $h$  depending *nonlinearly* on the ambient and surface temperatures.

We conclude that a general expression for flux input is

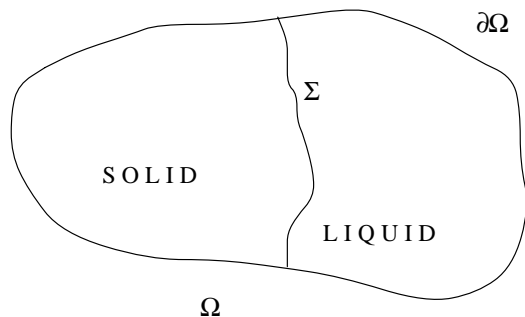
$$-k \frac{\partial T}{\partial \vec{n}_{in}} = h(T_{\infty}, T, t) \cdot [T_{\infty} - T], \quad \text{on } \partial\Omega, \quad t > 0, \quad (35)$$

where the heat transfer coefficient may depend nonlinearly on the imposed ambient temperature, the surface temperature, the time, as well as the emissivities, conductivities, geometry of the wall and air layers, and velocity and properties of the heat transfer fluid. Then (35) includes both (33) and (34). In addition, we can interpret  $h \rightarrow \infty$  in (33) as implying  $T = T_\infty$ , thus including the imposed temperature boundary condition (30). Finally  $h \equiv 0$  implies the insulated boundary case (32).

We close with the reminder that *different* boundary conditions may be imposed on *different* parts of the boundary. What is important is that **some** boundary condition must be imposed on **each** part of the boundary (PROBLEM 18).

### 1.2.E Interface Conditions

In a melting or solidification process, conforming to our assumptions in §1.2.B, the physical region  $\Omega$  occupied by the phase change material will be subdivided into two phases, liquid and solid, separated by a sharp interface  $\Sigma$  (of zero thickness, **Figure 1.2.7**).



**Figure 1.2.7.** Solid and liquid phases separated by a sharp interface.

According to our discussion in §1.2.C conservation of energy in each phase demands that a heat conduction equation (17) be satisfied there. In the liquid, the coefficients will be  $c_L$  and  $k_L$  and in the solid  $c_S$  and  $k_S$  (see §1.2.F); for simplicity in notation we shall not use different symbols for the temperatures of liquid and of solid. The interface constitutes part of the boundary of both the liquid and solid regions; hence we need a boundary condition from each side in order to complete the initial-boundary value problem in each phase. Since the temperature must always be continuous, and by Assumption 5 the interface is an isotherm at  $T_m$ , we have the interface conditions

$$\lim_{\substack{\vec{x} \rightarrow \text{interface} \\ \vec{x} \in \text{liquid}}} T(\vec{x}, t) = T_m \quad \text{and} \quad \lim_{\substack{\vec{x} \rightarrow \text{interface} \\ \vec{x} \in \text{solid}}} T(\vec{x}, t) = T_m, \quad (36)$$

that is, the temperature is prescribed there. If the interface location were known we would have enough conditions to determine the temperature inside the liquid and the solid regions. Since the location is unknown, we need one more condition to determine it. Such an additional condition results from energy conservation **across** the interface, and it can be derived in several ways. In order to avoid needless complications of notation we will postpone the derivation until §4.4 in **CHAPTER 4**. We will merely note that jump conditions for conservation laws can be derived in general as Rankine-Hugoniot “shock” conditions (Kotchine’s Theorem, see [TRUESDELL-TOUPIN], [SEGEL], [ARIS], [CHORIN-MARSDEN], [DELHAYE]). For a conservation law of the general form

$$A_t + \operatorname{div} \vec{B} = f, \quad (37)$$

the jump condition across a smooth surface (fixed in space-time),

$$\Sigma(\vec{x}, t) = 0, \quad (38)$$

can be shown to be

$$[[A]]_+^- N_t + [[\vec{B}]]_+^- \cdot \vec{N}_x = 0.$$

Here

$$\vec{N} = (\vec{N}_x, N_t) = (\nabla \Sigma, \Sigma_t) \frac{1}{\sqrt{\Sigma_t^2 + |\nabla \Sigma|^2}}$$

denotes the unit normal to the surface pointing towards the “+” side, and  $[[A]]_+^- = A^+ - A^-$  denotes the difference between the limiting value of a quantity  $A$  on  $\Sigma$  from the “+” side and its value on  $\Sigma$  from the “-” side. More conveniently, this may be expressed in terms of the

$$\text{normal velocity} \quad \mathbf{v} := \frac{d\vec{x}}{dt} \cdot \vec{n} = -\frac{\Sigma_t}{|\nabla \Sigma|} \quad (39)$$

of the moving surface (see next paragraph) as

$$[[A]]_+^- \mathbf{v} = [[\vec{B} \cdot \vec{n}]]_+^-, \quad (40)$$

where  $\vec{n} := \frac{\nabla \Sigma}{|\nabla \Sigma|}$  denotes the unit normal to the moving surface at each time.

Equation (39) may be seen as follows. Firstly (38) can be thought of either as representing a **fixed** surface in space-time, with unit normal  $\vec{N} = (\vec{N}_x, N_t)$ , or, a **moving** surface in space, with unit normal  $\vec{n} = \frac{\nabla \Sigma}{|\nabla \Sigma|}$  at each fixed time. From (38), we have  $\Sigma_t + \nabla \Sigma \cdot \frac{d\vec{x}}{dt} = 0$ , where  $\frac{d\vec{x}}{dt}$  is the velocity of a point on the surface. Hence  $\mathbf{v} := \frac{d\vec{x}}{dt} \cdot \vec{n}$  represents the normal component of the velocity of the moving interface and therefore

$$\mathbf{v} = \frac{d\vec{x}}{dt} \cdot \frac{\nabla \Sigma}{|\nabla \Sigma|} = - \frac{\Sigma_t}{|\nabla \Sigma|}.$$

Applying this to the energy conservation law, (15), we find

$$\llbracket \rho e \rrbracket_{\pm}^{\pm} \mathbf{v} = \llbracket \vec{q} \cdot \vec{n} \rrbracket_{\pm}^{\pm}. \quad (41)$$

Since both the energy,  $\rho e$ , and the flux,  $\vec{q}$ , across any surface  $\Sigma$  entirely inside the liquid (or the solid) are continuous within each one-phase region, the jumps  $\llbracket \rho e \rrbracket_{\pm}^{\pm}$  and  $\llbracket \vec{q} \rrbracket_{\pm}^{\pm}$  are both zero, and (41) degenerates to  $0 = 0$ . But, if  $\Sigma$  is the interface, then the jumps are *not* zero. Indeed, let us choose the liquid as “+” side and the solid as “-” side of the interface  $\Sigma$ . By (8), the enthalpy jump is  $\llbracket \rho e \rrbracket_{solid}^{liquid} = \rho L > 0$ , and therefore (41) becomes the so-called

$$\text{Stefan Condition:} \quad \rho L \mathbf{v} = \llbracket \vec{q} \cdot \vec{n} \rrbracket_{solid}^{liquid} \quad (42)$$

on the interface. This states that the latent heat released due to the interface displacement equals the net amount of heat delivered to (or from) the interface per unit area per unit time ( $\vec{q} \cdot \vec{n} =$  flux normal to the moving surface). Thus, the Stefan Condition is a statement of heat balance across the interface. For more general versions see §2.3.E and §2.4.F.

Now, we restrict our considerations to the 1-dimensional case and derive the Stefan Condition directly from *global* energy balance. Consider a slab of material,  $0 \leq x \leq l$ , of constant cross-sectional area  $A$ . Heat is input or output at the faces  $x = 0$  and  $x = l$  by some means, resulting in, say, liquid in  $0 \leq x < X(t)$  and solid in  $X(t) < x \leq l$ , separated by a sharp interface at  $x = X(t)$ , at each time  $t > 0$ . We assume constant density and phase-wise constant properties. The total enthalpy in the slab at time  $t > 0$ , referred to the melt temperature  $T_m$  (see PROBLEM 22) is

$$E(t) = A \left\{ \int_0^{X(t)} \{ \rho c_L [T(x, t) - T_m] + \rho L \} dx + \int_{X(t)}^l \rho c_S [T(x, t) - T_m] dx \right\}. \quad (43)$$

Global heat balance demands (see (16))

$$\frac{dE}{dt} = \text{net heat flow into the slab} = A \{ q(0, t) - q(l, t) \}, \quad (44)$$

where  $q(0, t)$  and  $-q(l, t)$  are the heat fluxes *into* the slab through the faces  $x = 0$  and  $x = l$ , respectively. Leibnitz's rule enables us to compute

$$\frac{1}{A} \frac{dE}{dt} = \rho c_L [T(X(t), t) - T_m] \cdot X'(t) + \int_0^{X(t)} \rho c_L T_t(x, t) dx$$

$$+ \rho L X'(t) - \rho c_S [T(X(t), t) - T_m] \cdot X'(t) + \int_{X(t)}^l \rho c_S T_t(x, t) dx. \quad (45)$$

Using  $T(X(t), t) = T_m$  and substituting the heat equation (21) for each phase we obtain

$$\frac{1}{A} \frac{dE}{dt} = k_L T_x(X(t)^-, t) - k_L T_x(0, t) + \rho L X'(t) + k_S T_x(l, t) - k_S T_x(X(t)^+, t),$$

where  $T_x(X(t)^{\mp}, t)$  denotes the values of  $T_x(x, t)$  as  $x \rightarrow X(t)^{\mp}$ , i.e. from the left or right. But,  $-k_L T_x(0, t)$  and  $+k_S T_x(l, t)$  are precisely the fluxes  $q(0, t)$  and  $-q(l, t)$ . Therefore, (44) yields the

$$\textbf{Stefan Condition:} \quad \rho L X'(t) = -k_L T_x(X(t)^-, t) + k_S T_x(X(t)^+, t), \quad (46)$$

expressing energy conservation across the interface  $x = X(t)$  in the 1-dimensional case. In fact, since the velocity of the interface is  $v = X'(t)$ , and

$$(q^{liquid} - q^{solid})|_{x=X(t)} = -k_L T_x(X(t)^-, t) + k_S T_x(X(t)^+, t),$$

we see that the 1-dimensional version of (42) is indeed (46).

The Stefan Condition says that the rate of change in latent heat  $\rho L X'(t)$ , equals the amount by which the heat flux jumps across the interface. In particular, the heat flux can be continuous across the interface if and only if either  $L = 0$  or the interface does *not* move. For an axially symmetric phase-change in a cylinder, or a spherically symmetric phase-change in a sphere, the Stefan condition across the interface  $r = R(t)$  has the same form, namely (PROBLEMS 24, 25)

$$\rho L R'(t) = -k_L T_r(R(t), t) + k_S T_r(R(t), t). \quad (47)$$

### 1.2.F The Stefan Problem

Now we have all the ingredients we need to state the mathematical problem modeling a phase-change process that satisfies the assumptions of §1.2.B. We will assume that no internal heating sources are present in the material.

As a very simple model process, we consider the following

**PHYSICAL PROBLEM.** A slab,  $0 \leq x \leq l$ , initially solid at temperature  $T_{init} < T_m$ , is melted by imposing a hot temperature  $T_L > T_m$  at the face  $x = 0$  and keeping the back face,  $x = l$ , insulated. We assume constant thermophysical parameters  $\rho$ ,  $c_L$ ,  $k_L$ ,  $c_S$ ,  $k_S$  (hence constant diffusivities  $\alpha_L = k_L/\rho c_L$  and  $\alpha_S = k_S/\rho c_S$ ), and a sharp interface  $x = X(t)$ .

A schematic picture of the process is shown in **Figure 1.2.8**. At each time  $t$ , liquid occupies  $[0, X(t))$  and solid  $(X(t), l]$ . The curve  $x = X(t)$  represents the interface location, schematically, demarcating the liquid and solid space-time regions. The



heat equation is to be satisfied in each phase-region and the initial and boundary conditions of the problem are shown.

The mathematical model for this process is the following

**Two-Phase Stefan Problem** (for a slab melting from the left):

Find the temperature  $T(x, t)$ ,  $0 \leq x \leq l$ ,  $t > 0$ , and interface location  $X(t)$ ,  $t > 0$ , such that the following are satisfied (**Figure 1.2.8**):

*Partial differential equations*

$$T_t = \alpha_L T_{xx} \quad \text{for } 0 < x < X(t), \quad t > 0 \quad (\text{liquid region}) \quad (48a)$$

$$T_t = \alpha_S T_{xx} \quad \text{for } X(t) < x < l, \quad t > 0 \quad (\text{solid region}) \quad (48b)$$

*Interface Conditions*

$$T(X(t), t) = T_m, \quad t > 0 \quad (49a)$$

$$\rho L X'(t) = -k_L T_x(X(t)^-, t) + k_S T_x(X(t)^+, t), \quad t > 0 \quad (49b)$$

*Initial Conditions*

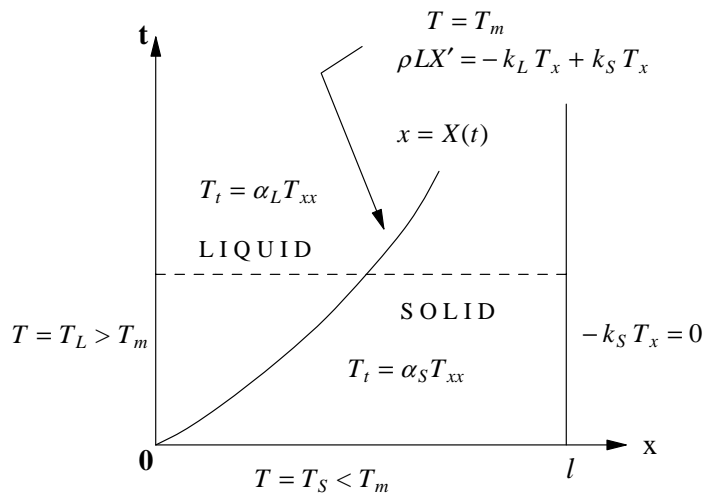
$$X(0) = 0 \quad (50a)$$

$$T(x, 0) = T_{\text{init}} < T_m, \quad 0 \leq x \leq l, \quad (\text{and initial state is solid}) \quad (50b)$$

*Boundary Conditions*

$$T(0, t) = T_L > T_m, \quad t > 0 \quad (\text{imposed temperature}) \quad (51a)$$

$$-k_S T_x(l, t) = 0, \quad t > 0 \quad (\text{insulated boundary}) \quad (51b)$$



**Figure 1.2.8.** Space-time diagram for the Two-Phase Stefan Problem.

**DEFINITION :** We say that the functions  $T(x, t)$ ,  $X(t)$  constitute a **classical solution of the above Stefan Problem** up to a time  $t^*$  if the functions have continuous derivatives to all orders appearing in the problem formulation and satisfy the conditions of the problem.

Here,  $t^*$  is the time up to which the solution is desired (global solution).

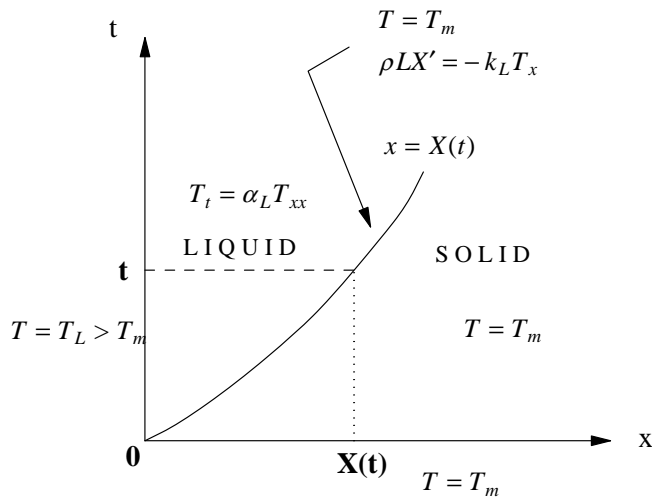
Clearly,  $T_{init}$  and  $T_L$  could be non-constant:  $T_{init}(x) \leq T_m$ ,  $T_L(t) \geq T_m$ . From the mathematical point of view, we could allow  $c_L$ ,  $c_S$ ,  $k_L$ ,  $k_S$  to be (known) functions of  $(x, t, T)$  by replacing the heat equations in (48) by heat conduction equations  $\rho c_i T_t = (k_i T_x)_x$ ,  $i = L, S$ . Naturally, the boundary conditions (51) can be replaced by any combination of the standard conditions described in §1.2.D.

All such generalizations of (48-51) are still referred to as Stefan Problems or **Stefan-type** problems. They serve as *prototypes* of the, so-called, **moving boundary problems** whose basic feature is that the regions in which the partial differential equations are to hold are unknown and must be found as part of the solution of the problem. This amounts to a **non-linearity of geometric nature**, apparent in (49a,b), even when the rest of the equations appear to be linear, and is the source of the mathematical difficulties that moving boundary problems present. Their non-linearity destroys the validity of the Superposition Principle, and “separation of variables” is no longer applicable ! The underlying geometric nonlinearity can be made to appear algebraically in the partial differential equations by a change of variables: replacing  $x$  by  $\xi = x / X(t)$  transforms the varying region  $0 < x < X(t)$  to the fixed region  $0 < \xi < 1$ , and the linear equation  $T_t = \alpha_L T_{xx}$  to the nonlinear equation  $X^2 T_t - \xi X X' T_\xi = \alpha_L T_{\xi\xi}$  (see §3.3).

The well-posedness (existence of a unique classical solution depending continuously on the data) of reasonably general 1-dimensional Stefan Problems without undue restrictions on the data was established only during the mid 1970's! (CANNON-HENRY-KOTLOW, see §4.4). We note that **local** solvability (meaning: there exists a time  $t^*$  up to which a unique classical solution exists) was already proved by Rubinstein in 1947 (see [RUBINSTEIN] for a historical survey of the mathematical development up to the mid 1960's). Of course, particular, well-behaved problems (those with a monotonic interface, like (52-55) below) were treated earlier by various methods.

Stefan-type problems can also be formulated classically in two or three dimensions (see §4.4), but such formulations may admit no (classical) solution, as the breakup of a piece of ice into two or more pieces indicates physically. Fortunately “weak” or “generalized” (“enthalpy”) formulations which are well-posed (and computable) came to the rescue in the early 1960's, as we shall see in CHAPTER 4. Let us also note that even 1-dimensional problems with either internal sources or variable  $T_m$  may develop mushy regions rendering the above sharp-front classical formulation inappropriate.

Certainly however, the great majority of phase-change processes lead to 1-dimensional Stefan Problems as just described. In fact one frequently deals with the so-called **One-Phase Stefan Problem**, in which only one “active” phase is present. If, in the physical problem, we assume that initially the slab is solid



**Figure 1.2.9.** Space-time diagram for the One-Phase Stefan Problem.

at the melt temperature:  $T_{init}(x) \equiv T_m$ , then we obtain the

**One-Phase Stefan Problem** (for a slab melting from the left):

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

$$T_t = \alpha_L T_{xx}, \quad 0 < x < X(t), \quad t > 0, \quad (\text{liquid region}) \quad (52)$$

$$T(X(t), t) = T_m, \quad t > 0, \quad (53a)$$

$$\rho L X'(t) = -k_L T_x(X(t), t), \quad t > 0, \quad (53b)$$

$$X(0) = 0, \quad (54)$$

$$T(0, t) = T_L(t) > T_m, \quad t > 0. \quad (55)$$

The temperature needs to be found only in the liquid  $0 < x < X(t)$ ,  $t > 0$ , because it is identically  $T_m$  in the solid, and there is no initial condition for  $T(x, t)$  because initially there is no liquid. Since the back face  $x = l$  now plays *no role*, the solid can be considered effectively semi-infinite, occupying  $(X(t), \infty)$ . The diagram for this problem is shown in **Figure 1.2.9**. Clearly few realistic phase-change processes will actually lead to the one-phase situation, with **ablation** (instantaneous removal of melt) and induced stirring of liquid while freezing, being notable exceptions. On the other hand, molecular diffusion, filtration, and other processes commonly lead to one-phase problems [RUBINSTEIN], [ELLIOTT-OCKENDON]. The inherent simplicity of one-phase problems makes them amenable to a variety of simple approximation methods, as we shall see in **CHAPTER 3**, and an entire book [HILL] is devoted to them.

## PROBLEMS

**PROBLEM 1.** Using relation (1) for the specific heat  $c(T)$  of water/ice, find the relation between the enthalpy  $e$  and the temperature  $T$ . Also express  $T$  as a function of  $e$  and plot.

**PROBLEM 2.** Recall ( §1.1) that a liquid is hypercooled if the sensible heat extracted from it is more than the latent heat. Show that its temperature should be no more than  $T_m - \frac{L}{c_L}$ .

**PROBLEM 3.** Describe an experiment for the determination of the thermal conductivity of a solid; of a liquid. On what factors do you expect it to depend? [CHAPMAN], [ECKERT-DRAKE].

**PROBLEM 4.** The thermal conductivity of aluminum is  $k = .213 \text{ kJ/m s}^\circ\text{C}$ . Assuming that the temperature distribution through a plate of Aluminum is a straight line, how thick should the plate be in order that a  $100^\circ\text{C}$  temperature drop across the plate will induce a heat flux of  $q = 1000 \text{ kJ/m}^2 \text{ s}$  ?

**PROBLEM 5.** A heat source has been placed at the center of an aluminum ball of radius 10 cm emitting heat at a rate of  $1000 \text{ kJ/s}$ . What should the flux of heat at the surface of the ball be under the condition that the ball contains no heat sources or sinks?

**PROBLEM 6.** What is the heat flux along an isotherm for an isotropic medium? What if the medium is not isotropic?

**PROBLEM 7.** Derive (15) as the limiting case of energy conservation on a box  $x_0 \leq x \leq x_0 + \Delta x$ ,  $y_0 \leq y \leq y_0 + \Delta y$ ,  $z_0 \leq z \leq z_0 + \Delta z$  over a time interval  $t_0 \leq t \leq t_0 + \Delta t$  as  $\Delta x, \Delta y, \Delta z, \Delta t \rightarrow 0$  [WHITAKER] , [BIRD et al].

**PROBLEM 8.** The thermal diffusivity of most materials is a non-constant function of the temperature. Describe in qualitative terms under what conditions you could “safely” pass from the nonlinear equation of (21) to the linear equation (22) without making too great an error.

**PROBLEM 9.** Show that the initial value problem  $y' = \sqrt{y}$ ,  $y(0) = 0$  is *not* well-posed.

**PROBLEM 10.** Using separation of variables, derive the solution (24c) for the problem of EXAMPLE 1, §1.2.C. Verify (at least formally) that it is indeed a solution.

**PROBLEM 11.** Derive the solution to Problem (25) of EXAMPLE 2, §1.2.C.

**PROBLEM 12.** Derive the solution to Problem (26) of EXAMPLE 3, §1.2.C.

**PROBLEM 13.** Show that the error function, (29), EXAMPLE 4, §1.2.C, satisfies  $\operatorname{erf}(0) = 0$ ,  $\operatorname{erf}(\infty) = 1$ . [ABRAMOWITZ-STEGLUN].

**PROBLEM 14.** (a) Seek the solution to Problem (27), EXAMPLE 4, §1.2.C, in the form  $T(x, t) = F(\xi)$  with  $\xi = x/2\sqrt{\alpha t}$  (similarity solution). Show that the unknown  $F(\xi)$  must satisfy  $F'' + 2\xi F' = 0$ ,  $F(0) = T_L$ ,  $F(\infty) = T_0$ . Solve this ODE to obtain (28). (b) Verify that (28) solves problem (27).

**PROBLEM 15.** Using the value  $T_0$  as the reference temperature for zero energy, find the total energy of the semi-infinite slab of EXAMPLE 4, §1.2.C, as a function of time (see PROBLEM 17, §2.2). [Answer:  $E(t) = 2(T_L - T_0)(\rho c k t / \pi)^{1/2}$ ].

**PROBLEM 16.** Verify that the function

$$T(x, t) = A + B \left( 1 - e^{-\frac{U}{\alpha}(x - Ut)} \right) \quad (56)$$

solves the heat equation (22), for any constants  $A$ ,  $B$ ,  $U$ . It represents a (thermal) front traveling with constant speed  $U$  (to the right if  $U > 0$ , to the left if  $U < 0$ ).

**PROBLEM 17.** Leave a cup of hot coffee to cool in a room while using a thermometer to monitor its temperature  $T(t)$  with passing time  $t$ . Taking Newton's Law of cooling in the form  $T'(t) = h(T_{room} - T(t))$ , find  $h$  for your cup of coffee, where  $T_{room}$  is the room temperature.

**PROBLEM 18.** A solid slab  $0 \leq x \leq l$  is initially at a uniform temperature  $T_{init} < T_m$ . Heat is withdrawn from the front face,  $x = 0$ , and an experimenter can measure both the temperature,  $T(0, t)$  (by a thermocouple) and the flux  $q(0, t)$  (by a flux meter) at this face. The experimenter wants to determine the temperature distribution  $T(x, t)$  in the slab. Unfortunately, the back face  $x = l$ , is inaccessible, so the only known data are  $T(x, 0) = T_{init}$ ,  $0 \leq x \leq l$ ,  $T(0, t) = T_{face}(t)$ , and  $-k T_x(0, t) = q_{face}(t)$ ,  $t > 0$ . Explain why he **cannot** determine  $T(x, t)$  throughout the slab without any information about  $x = l$ .

**PROBLEM 19.** One of the more important and elusive types of information that we should be able to extract from models of physical processes is the sensitivity of these processes with respect to the system specifications. For example, one might wish to obtain information about the dependence of the temperature distribution history on the conductivity of a material. For the case of constant thermophysical properties and heat transfer in a finite slab use the heat equation to find relations that will yield the dependencies of the temperature and total heat content of the slab with respect to each of the parameters  $\alpha$ ,  $k$ ,  $c$ ,  $\rho$  and the slab length.

**PROBLEM 20.** Verify the units in equations (43), and (45).

**PROBLEM 21.** Derive the Stefan Condition for a slab,  $0 \leq x \leq l$ , freezing from the left. [Hint: Proceed as in (43-46)].

**PROBLEM 22.** Let  $T_{ref} < T_m$  be a reference temperature. Show that the total energy in the slab  $0 \leq x < l$  at any time  $t > 0$ , referred to the temperature  $T_{ref}$  is

$$E(t) = A \left\{ \int_0^{X(t)} [\rho c_S(T_m - T_{ref}) + \rho c_L(T - T_m) + \rho L] dx + \int_{X(t)}^l \rho c_S(T - T_{ref}) dx \right\}.$$

Compare with (43).

**PROBLEM 23.** Show that the Stefan Condition remains unchanged no matter what we choose as reference temperature. [see the previous problem, proceed as in (43-46)].

**PROBLEM 24.** Derive the Stefan Condition, (47), across the interface  $r = R(t)$  for an axially symmetric phase-change process in a cylinder. For definiteness, consider  $0 < r < R(t)$  as liquid and  $R(t) < r < R_0$  as solid. Note that the total enthalpy (per unit height) may be written as

$$\int_0^{R(t)} \{ \rho c_L [T(r, t) - T_m] + \rho L \} 2\pi r dr + \int_{R(t)}^{R_0} \rho c_S [T(r, t) - T_m] 2\pi r dr.$$

**PROBLEM 25.** Derive the Stefan Condition across the interface  $r = R(t)$  for a spherically symmetric phase-change process in a sphere. For definiteness, consider  $0 < r < R(t)$  as liquid and  $R(t) < r < R_0$  as solid. Then we have

$$E(t) = \int_0^{R(t)} \{ \rho c_L [T(r, t) - T_m] + \rho L \} 4\pi r^2 dr + \int_{R(t)}^{R_0} \rho c_S [T(r, t) - T_m] 4\pi r^2 dr.$$

**PROBLEM 26.** Consider the 1-phase Stefan Problem for the slab (when the material is initially solid at its melt temperature  $T = T_m$ ). Using the fact that the phase change front is an isotherm, show that along the front we have

$$T_{xx} = \frac{c_L}{L} T_x^2 \quad (57)$$

exhibiting vividly the nonlinearity of the problem. Observe that (57) is a special case of (40) for one space dimension and one phase, if we regard the interface as an isotherm for the temperature, permitting the function  $\Sigma$  of (40) to be defined as  $\Sigma = T - T_m$ .

**PROBLEM 27.** A slab  $0 < x < l$  is filled with material having melting temperature  $T_m$ . The material has constant thermophysical parameters, different for liquid and solid phases. At  $x = 0$  a temperature  $T_0 < T_m$  is imposed for all time, while at  $x = l$  a temperature  $T_l > T_m$  is imposed for all time. Find the *steady state* temperature distribution and the location of the front separating solid and liquid phases.

**PROBLEM 28.** (A 1-phase Stefan Problem with straight-line interface)

Fix  $U = \text{constant}$  and assume a straight-line interface  $X(t) = Ut$ , separating liquid in  $0 \leq x < X(t)$  from solid at the melt temperature  $T_m$  (for  $x > X(t)$ ).

- (a) Determine the constants  $A, B$  so that the traveling-front solution (56) also satisfies the interface conditions (53). Then, the resulting  $T(x, t)$  will satisfy (52-53), with  $X(t) = Ut$ .
- (b) Show that the boundary temperature,  $T_L(t)$ , necessary for the  $T(x, t)$  (found in (a)) to satisfy the 1-phase problem (52-55) is an exponentially increasing function of time, given by

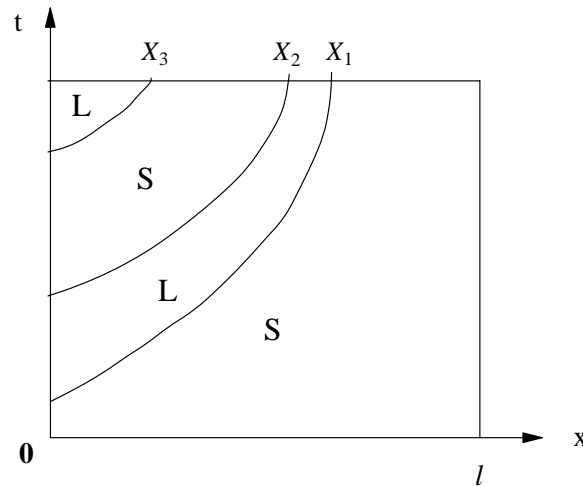
$$T_L(t) = T_m - \frac{L}{c_L} [1 - e^{U^2 t / \alpha}], \quad t > 0 .$$

### 1.3. GENERAL MELTING AND SOLIDIFICATION PROCESSES

The mathematical model of a melting process formulated in §1.2 is disarmingly simple, since it concerns a process for which, at any time there are two distinct regions, one solid, the other liquid, separated by a single phase front  $X(t)$  (Figures 1.2,6,7). Moreover the phase boundary is always moving in the same direction, while the temperature at any point is always rising. Such simplicity is not typical of the kinds of problems that arise in melt/freeze scenarios. Thus for example, molten metal placed in a cast will partly contract away from the cast wall because of the increase in density upon solidification; this reduces the cooling effect of the cast and can induce remelting of the solid skin of the metal adjacent to the cast. More dramatically, in latent heat thermal energy storage applications where we might wish to store solar energy as the latent heat of melting of a PCM during daylight hours for use at night, the PCM will go through repeated melt/freeze cycles possibly producing a multitude of phase change fronts separating zones of liquid and solid. Similarly, placing two cold ice cubes sufficiently close to each other in water can induce the formation of an “ice bridge” linking them, due to local freezing of the water; if the water is sufficiently warm this bridge, together with the cubes themselves, will melt.

Let us examine the possibility of multiple melt/freeze fronts for a process in which a material is subjected alternatively to temperatures above and below its melt temperature.

**EXAMPLE 1.** A slab of length  $l$  is intermittently heated and cooled to the extent that freezing and melting take place. The periods of heat input are referred to as *charging times* while those of heat withdrawal are *discharging*



**Figure 1.3.1.** Repeated melting and freezing of a slab.

*times*. Assume that heat input and withdrawal are always carried out at the left-hand face of the slab, while the right-hand face is insulated (**Figure 1.3.1**). Let the slab be entirely solid at the beginning of our scenario.

Suppose that heat is input to the slab over a period of time  $t_1^C$  with the superscript  $C$  corresponding to the “charging” mode. If the initial temperature was not too low, and the heat flux into the slab is not too small, a melt front will appear at  $x=0$  moving monotonically into the slab. For an imposed temperature the front will appear at  $t=0$  while for flux, convection or radiation input, the front will only appear when the material temperature at the face  $x=0$  has reached  $T_m$ . In any event, a front  $X_1$  with liquid on its left and solid at its right may well appear before the end of the first charge interval,  $t=t_1^C$ .

Now suppose that the material begins to discharge heat at time  $t=t_1^C$  in a process whose duration is  $t_1^D$  (the superscript  $D$  representing “discharge”). Depending on the mechanism of heat withdrawal, a new front  $X_2$  will appear at some time  $t > t_1^C$  separating solid material (on its left) from liquid material (on its right). Meanwhile the earlier appearing melt front  $X_1$  will continue to move into the solid; the velocity of this front will be far less than it was during the charging process, since its driving force (the surface heat flux into the slab) has now been replaced by the low temperature gradient in the liquid. Eventually, it will stop advancing (if the right-hand face were cooled instead of being insulated, it could even move leftward!) Hence during the time of discharge several possible events may occur, two of which are: a) the freezing front  $X_2$  moving to the right meets the melt front  $X_1$ ; when this occurs the liquid region formed during the charge interval will disappear, as will both fronts; b) the freezing front  $X_2$  will move to the right, but *not* overtake  $X_1$  before the discharge period ends. Now when the new



charge period begins we may find ourselves in the situation shown in **Figure 1.3.1**, wherein three fronts separating four zones exist: the first melt front  $X_1$ , the second freeze front  $X_2$ , and a third melt front  $X_3$ . As the number of cycles increases a myriad of possible phase configurations may occur because of variations in heat input and extraction rates and durations.

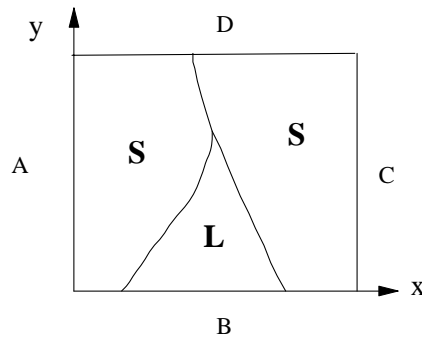
EXAMPLE 1 was concerned with a one-dimensional problem. For two or three dimensions the complexity of the geometry of the phase regions and their boundaries goes beyond the stage where simple physical intuition can be of much use. A hint of what may occur in two space dimensions is given in EXAMPLE 2, concerned with a charge-discharge cycle with a reversal of flow of the heat transfer fluid.

**EXAMPLE 2. Two Dimensional Phase Change:** Consider a two-dimensional material slab as seen in **Figure 1.3.2**. Heat exchange with a transfer fluid channel will take place at face  $A$  while faces  $B, C, D$  are assumed insulated. We also assume that the material is initially solid. During a charge period a hot transfer fluid is to flow upward- in the direction of increasing  $y$ ; as the transfer fluid flows upward it will cool down; thus a melt front will be formed, as seen in the Figure, moving further into the slab for smaller  $y$  than for larger  $y$ . If the discharge process is carried out with a downward flow of a cold transfer fluid, then at the end of the discharge cycle, we may well find a “V” shaped front extending only partly in the  $y$  direction. Clearly further cycles, if they correspond to intermittent heat sources and sinks, may well result in isolated regions of one phase, within material of the second phase.

Note that the qualitative description of EXAMPLE 2 is not surprising. If one were to immerse an ice-sculpture of, say, a unicorn, in a hot- water bath, we might well find after some moments that the single ice statue has melted in such a way that several distinct pieces of ice result.

Our examples imply that in processes involving alternate melt-freeze cycles we must seek modeling techniques in which we do not have to know apriori the qualitative behavior of the process. In general, we will encounter multiple fronts, disappearing phases, and extremely complex geometries. Whether the actual physical process would yield such multiple solid/liquid regions depends on the physical makeup of the material and the conditions of the process. Thus for example in a microgravity space environment one could expect a much reduced tendency for solid particles to float or settle in the liquid.

Of course the complexity of the phase change process is only increased when other, sometimes extremely realistic physical phenomena are taken into account. Thus for example liquid paraffin wax easily dissolves air; on solidification the air is entrapped in the solid. On melting, the solid particles are alternately buoyant-when they contain bubbles of air, and sink in the liquid when the bubbles are released from the melting solid. In engineering applications one may have to accommodate such behavior, if possible, through suitable assumptions in a model not explicitly incorporating the phenomenon, or in the development of a more complete model.



**Figure 1.3.2.** A two-dimensional charge/discharge process.

### PROBLEMS

- PROBLEM 1.** Discuss the phase change history of a sample of radioactive material placed in an insulated container. Assume that the sample is cubically shaped and that it is initially at a temperature  $T_S$  below its melt temperature  $T_m$ . Will any phase change front appear in the material?
- PROBLEM 2.** In addition to the radioactive decay of PROBLEM 1 internal heating may arise from radiative transfer through semi-transparent materials. Describe a charge-discharge process similar to that in Example 1, but with radiation taken into account.
- PROBLEM 3.** Two samples of a material, one of them liquid at a high temperature, the second solid at a low temperature, are placed in contact. Discuss what factors will determine whether the liquid freezes or the solid melts.
- PROBLEM 4.** For several days the temperature in the town was on the average  $0^\circ F$ . Then suddenly the weather changed, the temperature rose to the low 40's and an ice layer formed on all the streets, paralyzing movement of cars and people for a while. What happened?