SIMAI
e-Lecture Notes
ISSN 1970-4429

Parabolic Free Boundary Problems in Industrial and Biological Applications

Antonio Fasano

Dipartimento di Matematica ”U. Dini‘
Università degli Studi di Firenze, Italy
fasano@math.unifi.it

Vol. 9 - 2011

ISBN-A: 10.978.88905708/89

Published by:
SIMAI - Società Italiana di Matematica Applicata e Industriale
Via dei Taurini, 19 c/o IAC/CNR
00185, ROMA (ITALY)

SIMAI e-Lecture Notes
ISSN: 1970-4429

Parabolic Free Boundary Problems
in Industrial and Biological Applications
Volume 9, 2011
ISBN-13: 978-88-905708-8-9
ISBN-A: 10.978.88905708/89

Abstract.

Diffusive phenomena including free boundaries occur in an impressive number of processes relevant to industry, biology, medicine, environment, etc. Here a small selection of problems in this class is presented. In general the emphasis will be on the derivation of a mathematical model, also discussing its range of applicability. The mathematical structure of the problems will usually be treated in a concise way. The Stefan problem (phase change) has been given a larger space, since it is the most representative example in this class. Some basic material concerning the necessary mathematical background is included, to make these notes accessible to non-mathematicians.

Preface

These notes have been inspired by a series of lectures I have taught during the last years at the Scuola Normale Superiore in Pisa. The lectures were addressed to the students of the Ph.D. Programme "Mathematics for Industrial Technologies". Their general purpose was to provide several examples of how a mathematical model for a given process can be formulated, starting from the raw material, i.e. some basic physical information. Thus particular attention was devoted to the modelling stage, still keeping the necessary level of mathematical rigour. Topics like *rescaling* (the selection of suitable dimensionless variables), usually not a main concern for mathematicians, find here some emphasis to point out that solving real world problems requires quite often more than the knowledge of fundamental theorems. Not only one has to understand the physical (or biological, etc.) nature of the problem, but even after one has come up with a sensible set of equations, then practical questions arise that are not discussed in mathematical books; for instance: how to discriminate between effects which are really dominant and those which are simply negligible. This is normally crucial, because modelling is in many cases the result of a compromise and it is very important to know the relative weight of the various ingredients entering the final equations. Also it may happen that a process can have concurrent phenomena taking place at time and space scales very different from each other and that it goes through several stages in which the relative importance of the various simultaneous mechanisms changes, sometimes producing a radical modification of the mathematical structure of the model. All these circumstances contribute to make the *technomathematician* (so to speak) a very peculiar character that needs also a very peculiar training. This motivates the many digressions the reader will find.

In this notes I have selected some topics having diffusion as a common denominator. Even more specifically, for obvious reasons of space I further restricted my attention to problems exhibiting free (i.e. unknown) boundaries, which occur with great frequency in a variety of applications. Diffusion is ubiquitous in nature and plays a fundamental role in innumerable processes quite relevant to many applied sciences and to industrial technologies. Diffusion is also responsible for evolution of biological organisms, since it intervenes in transmitting the chemical signals regulating e.g. growth mechanism and the formation of coloured patterns in animals coat.

As a mechanism of mass transfer (but the same applies for instance to the propagation of heat) diffusion is a macroscopic phenomenon having its roots in the seemingly chaotic motion of molecules. The latter, however, does not take place in the absence of rules, but is governed by probabilistic laws. Defining in an appropriate way the average of microscopic quantities, it is often possible to derive the laws obeyed by such averages, which can receive a more familiar interpretation on the macroscopic scale. This is precisely the way Statistical Mechanics leads from the immensely complex mechanics of a huge number of particles to the laws of thermodynamics.

With techniques of the same kind it is possible to show that Fick's law [a] (the basic law of mass transfer in dilute solutions, stating that mass flux is proportional to the gradient of mass concentration), is the eventual macroscopic interpretation of the Brownian motion of inhomogeneously distributed molecules of the same species.

The parallel law governing heat transport (heat flux proportional to temperature gradient) is known as Fourier's law [b]. We will not enter the discussion about the validity of these linear laws, which however work quite well in not too extreme situations. Fick's and Fourier's laws belong to a class of experimental laws in which the gradient of some quantity plays the role of a driving force. Another member of this class is Darcy's law [c] (describing how liquids move through porous materials like sand), which we will also consider.

In these notes we will not deal with processes deviating from the Fickian behaviour. In the Appendix we will shortly illustrate how Fick's law is related to a stochastic process like *random walk*.

The prototype of free boundary problems for the heat equation is the celebrated Stefan problem (heat conduction with phase change), on which we will spend some more time, although for reasons of space our approach will be far from being encyclopedic. On the other hand there are several books, partially or totally devoted to this subject and many survey papers (see[24,37,38,41,46,49,84,100,104,119,131,133,134]).

We start with an overview of the Stefan problem. There are many reasons for that:

1) Phase change takes place in an impressive number of industrial processes (metal casting, mould injection, crystal growth, etc.).

2) The standard Stefan problem has a simple mathematical formulation and has been studied extensively.

3) Many other processes of different physical nature can be reduced to a problem of Stefan type.

On the other hand we will have the opportunity to see that the occurrence of free boundaries in mass or heat transport processes is quite frequent and gives rise to an amazing variety of mathematical problems. Indeed we will illustrate a number of problems of industrial relevance (either quite classical or very recent) having the structure of a boundary value problem for a parabolic partial differential equation (i.e. in the same class as the equation governing diffusion) to be solved in a domain whose boundary is partly unknown. Having already illustrated the fundamental mathematical aspects for the Stefan problem, the emphasis in the remaining parts

---

[a] Adolf Eugen Fick (1829-1901), German physiologist. He formulated his law of diffusion in 1855. Inventor of the contact lens (1887). Also known for the Fick Principle which allows to calculate the heart output from the oxygen uptake and the carbon dioxide output during breathing.

[b] Joseph Fourier (1768-1830), the famous mathematician. His treatise on the Analytical Theory of Heat appeared in 1822.

[c] Henry Darcy (1803-1858), French hydrologist. He formulated his law in 1855.

of the notes will be on modelling.

Keeping in mind the purpose of these notes we will confine to problems whose nature is relatively easy to explain, once the basic facts about the classical Stefan problem are known. However, at the same time we will at least take the opportunity to quote more complicated problems in the same area, with the aim of arising the curiosity of the reader.

We hope that these notes can provide some teaching material for higher courses in applied mathematics and can anyway be helpful to students (even not mathematicians!) having an interest for genuine applications of mathematics. For the latter reason we have treated with perhaps excessive attention some introductory details.

Having focused so much on a very particular class of free boundary problems we feel the obligation to point out that free boundaries appear in a really great variety of phenomena described by differential equations and systems, most of the time of remarkable difficulty. For reasons of space here we adopt a very restricted view, even within the class of free boundary problems for parabolic equations. Thus the reader must be aware that *this is not a book*, in the sense that completeness and full generality are out of our scopes, and references are also given sparingly.

An impressively large collection of references on free boundary problems (which includes many thousands of titles) has been assembled by Professor Domingo A. Tarzia and is available at the address http:\\www.austral.edu.ar\fce\archives \mat\Tarzia-MAT-SerieA-2(2000).pdf.
Prof. Tarzia was the one who first pushed me to write these notes, which first appeared in the Argentinean journal MAT, Serie A, 11 (2005). It is a great honor for me that SIMAI wanted them to be published in its own series of e-lecture notes. Through SIMAI's initiative this material has acquired a new life, in the sense that it has become possible to update it periodically.

(last update: 01.01.2011)

Keywords: Mathematical modelling of industrial processes, Biomathematics, Porous media, Free Boundary problems.

Contents

Chapter 1

Balance equations

1.1. General balance laws

Let G be any physical quantity for which we may define a *density* $u(\vec{x},t)$ and a *current density* (or *flux vector*) $\vec{j}(\vec{x},t)$. If $d\sigma$ is a surface element with normal unit vector $\vec{n}$, the amount of G crossing $d\sigma$ per unit time is $\vec{j}\cdot\vec{n}\, d\sigma$.

While the procedure to define u is standard, the definition of $\vec{j}$ has an experimental basis and is one of the main elements in formulating the mathematical model for the evolution of G.

The simplest case is the one in which G is just transported in a velocity field $\vec{v}$: then we have the *advection* current $\vec{j}_c = u\vec{v}$. This happens for instance in the case in which g is the mass density ρ of a moving medium.

It is well known that mass conservation is expressed by the continuity equation

$$\frac{\partial\rho}{\partial t} + div(\rho\vec{v}) = 0, \tag{1.1.1}$$

which is a particular case of a more general conservation law, deducible on the basis of the same arguments leading to (1.1.1) . Such a law, referred to the quantities u, $\vec{j}$ reads

$$\frac{\partial u}{\partial t} + div\vec{j} = 0. \tag{1.1.2}$$

If instead of being conserved G is produced (or eliminated) at a rate f in the unit volume, a source term appears in the balance law [a]:

$$\frac{\partial u}{\partial t} + div\vec{j} = f. \tag{1.1.3}$$

---

[a] The derivation of (1.1.3) is quite simple and well known. If one is not familiar with it, it is a useful exercise to count molecules of a chemical species which migrate with a velocity field $\vec{v}(\vec{x},t)$ and are produced at the rate of $f(\vec{x},t)$ moles $cm^{-3}\,\sec^{-1}$. At time t consider a domain of volume V containing N moles and follow the motion of the domain to a new configuration occupying a volume $V+\Delta V$ after a time Δt. The Lagrangian derivative $\frac{dn}{dt}$ of the concentration $n=\frac{N}{V}$ (we refer to the average concentration, but it may represent the actual concentration if V is taken "infinitesimal"), is the limit as $\Delta t\to 0$ of the ratio $\frac{1}{\Delta t}\left[\frac{N+\Delta N}{V+\Delta V}-\frac{N}{V}\right]$, where $\Delta N = V\overline{f}\Delta t$ at the first order ($\overline{f}$ is the average of f over V).

This can be rewritten as $\frac{\Delta N}{\Delta t}\frac{1}{V+\Delta V}-\frac{N}{V+\Delta V}\frac{\Delta V/\Delta t}{V}$.

The ratio $\frac{\Delta V/\Delta t}{V}$ is the specific dilation rate and thus tends to $div\ \vec{v}$, while $\frac{\Delta N}{\Delta t}\frac{1}{V+\Delta V}$ tends to $\overline{f}$. Therefore the limit $\Delta t\to 0$, $V\to 0$ gives $\frac{dn}{dt}+n\ div\ \vec{v}=f$, or $\frac{\partial n}{\partial t}+\ div\ (n\vec{v})=f$.

Quite frequently the evolution of G is associated to the motion of a continuum medium of density ρ and velocity $\vec{v}$. Then we must keep in mind the following facts.

(i) The density (or concentration) of G is defined through a specific capacity w (the amount of G per unit mass of the supporting medium) via the equality

$$u = \rho w, \tag{1.1.4}$$

(ii) The current density is the sum of the advection term

$$\vec{j}_c = \rho w \vec{v} \tag{1.1.5}$$

and of another term, due to a specific transport mechanism of G (for instance diffusion), that we denote by $\vec{j}'$:

$$\vec{j} = \vec{j}_c + \vec{j}'. \tag{1.1.6}$$

If we use (1.1.4), (1.1.5), (1.1.6) and mass conservation (1.1.1), we re-interpret (1.1.3) as follows:

$$\rho \left[\frac{\partial w}{\partial t} + \vec{v} \cdot \nabla w \right] + div \vec{j}' = f, \tag{1.1.7}$$

to which (1.1.1) has still to be associated, together with the evolution equation for $\vec{v}$ (momentum balance), if the velocity field is not prescribed.

In all equations above we have tacitly supposed that we were dealing with differentiable functions. Let us examine what happens in the presence of discontinuities.

1.2. Propagation of discontinuities

We still refer to the generic conservation law (1.1.2). Suppose that a moving regular surface $\zeta(t)$ is a set of discontinuity for u and $\vec{j}$, which are C^1 on both sides of ζ. We define the positive and the negative side of ζ by choosing the orientation of the unit normal vector $\vec{n}$ and we denote by $u^{\pm}$, $\vec{j}^{\pm}$ the limits for $(\vec{x}, t)$ tending to $\zeta^{\pm}$.

The jumps $[u]$, $\left[\vec{j}\right]$ are defined by

$$[u] = u^+ - u^-, \ \left[\vec{j}\right] = \vec{j}^+ - \vec{j}^-. \tag{1.2.1}$$

Let $\vec{V}(\vec{x}, t)$ be the propagation velocity of $\zeta(t)$. An element $d\sigma$ on ζ sweeps the volume $\vec{V} \cdot \vec{n}$ $d\sigma\ dt$ in the time interval $(t, t + dt)$. If for instance on $d\sigma$ we have $u^+ > u^-$, $\vec{V} \cdot \vec{n} > 0$, then the expression

$$\vec{V} \cdot \vec{n}\ \ [u]\, d\sigma$$

represents the loss rate of our quantity, due to the displacement of $\zeta(t)$ (if one of the inequalities is reversed we have a gain rate).

If we still impose that the quantity G has to be conserved, we must say that the loss (or gain) rate equals the difference between the local outgoing current $\vec{j}^+ \cdot \vec{n}\ d\sigma$ and the incoming current $\vec{j}^- \cdot \vec{n}\ d\sigma$: the current density field takes away from ζ^+ more (less) material than it brings to ζ^-.

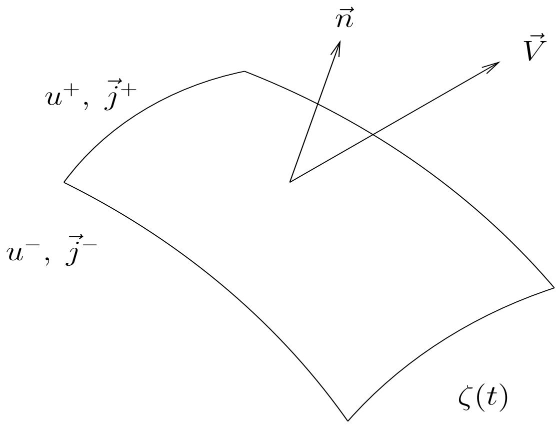


Figure 1.2.1. *Propagation of discontinuities.*

Thus the conservation law on the moving discontinuity surface $\zeta(t)$ is expressed by the well known *Rankine-Hugoniot condition:*

$$[u]\ \vec{V}\cdot\vec{n} = \left[\vec{j}\right]\cdot\vec{n}. \tag{1.2.2}$$

Note that the presence of possible (bounded) sources has no influence.

If ζ is a discontinuity surface for the mass density in a medium with velocity field $\vec{v}$, the conservation condition (1.2.2) accompanying (1.1.1) is

$$[\rho]\ \vec{V}\cdot\vec{n} = [\rho\vec{v}]\cdot\vec{n}. \tag{1.2.3}$$

Using the identity $[ab] = [a]\,b^+ + a^-\,[b] = [a]\,b^- + a^+\,[b]$, we see that (1.2.3) shows how the jump $[\vec{v}]\cdot\vec{n}$ is related to $[\rho]$ and to the relative velocity of the medium with respect to the discontinuity surface ζ:

$$[\rho]\left(\vec{V}-\vec{v}^+\right)\cdot\vec{n} = \rho^-\,[\vec{v}]\cdot\vec{n}, \tag{1.2.4}$$

$$[\rho]\left(\vec{V}-\vec{v}^-\right)\cdot\vec{n} = \rho^+\,[\vec{v}]\cdot\vec{n}.$$

Note that (1.2.4) are frame invariant.

If $\zeta(t)$ is represented by the equation

$$S(\vec{x},t) = 0, \tag{1.2.5}$$

we have

$$\vec{V}\cdot\nabla S + \frac{\partial S}{\partial t} = 0 \tag{1.2.6}$$

and multiplying (1.2.2) by $|\nabla S|$, we may write it in the equivalent form:

$$-\,[u]\,\frac{\partial S}{\partial t} = \left[\vec{j}\right]\cdot\nabla S.$$

In the situation described by (i), (ii) of the previous section, i.e. when G evolves in a medium of density ρ and velocity $\vec{v}$, using (1.1.4), (1.1.5), (1.1.6) and (1.2.4) we may rewrite (1.2.2) in the form

$$\rho^-\left(\vec{V}-\vec{v}^-\right)\cdot\vec{n}\,[w] = \left[\vec{j}'\right]\cdot\vec{n} \tag{1.2.7}$$

or equivalently

$$\rho^+ \left(\vec{V} - \vec{v}^+\right) \cdot \vec{n}\,[w] = \left[\vec{j}'\right] \cdot \vec{n}. \tag{1.2.8}$$

As we said, the presence of (bounded) distributed sources or sinks does not affect (1.2.2). However, there are cases in which non-preserving phenomena occur on an interface and the situation is completely different from the one we have illustrated so far. A clear example is provided by fast chemical reactions between two diffusing species. Diffusion of a diluted substance in a still enviroment is governed by Fick's law:

$$\vec{j} = -d\nabla c \tag{1.2.9}$$

where c is the substance concentration and $d > 0$ is the diffusion coefficient.
On an interface separating two diffusing species of concentrations c_1, c_2 which react infinitely fast we have the following conditions:

$$c_1 = c_2 = 0, \tag{1.2.10}$$

$$\alpha \vec{j}_1 \cdot \vec{n} = -\vec{j}_2 \cdot \vec{n}, \tag{1.2.11}$$

α being the ratio of the mass involved in the reactions, expressing the fact that the reaction is sustained by the two diffusive fluxes at the reaction site.

1.3. Heat conduction

The heat capacity of a thermal conductor at a temperature T is defined by the relationship

$$dQ = C(T)\ dT, \tag{1.3.1}$$

where dQ is the amount of heat that must be supplied to the body to raise its temperature from T to $T + dT$. The heat capacity of the unit mass, namely the specific heat $c\,(t)$, is a property of the material of which the conductor is made, but it also depends on the way the amount of heat is supplied.

If we recall the first principle of thermodynamics

$$dQ = dU + dL \tag{1.3.2}$$

(dU variation of internal energy, dL work made by the system during the transformation), we can easily emphasize the difference between the heat capacity at constant volume (C_v), corresponding to $dL = 0$, and the heat capacity at the constant pressure (C_p), in which we have the contribution of $dL = P\ dV$ (P pressure, dV volume variation).

The definition of internal energy may be complicated, because it involves the potential energy of molecules interaction, but for ideal gases we know that $U = \dfrac{3}{2}NkT$ (N number of molecules, k Boltzmann's constant) [b]. Thus $C_v = \frac{3}{2}Nk$.

---

[b] Remembering that $N = N_m N_A$ (N_m: number of moles, N_A: Avogadro's number) and that the universal gas constant is $R = kN_A$, the product kN can be also expressed as $N_m R$.

In the case of constant pressure we have

$$dQ = d(U + PV) = dH, \tag{1.3.3}$$

where H is the *enthalpy* of the system, which we may define as

$$H(T) = \int_{T_0}^{T} C_p\,(\xi)\,d\xi, \tag{1.3.4}$$

up to a constant (the selection of the temperature T_0 is arbitrary).

At this point we try to use equations (1.1.4) – (1.1.7) to write down the heat balance equation at constant pressure. We identify the quantity w with the specific enthalpy

$$h(T) = \int_{T_0}^{T} c_p\,(\xi)\,d\xi, \tag{1.3.5}$$

i.e. the enthalpy of the unit mass, and we define the non-convective enthalpy current density by means of the *Fourier's law*

$$\vec{j}' = -k(T)\nabla T, \tag{1.3.6}$$

$k > 0$ being the heat conductivity of the material.

Thus in our case (1.1.7) becomes (neglecting the work of thermal dilation[c])

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p \vec{v} \cdot \nabla T - div\,(k\,(T)\,\nabla T) = 0 \tag{1.3.7}$$

where ρ has to be prescribed as a function of T (since we are considering an isobaric process). We will review some basic facts about the linear version of (1.3.7) (i.e. constant coefficients) in the next Chapter.

A very important procedure when dealing with real problems is *rescaling*, i.e. choosing appropriate dimensionless variables.

Let us consider for simplicity the case of constant coefficients. Looking at the shape of the heat conducting body it is usually clear how to select a reference length L[d]. Likewise the initial or boundary conditions indicate a reference temperature T_0. We denote by $\overline{\nabla}$ and by $\overline{\Delta}$ the gradient and the Laplacian in the non-dimensional coordinates and we put $\overline{T} = \dfrac{T}{T_0}$.

Velocity can be rescaled by v_0, e.g. the maximum modulus of $\vec{v}$. Thus we define the nondimensional vector $\overline{\vec{v}} = \dfrac{\vec{v}}{v_0}$. The choice of time scale is generally more delicate. For the moment we set $\bar{t} = \dfrac{t}{t_0}$ with t_0 to be defined. Adopting the new variables, equation (1.3.7) takes the form

$$\frac{\partial \overline{T}}{\partial \bar{t}} + \frac{v_0}{L/t_0} \overline{\vec{v}} \cdot \overline{\nabla T} - \frac{t_0}{t_d} \overline{\Delta T} = 0, \tag{1.3.8}$$

where $t_d = \dfrac{\rho c L^2}{k}$ is the natural time scale associated to heat diffusion.

---

[c] Again we are taking a simplified approach to heat diffusion. Thermal dilation not only affects energy balance, but is the cause of buoyancy effects in fluids. For a description of the general theory see[120]

[d] It may happen that the geometry of the body suggests different rescalings for different spatial coordinates. This is the case for a *thin layer* or a *slender body* (e.g. a thin rod). Proceeding in this way it is often possible to obtain significant simplifications

If we select $t_0 = t_d$ and we put $L/t_d = v_d$, (1.3.8) reduces to

$$\frac{\partial \overline{T}}{\partial \overline{t}} + \frac{v_0}{v_d}\overline{\vec{v}} \cdot \overline{\nabla T} - \overline{\Delta T} = 0. \tag{1.3.9}$$

The number

$$P_e = \frac{v_0}{v_d} = \frac{v_0 L \rho c}{k}$$

is called *Peclet number* and it expresses the relative importance of advection vs. diffusion. If $P_e << 1$, then the advection term can be neglected and (1.3.8) simplifies to

$$\frac{\partial \overline{T}}{\partial \overline{t}} - \overline{\Delta T} = 0. \tag{1.3.10}$$

If on the contrary $P_e >> 1$, then we expect that diffusion has little importance and the choice of time scale should be changed.

In this case the natural choice is the one which reduces to 1 the coefficient of $\overline{\vec{v}} \cdot \overline{\nabla T}$ in (1.3.8), namely $t_0 = \left(\frac{v_0}{L}\right)^{-1}$. At the same time we have now $\frac{t_0}{t_d} = \frac{k}{\rho c v_0 L} = \frac{1}{P_e} << 1$ and we replace (1.3.8) by

$$\frac{\partial \overline{T}}{\partial \overline{t}} + \overline{\vec{v}} \cdot \overline{\nabla T} = 0. \tag{1.3.11}$$

However, we must notice that this time we have changed the character of the equation (from a second order parabolic equation to a first order (hyperbolic) equation). Such a modification has substantial implications. For instance, when we solve (1.3.8) in a bounded spatial domain Ω with regular boundary $\partial\Omega$ we must specify the temperature $\overline{T}\,(\overline{x}, 0)$ and e.g. the temperature on the whole boundary $\partial\Omega$ during a given time interval. When we come to equation (1.3.11), besides the initial temperature we must assign $\overline{T}$ only on those points of $\partial\Omega$ such that $\vec{n} \cdot \overline{\vec{v}} < 0$ ($\vec{n}$ normal to $\partial\Omega$ pointing outwards: the material enters the domain and we have to say with what temperature). The data formerly prescribed on the complementary part of $\partial\Omega$ for equation (1.3.8) will not generally match the solution of (1.3.11).

Such a conflict is originated by the fact that the approximation leading to (1.3.11) does not respect the nature of the original problem and is in fact admissible as long as $\overline{\Delta T}$ does not become so large to compensate the smallness of $\frac{1}{P_e}$.

A circumstance like this occurs any time we introduce approximations deeply affecting the mathematical structure of a differential equation (for instance, also for ordinary differential equations, if we neglect the leading order term). We say that we have a *singular perturbation* and we are forced to study the original (unmodified) equation in a *boundary layer.* This is a large and important branch of mathematics [e].

Continuing our analysis of equation (1.3.8), there may be cases in which the natural time scale t_0 is suggested by another parallel process. For instance another diffusive process of Fickian type in which the (material) diffusivity d is much smaller than the *heat diffusivity* $\alpha = \frac{k}{\rho c}$. In that case it may be convenient to rescale time by $\hat{t}_d = \frac{L^2}{d}$. Now the coefficient of the Laplacian in (1.3.8) is $\frac{\hat{t}_d}{t_d} = \frac{\alpha}{d} >> 1$ and we rewrite (1.3.8) in the form

---

[e] See e.g. the recent book by S. Howison[92] and the very classical book by H. Schlichting and K. Gersten.[120]

$$\frac{d}{\alpha}\frac{\partial\overline{T}}{\partial\overline{t}} + \frac{v_0 L}{\alpha}\overline{\vec{v}} \cdot \overline{\nabla T} - \overline{\Delta T} = 0,$$

where $\dfrac{v_0 L}{\alpha} = P_e$. Thus, if $P_e << 1$, this time we are led to conclude that we may simplify (1.3.8) to

$$\overline{\Delta T} = 0. \tag{1.3.12}$$

In this case the time evolution of the thermal field is so fast (in the chosen time scale) that we may consider it *quasi-steady.* Time variations of the temperature are driven only by the boundary data (provided they are slow enough!).

Once more we have changed the nature of the equation (from parabolic to elliptic). An obvious consequence is that we are not allowed to prescribe initial data. If we need to describe the correct time evolution from $t = 0$ we must revert to the time scale t_d and compute the solution for a time interval (which will anyway be much smaller than $\overset{\wedge}{t_d}$) long enough for $\overline{T}$ to obey (1.3.12).

Remark 1.3.1. We will always assume, without mentioning it, that ρ, c, k are strictly positive. In deriving equation (1.3.7) we have excluded that any phase change takes place. $\square$

1.4. Inflow and outflow boundary conditions

It frequently happens to consider diffusion problems within domains which are crossed by a liquid (typically the solvent). Here we discuss very briefly what kind of boundary conditions should be imposed in those cases.

We suppose to work in a frame of reference in which the boundary of the domain is at rest. If $\vec{n}$ is the outer normal unit vector and $\vec{v}$ is the fluid velocity then we have inflow if $\vec{v} \cdot \vec{n} < 0$ and outflow if $\vec{v} \cdot \vec{n} > 0$. We refer to the case of solutions, but the extension to heat conduction-advection is obvious.

(i) *"Standard" conditions.* It is always possible to impose the value of concentration (Dirichlet) or of its normal derivative (Neumann) or of a linear combination of the two. This is what can be found in any book on PDE's. We will return to the question of the initial-boundary-value problems for parabolic equations in the next chapter. However we take the opportunity here to point out that even this seemingly innocent subject can hide unexpected difficulties. Suppose for instance that in a layer $0 < x < l$ it is possible to guarantee that concentration takes a value $c_0(t)$ at $x = 0$, while at $x = l$ the extraction rate of the solute is prescribed as $-D\dfrac{\partial c}{\partial x} = \varphi_0 > 0$. Here we suppose that φ_0 is the maximum rate attainable in the process under consideration. To make the problem even simpler we take $v = 0$. Of course the initial concentration $c_{in}(x) \geq 0$ must be prescribed and the governing differential equation is $\dfrac{\partial c}{\partial t} - D\dfrac{\partial^2 c}{\partial x^2} = 0$. This problem is absolutely standard, but we must be aware that, since we are dealing with a concentration, the constraint $c(x,t) \geq 0$ must always be fulfilled. If we just solve the stated problem blindly, depending on the data it may happen that, starting from $x = l$, a negativity set appears at some time t^*. Clearly we are entering a non-physical stage, because we are imposing an extraction rate no longer compatible with the amount of solute actually present in the solution. Therefore, for $t > t^*$ we have to replace the flux boundary condition with the Dirichlet condition $c(l,t) = 0$. Once we have done this, we should still keep the outgoing flux $-D\dfrac{\partial c}{\partial x}$ under surveillance. Indeed, it may happen that if the boundary concentration $c_0(t)$ increases fast enough, the extraction rate needed to keep $c(l,t) = 0$ exceeds the value φ_0. In that case we have to switch to the former condition $-D\dfrac{\partial c}{\partial x} = \varphi_0 > 0$, and so on. Thus the problem turns out to obey the unilateral constraints $c(l,t) \geq 0$, $-D\dfrac{\partial c}{\partial x}|_{x=l} \leq \varphi_0$, according to which the *active* boundary condition must be selected.

(ii) *Contact with a well-stirred reservoir.*

For simplicity we consider a layer $0 < x < l$ with permeable walls (see fig. 1.4.1).

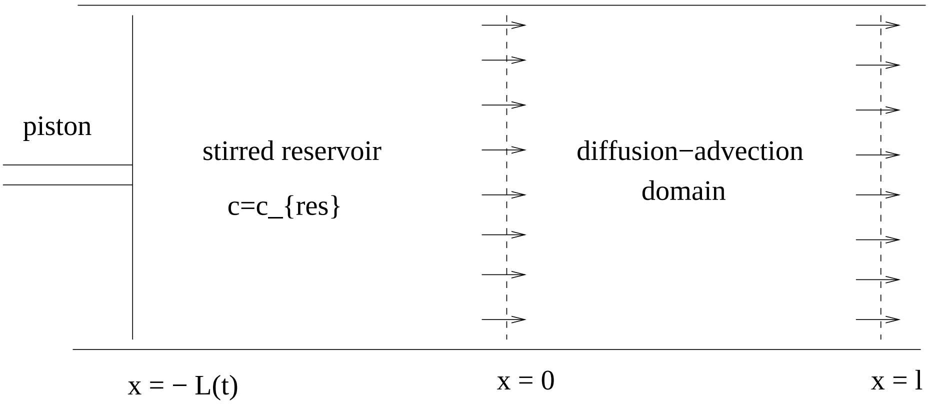


Figure 1.4.1. *Injection of a solution from a well stirred reservoir.*

(a) *Inflow.*

Fluid is injected with velocity v through $x = 0$ (we consider a portion of the inflow surface of area S). The well stirring hypothesis means that the concentration c_{res} in the reservoir depends on time only. The thickness L of the reservoir decreases in time.

The mass balance in the reservoir is

$$\frac{d}{dt}\left(Lc_{res}\right) = LF - j, \tag{1.4.1}$$

where F is the possible supply rate to the reservoir (per unit volume) and j is the solute mass flow rate in the domain considered. The latter is

$$j = \left(-D\frac{\partial c}{\partial x} + cv\right)\Big|_{x=0^+}. \tag{1.4.2}$$

Clearly $L = L_0 - \int_0^t v(\tau)\,d\tau$ and $\dot{L} = -v$, so (1.4.1) is explicitly written as

$$L(t)\left(\dot{c}_{res} - F\right) = D\frac{\partial c}{\partial x} + v\left(c_{res} - c\right). \tag{1.4.3}$$

It is evident that this equation is not sufficient, because both c_{res} and c are unknown, if we exclude the limit cases in which either c_{res} or c are prescribed. The missing condition is usually expressed in the form of the diffusive mass exchange rate

$$D\frac{\partial c}{\partial x} = h\left(c - c_{res}\right), \tag{1.4.4}$$

where $h > 0$ measures the exchange efficiency (it has the dimension of a velocity)[f].

A justification of (1.4.4) can be obtained by assuming that agitation in the reservoir produces a uniform distribution c_{res} everywhere with the exception of a boundary layer near $x = 0$, having thickness εl, where $\varepsilon \ll 1$ depends on the agitation speed. There we have a concentration $c_b(x,t)$, obeying

$$\frac{\partial c_b}{\partial t} - D_b\frac{\partial^2 c_b}{\partial x^2} + v\frac{\partial c_b}{\partial x} = 0, \qquad -\varepsilon l < x < 0$$

and satisfying $c_b(-\varepsilon l, t) = c_{res}(t)$, $c_b(0,t) = c(0,t)$.

If we take dimensionless variables, $\overset{\wedge}{c_b}$, ξ, τ with $\xi = x/\varepsilon l$, $t/\tau = l^2/D$, we obtain

$$\frac{D}{l^2}\frac{\partial \overset{\wedge}{c_b}}{\partial \tau} - \frac{D_b}{\varepsilon^2 l^2}\frac{\partial^2 \overset{\wedge}{c_b}}{\partial \xi^2} + \frac{v}{\varepsilon l}\frac{\partial \overset{\wedge}{c_b}}{\partial \xi} = 0, \qquad -1 < \xi < 0,$$

or

$$\varepsilon\frac{D}{D_b}\frac{\partial \overset{\wedge}{c_b}}{\partial \tau} - \frac{\partial^2 \overset{\wedge}{c_b}}{\partial \xi^2} + \frac{\varepsilon l v}{D_b}\frac{\partial \overset{\wedge}{c_b}}{\partial \xi} = 0.$$

Since $\dfrac{D}{D_b} = O(1)$ and $\dfrac{\varepsilon l v}{D_b}$ plays the role of a Peclet number in the boundary layer, we can say that, if the main transport process in $0 < x < l$ is not advection-dominated and thus $\dfrac{lv}{D}$ is not large, then the mass transport in the boundary layer is quasi-steady and diffusion-dominated, i.e. $\dfrac{\partial^2 \overset{\wedge}{c_b}}{\partial \xi^2} \simeq 0$. Thus

$$\overset{\wedge}{c_b} = \hat{c}_{res}\,(1 - \xi) + \hat{c}\,\xi \Rightarrow \frac{\partial \overset{\wedge}{c_b}}{\partial \xi} = \hat{c} - \hat{c}_{res}$$

and returning to the original variables

$$D_b\frac{\partial c_b}{\partial x} = \frac{D_b}{\varepsilon l}\left(c - c_{res}\right) = D\frac{\partial c}{\partial x}, \tag{1.4.5}$$

which identifies the coefficient h in (1.4.4) :

$$h = \frac{D_b}{\varepsilon l}.$$

Thus mass exchange is more efficient if the boundary layer is thinner.

(b) *Outflow.*

A typical case is when the fluid flowing out is eliminated. Then the outgoing solute mass flux is cv and equating cv to the incoming flux, i.e. $-D\dfrac{\partial c}{\partial x} + cv$, we conclude that the correct condition to be imposed is

$$\left.\frac{\partial c}{\partial x}\right|_{x=L} = 0. \tag{1.4.6}$$

---

[f] Show that as long as $L/l \gg 1$ and $F = 0$, from (1.4.3) we can deduce $c_{res} \simeq$ constant (hint: rescale x by l and t by l^2/D).

Of course we can also consider the case in which the outgoing fluids enters another reservoir. Then the analysis goes exactly as for the inflow case.

1.5. An example of singular perturbation

As we said, we have no space to deal with the theory of singular perturbations, particularly for p.d.e.'s. Just to explain the main ideas, let us consider a classical case from mechanics. The equation

$$m\ddot{x} + \lambda\dot{x} + \kappa x = 0 \tag{1.5.1}$$

describes the motion of a point of mass m under the action of an elastic force of constant κ and with a viscous damping of constant λ.

We may rescale x by some length L $\left(\tilde{x} = x/L\right)$ and time by $t = \tilde{t}\,\tau$, so that (1.5.1) becomes

$$\frac{m}{\tau^2}\frac{d^2\tilde{x}}{d\tilde{t}^2} + \frac{\lambda}{\tau}\frac{d\tilde{x}}{d\tilde{t}} + \kappa\tilde{x} = 0 \tag{1.5.2}$$

and if we choose $\tau = \frac{\lambda}{\kappa}$ and we set $\epsilon = \frac{m}{\kappa\tau^2} = \frac{m\kappa}{\lambda^2}$, we obtain

$$\epsilon\frac{d^2\tilde{x}}{d\tilde{t}^2} + \frac{d\tilde{x}}{d\tilde{t}} + \tilde{x} = 0. \tag{1.5.3}$$

Of course we can associate to (1.5.1) any pair of conditions

$$x(0) = x_0, \qquad \dot{x}(0) = v_0, \tag{1.5.4}$$

which in the dimensionless form become

$$\tilde{x}(0) = \tilde{x}_0 = \frac{x_0}{L}, \qquad \left.\frac{d\tilde{x}}{d\tilde{t}}\right|_{\tilde{t}=0} = \tilde{v}_0 = \frac{v_0}{v^*}, \qquad v^* = \frac{L}{\tau} \tag{1.5.5}$$

and we always find one unique solution.

However, we are interested in the case in which m is *small*, in the sense that $\epsilon << 1$. We wonder whether the solution can be approximated by taking $\epsilon = 0$ in (1.5.3). Thus we are led to consider the so-called *outer solution* x_{out}, governed by the equation without the inertia term

$$\frac{dx_{out}}{d\tilde{t}} + x_{out} = 0, \tag{1.5.6}$$

which however cannot match the original data (1.5.5) for the simple reason that it is a first order equation whose general integral is $x_{out}\left(\tilde{t}\right) = ce^{-\tilde{t}}$. Therefore we need to put a magnifying lens on what happens in a short time close $t = 0$ and to describe the so-called *inner solution* x_{in}. Returning to (1.5.3) we use the different rescaling $\hat{t} = \frac{\tilde{t}}{\varepsilon}$, leading to

$$\frac{1}{\varepsilon}\left(\frac{d^2x_{in}}{d\hat{t}^2} + \frac{dx_{in}}{d\hat{t}}\right) + x_{in} = 0. \tag{1.5.7}$$

Treating (1.5.6) and (1.5.7) is not difficult, but it is delicate.

In this particularly simple case it is possible to calculate the exact solution of (1.5.3), (1.5.4) and its first order approximation in ε, which can be used to check the validity of the expression we will derive for x_{out}, x_{in}. The exact solution is

$$\frac{\left(\varepsilon\,\tilde{v}_0 + \frac{1}{2}\left(1+\sqrt{1-4\varepsilon}\right)\tilde{x}_0\right)}{\sqrt{1-4\varepsilon}}\exp\left[\left(\frac{-1+\sqrt{1-4\varepsilon}}{2\varepsilon}\right)\tilde{t}\,\right]+$$

$$+\frac{\frac{1}{2}\left(-1+\sqrt{1-4\varepsilon}\right)\tilde{x}_0 - \varepsilon\,\tilde{v}_0}{\sqrt{1-4\varepsilon}}\exp\left[\left(-\frac{1+\sqrt{1-4\varepsilon}}{2\varepsilon}\right)\tilde{t}\,\right]\simeq \tag{1.5.8}$$

$$\left[\tilde{x}_0 + \varepsilon\left(\tilde{x}_0 + \tilde{v}_0\right)\right]e^{-(1+\varepsilon)\tilde{t}} - \varepsilon\left[\tilde{x}_0 + \tilde{v}_0 + \varepsilon\left(3\,\tilde{x}_0 + 2\,\tilde{v}_0\right)\right]e^{-\left(\frac{1}{\varepsilon}-1-\varepsilon\right)\tilde{t}},$$

to the first order in ε.

It is easy to check that both the differential equation and the initial conditions are satisfied to the first order in ε by this approximation (note that the coefficient of the second exponential must be calculated to the second order in ε order to compute its first order contribution to velocity).

Let us go back to the problem of computing x_{out}, x_{in}.
Looking for the inner solution we may write

$$x_{in}\left(\hat{t}\right) = y_0\left(\hat{t}\right) + \varepsilon y_1\left(\hat{t}\right)$$

imposing that (1.5.7) is satisfied with initial conditions

$$x_{in}(0) = \tilde{x}_0, \qquad \frac{dx_{in}}{dt}\Big|_{\hat{t}=0} = \varepsilon\tilde{v}_0 \tag{1.5.9}$$

in the sense that

$$y_0'' + y_0' = 0, \quad y_0(0) = \tilde{x}_0, \quad y_0'(0) = 0 \Rightarrow y_0\left(\hat{t}\right) = \tilde{x}_0$$

$$y_1'' + y_1' + \tilde{x}_0 = 0, \quad y_1(0) = 0, \quad y_1'(0) = \tilde{v}_0 \Rightarrow y_1 = \left(\tilde{x}_0 + \tilde{v}_0\right)\left(1 - e^{-\hat{t}}\right) - \tilde{x}_0\hat{t}\ .$$

Thus we find the expression

$$x_{in}\left(\hat{t}\right) = \tilde{x}_0 + \varepsilon\left\{\left(\tilde{x}_0 + \tilde{v}_0\right)\left(1 - e^{-\hat{t}}\right) - \tilde{x}_0\hat{t}\right\}, \tag{1.5.10}$$

which clearly agrees with (1.5.8) to the first order in ε, once we put $\hat{t} = \frac{\tilde{t}}{\varepsilon}$.

Coming to the outer solution, we note that it should lose the memory of the initial velocity. Indeed if we now match for $\varepsilon \ll \tilde{t} \ll 1$ the function $x_{out} \simeq ce^{-\tilde{t}}$ with $x_{in} \simeq \tilde{x}_0 + \varepsilon\left\{\left(\tilde{x}_0 + \tilde{v}_0\right)\left(1 - e^{-\frac{\tilde{t}}{\varepsilon}}\right) - \frac{1}{\varepsilon}\,\tilde{x}_0\tilde{t}\right\} \simeq \tilde{x}_0\left(1 - \tilde{t}\right)$ we get $c = \tilde{x}_0$, as expected, and thus simply

$$x_{out}\left(\tilde{t}\right) = \tilde{x}_0\,e^{-\tilde{t}}. \tag{1.5.11}$$

The transition from x_{in} to x_{out} takes place in a time interval in which $\tilde{t}$ is small while $\hat{t}$ is large. For instance if $\varepsilon \simeq 10^{-4}$ we can have $\tilde{t} = 10^{-2}$, $\hat{t} = 10^{2}$. Check that x_{in}, x_{out} do match for these numerical values.

1.6. Phase change. The Stefan condition

We refer to the specific case of melting or solidification at constant pressure. The peculiar feature of such phase transitions is that they are accompanied by a jump of the specific enthalpy.

For simplicity here we suppose that there is a fixed temperature T_m (the melting point) above which the material is liquid and below which it is solid [g]. For pure substances this is actually the case (T_m depends on pressure, which however is constant in our case), although usually the solid may be (slightly) overheated and the liquid may be (largely) undercooled. For systems such as alloys or polymers the situation is much more complicated, but in this chapter we are not going to deal with such cases.

If we take T_m as the reference temperature in the definition (1.3.5) of the specific enthalpy, we write

$$h_s(T) = \int_{T_m}^{T} c_s\,(\eta)\,d\eta, \qquad T < T_m \tag{1.6.1}$$

and

$$h_l(T) = \int_{T_m}^{T} c_l\,(\eta)\,d\eta + \lambda, \qquad T > T_m \tag{1.6.2}$$

where $\lambda > 0$ is the so-called *latent heat* and the indices s, l refer to the solid and liquid phase, respectively.

We want to derive the mathematical model for two heat conducting phases separated by a sharp and regular interface Γ, defined as the set $\{T = T_m\}$.

All we have to do is to write down the enthalpy conservation law on the moving interface (i.e. the Rankine-Hugoniot condition for enthalpy), which is obtained from (1.2.7) with $w = h$, $[h] = \lambda$, $\vec{j}' = -\kappa \nabla T$.

Note that $[h] = \lambda$ is consistent with the normal $\vec{n}$ to Γ pointing towards the liquid phase. The resulting equation is the so-called *Stefan condition*, which can be formulated either as

$$\lambda\ \rho_s\ (\vec{V} - \vec{v}_s)\ \cdot\ \vec{n} = -\kappa_l \frac{\partial T_l}{\partial n} + \kappa_s \frac{\partial T_s}{\partial n}, \tag{1.6.3}$$

or as

$$\lambda\ \rho_l\ (\vec{V} - \vec{v}_l)\ \cdot\ \vec{n} = -\kappa_l \frac{\partial T_l}{\partial n} + \kappa_s \frac{\partial T_s}{\partial n}, \tag{1.6.4}$$

to be coupled with

$$T_s = T_l = T_m \quad \text{on } \Gamma. \tag{1.6.5}$$

If we may neglect deformations in the solid phase and we take a frame of reference in which the solid phase is at rest, equation (1.6.3) simplifies to

$$\lambda\ \rho_s \vec{V}\ \cdot\ \vec{n} = -\kappa_l \frac{\partial T_l}{\partial n} + \kappa_s \frac{\partial T_s}{\partial n}, \qquad (\vec{v}_s = 0) \tag{1.6.6}$$

and if Γ is described as the set $S(\vec{x}, t) = 0$, we can also write

$$-\lambda\ \rho_s \frac{\partial S}{\partial t} = [-\kappa \nabla T]\ \cdot\ \nabla S. \tag{1.6.7}$$

---

[g] See Remark (1.6.2) below.

Let us consider in particular the one-dimensional case with the only space coordinate x. If we put $S(x,t) = x - s(t)$, then (1.6.6) is

$$\lambda\ \rho_s\ \dot{s}\ (t) = -\kappa_l \frac{\partial T_l}{\partial x} + \kappa_s \frac{\partial T_s}{\partial x}. \qquad (\vec{v}_s = 0) \tag{1.6.8}$$

When we have no variation of T_m it makes sense to consider **one-phase problems**:

a) *melting of solid at* $T \equiv T_m$ *(with liquid at rest)*

$$\lambda\ \rho_l\ \dot{s} = -\kappa_l \frac{\partial T}{\partial x} \qquad (\vec{v}_l = 0) \tag{1.6.9}$$

(remembering (1.2.3) we see that $\rho_l\ \dot{s} = \rho_s(\dot{s}\ - v_s)$, explaining that when $v_l = 0$ the solid is displaced with the velocity given by: $(\rho_l - \rho_s)\ \dot{s} = -\rho_s v_s$. In the frame with the solid at rest in (1.6.9) ρ_l is replaced by ρ_s (see(1.6.8)).

b) *solidification of liquid at* $T \equiv T_m$ *(with solid at rest)*

$$\lambda\ \rho_s\ \dot{s} = \kappa_s \frac{\partial T}{\partial n} \qquad (\vec{v}_s = 0) \tag{1.6.10}$$

(with $v_s = 0$ the liquid phase is diplaced with the velocity $v_l = (1 - \frac{\rho_s}{\rho_l})\ \dot{s}$).

Remark 1.6.1. The sign of the one-phase one-dimensional Stefan condition indicates which phase is conducting and which is identically at the phase transition temperature. □

As we shall see, in one-phase problems the conducting phase is always advancing over the isothermal phase.

So far we have excluded superheating or supercooling. However, the model above still makes sense if the liquid is below freezing and/or the solid is above melting temperature, provided we impose that phase change occurs only at $T = T_m$.

For instance we may use (1.6.9) to describe solidification of a supercooled liquid ($T < T_m$) or (1.6.10) to describe melting of a superheated solid ($T > T_m$). In such cases however the conducting phase shrinks in favour of the isothermal phase which increases its volume.

More generally the temperature at the interface is not constant but depends on its curvature (through surface tension effects) or on its velocity (kinetic supercooling). We will not deal with such cases, nor with processes with variable pressure (the typical case of mould injection processes).

Concerning rescaling we have several options.

Considering the one-phase one-dimensional melting problem

$$\rho c \frac{\partial T}{\partial t} - \kappa \frac{\partial^2 T}{\partial x^2} = 0, \qquad \rho\lambda\ \dot{s} = -\kappa\ \frac{\partial T}{\partial x}\bigg|_{x=s}, \qquad T|_{x=s} = T_m, \tag{1.6.11}$$

with constant coefficient, we can introduce the dimensionless variables

$$\theta = \frac{T - T_m}{T_0 - T_m}, \quad \xi = \frac{x}{L}, \quad \sigma = \frac{s}{L}, \quad \tau = \frac{t}{t_m}, \quad t_m = \frac{\rho \lambda L^2}{\kappa\,(T_0 - T_m)}, \quad t_d = \frac{\rho c L^2}{k} \tag{1.6.12}$$

obtaining

$$\frac{\partial \theta}{\partial \tau} - \frac{t_m}{t_d}\frac{\partial^2 \theta}{\partial \xi^2} = 0, \qquad \frac{d\sigma}{d\tau} = - \left.\frac{\partial \theta}{\partial \xi}\right|_{\xi=\sigma(\tau)}, \qquad \theta|_{\xi=\sigma(\tau)} = 0. \tag{1.6.13}$$

The temperature T_0 may be a typical value of the boundary temperature. In this way we have selected a time scale linked with the phase change process. The dimensionless ratio

$$Ste = \frac{c\,(T_0 - T_m)}{\lambda} \tag{1.6.14}$$

is called the *Stefan number* and it coincides with $\frac{t_d}{t_m}$: it does not depend on the geometry, but it compares the heat required to take the unit mass of the material from T_0 to T_m, and the latent heat.

By adopting the different rescaling

$$\theta = \frac{T - T_m}{T^*}, \qquad \tau = \frac{t}{t_d}, \qquad \xi = \frac{x}{L}, \qquad \sigma = \frac{s}{L}, \tag{1.6.15}$$

we reduce (1.6.11) to the simpler form

$$\frac{\partial \theta}{\partial \tau} - \frac{\partial^2 \theta}{\partial \xi^2} = 0, \qquad \frac{d\sigma}{d\tau} = - \left.\frac{\partial \theta}{\partial \xi}\right|_{\xi=\sigma}, \qquad \theta|_{\xi=\sigma} = 0, \tag{1.6.16}$$

provided $T^* = \dfrac{\lambda}{c}$. Of course we can get the same result performing a further rescaling of (1.6.13).

Note that in (1.6.13) the thermal field θ can be considered quasi-steady (hence linear in ξ) if $Ste << 1$ (meaning that the latent heat is large with respect to the amount of heat required to take the unit mass from the temperature T_0 to the temperature T_m). In this case phase change dictates the time scale of the interface evolution, which is very slow compared to that of conduction. For this reason the temperature in the conducting phase reaches a linear profile before the interface has made any significant progress.

Example 1.6.1. For water

$\rho = 1\,gr/cm^3, \qquad c = 1\,cal/g^\circ K, \qquad \kappa \simeq 1.5 \times 10^{-3}\,cal/\sec\, cm\,^\circ K,$

$\lambda = 80\,cal/g, \qquad L = 10cm\ \ [L = 1cm], \qquad T_0 = 283\,^\circ K, \qquad T_m = 273\,^\circ K$

$\Longrightarrow$

$t_d = \frac{\rho \lambda L^2}{\kappa} \simeq 6.64 \times 10^4 \sec\ \left[6.64 \times 10^2 \sec\right]$

$t_m = \frac{\rho \lambda L^2}{\kappa(T_0 - T_m)} \simeq 5.33 \times 10^5 \sec\ \left[5.33 \times 10^3 \sec\right]$

$Ste \simeq 1.25 \times 10^{-1}$

For $T_0 = 323\,^\circ K$, t_m is reduced by $\frac{1}{5}$ and $Ste \simeq 6.25 \times 10^{-1}$.

Remark 1.6.2. We recall that only solidification (and melting) accompanied by the formation (or destruction) of crystals gives rise to a discontinuity of enthalpy (i.e. involving release or absorption of latent heat). When the solid phase is amorphous no latent heat is released upon solidification and this process is more appropriately called *glassy transition.* During a glassy transition molecules do not enter a crystalline structure, but we can say that their mobility is strongly reduced by a large increase of viscosity. In other words, amorphous solids (like glass) can be considered fluids with an extremely high viscosity. Indeed glass viscosity changes by order of magnitudes from temperatures typical of molten glass in a furnace, to room temperature, according to an exponential law, known as the Vogel-Fulcher-Tamman formula.[122] Glass manufacturing is an incredible source of mathematical problems of considerable difficulty and of great importance for industry. For this important subject in the sector of diffusion see the Lecture Notes.[45] □

1.7. Weak version of balance laws

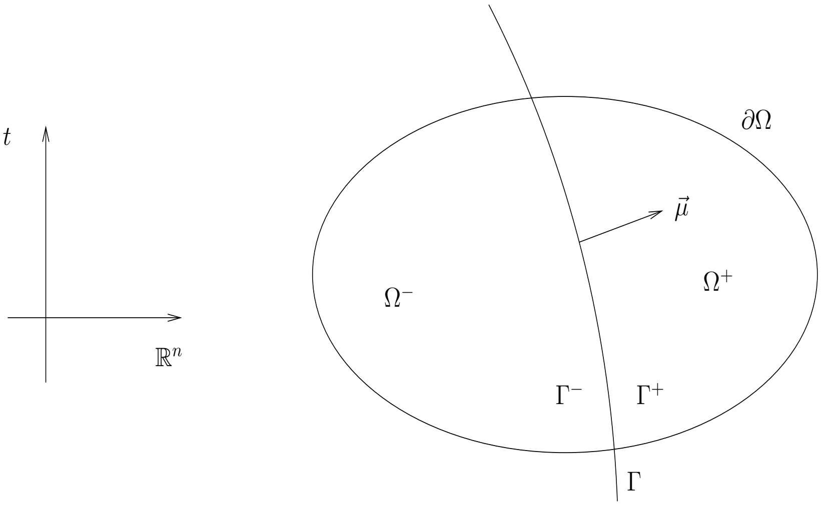


Figure 1.7.1. *Weak formulation of balance laws.*

Let us come back to the balance law (1.1.3) in the presence of a discontinuity surface $\Gamma \subset \mathbb{R}^{n+1}$, to which the Rankine-Hugoniot condition (1.2.2) applies.

We want to show that we may interpret (1.1.3) in a generalized way, so that it incorporates (1.2.2). Such a generalized version of (1.1.3) holds in any domain including Γ and replaces the system (1.1.3), (1.2.2). This approach presents several advantages:

(i) We can deal with non-smooth functions (thus we may consider for instance a larger class of data),

(ii) in many cases (like in the Stefan problem) the surface Γ is unknown (i.e. it is a free boundary) and the weak formulation does not make it appear explicitly, since it is identified simply as a level set of the solution,

(iii) numerical methods can be set up for the weak version, based on smoothing approximation procedures.

We will discuss in more details such aspects when we will deal with the weak form of the Stefan problem. Here we want to say a few general things about the weak version of (1.1.3), (1.2.2).

Let us suppose that u, $\vec{j}$ satisfy (1.1.3), (1.2.2) in the usual sense (*classical* version). We select a *test function* $\varphi(\vec{x},t)$ having compact support in a smooth domain $\Omega \subset \mathbb{R}^{n+1}$ in which (1.1.3), (1.2.2) are satisfied and which intersects Γ. With reference to fig. 1.7.1 we define the domains Ω^-, Ω^+, where $\vec{\mu}$ is the unit vector normal to Γ in $\mathbb{R}^{n+1}$.

For the moment we suppose that φ is a C^∞ function.

For a vector function $\vec{z}(\vec{x},t) \in \mathbb{R}^{n+1}$ we define the divergence operator $div_{n+1}\vec{z} = \sum_{i=1}^{n} \frac{\partial z_i}{\partial x_i} + \frac{\partial z_{n+1}}{\partial t}$. We take $\vec{z} = \left(\varphi\vec{j}, \varphi u\right)$, so that

$$div_{n+1}\vec{z} = \varphi\left(div\vec{j} + \frac{\partial u}{\partial t}\right) + \vec{j}\cdot\nabla\varphi + u\frac{\partial\varphi}{\partial t} \tag{1.7.1}$$

$$= f\varphi + \vec{j}\cdot\nabla\varphi + u\frac{\partial\varphi}{\partial t} \quad \text{in} \quad \Omega^- \cup \Omega^+.$$

Clearly

$$\int_{\Omega^\pm} div_{n+1}\vec{z}\, d\vec{x}\, dt = \int_{\partial\Omega^\pm} \vec{z}\cdot\vec{\nu}_\pm\, d\sigma, \tag{1.7.2}$$

where $\vec{\nu}_\pm$ is the outer unit normal to $\partial\Omega^\pm$.

Due to the choice of φ, $\vec{z}$ vanishes on $\partial\Omega$. Therefore the only contributions to (1.7.2) come from the sides Γ^-, Γ^+ of $\Gamma\cap\Omega$. For Γ^- we have $\vec{\nu}_- = \vec{\mu}$, for Γ^+ we have $\vec{\nu}_+ = -\vec{\mu}$.

Hence (1.7.2) gives

$$\int_{\Omega^\pm} div_{n+1}\vec{z}\, d\vec{x}\, dt = \mp\int_{\Gamma^\pm} \vec{z}\cdot\vec{\mu}\, d\sigma, \tag{1.7.3}$$

We are now ready to evaluate

$$\int_{\Omega^+\cup\Omega^-} div_{n+1}\vec{z}\, d\vec{x}\, dt = \int_{\Omega}\left\{u\frac{\partial\varphi}{\partial t} + \vec{j}\cdot\nabla\varphi + f\varphi\right\} d\vec{x}\, dt = -\int_{\Gamma\cap\Omega} [\vec{z}]\cdot\vec{\mu}\, d\sigma. \tag{1.7.4}$$

Since φ is continuous across Γ, we have

$$[\vec{z}]\cdot\vec{\mu} = \varphi\left\{\left[\vec{j}\right]\cdot\vec{\mu}_n + [u]\,\mu_t\right\} \tag{1.7.5}$$

where $\vec{\mu}_n$ is the projection of $\vec{\mu}$ into $\mathbb{R}_n$ and μ_t is the $(n+1)$-th component of $\vec{\mu}$ (i.e. time).

If Γ has the equation $S(\vec{x},t) = 0$, $\vec{\mu}$ is parallel to the $(n+1)$-dimensional vector $\left(\nabla S, \frac{\partial S}{\partial t}\right)$.

If we use $S(\vec{x},t) = 0$ to define $\vec{x}(t)$ in $\mathbb{R}^n$, we have $\dot{\vec{x}} = \vec{V}$ (with the notation of Sect. 2), and $\vec{V}\cdot\nabla S + \frac{\partial S}{\partial t} = 0$.

Setting $\Sigma = \left(|\nabla S|^2 + (\frac{\partial S}{\partial t})^2\right)^{\frac{1}{2}}$, we see that

$$\Sigma\vec{\mu} = \pm\left(\nabla S, \frac{\partial S}{\partial t}\right) = \pm\,|\nabla S|\left(\vec{n}, -\vec{V}\,\cdot\,\vec{n}\right),$$

$\vec{n}$ being the unit normal vector to the surface $S\,(\vec{x}, t) = 0$ in $\mathbb{R}^n$.

Thus (1.7.5) becomes

$$\Sigma\,[\vec{z}\,\cdot\,\vec{\mu}] = \pm\,|\nabla S|\left\{\left[\vec{j}\right]\,\cdot\,\vec{n} - [u]\,V\,\cdot\,\vec{n}\right\}\varphi = 0 \tag{1.7.6}$$

because of (1.2.2).

The conclusion is that if the pair $u, \vec{j}$ satisfies the system (1.1.3), (1.2.2) we have

$$\int\limits_{\Omega}\left\{u\frac{\partial\varphi}{\partial t} + \vec{j}\,\cdot\,\nabla\varphi + f\varphi\right\}\,d\vec{x}\,dt = 0 \tag{1.7.7}$$

for all $\varphi \in C_0^\infty\,(\Omega)$.

Now we may replace (1.1.3), (1.2.2) with the requirement that (1.7.7) is satisfied in the above sense. At this point we should be more precise about function spaces. Equation (1.7.7) makes sense if we look for $u \in L^2$, $\vec{j} \in \left(L^2\right)^n$, and accordingly the space of test functions can be identified with $H_0^1\,(\Omega)$.

Note that f is then to be taken in $H^{-1}\,(\Omega)$: in a sense we can say that the source term has no role in balancing the singularities at a discontinuity surface, provided it belongs to $H^{-1}\,(\Omega)$.

However, if e.g. u is just an L^2 function, we are no longer able to specify for instance its initial value (which is always essential in evolution problems). Initial data must be incorporated in the problem statement (weak version) by suppressing the requirement $\varphi = 0$ for $t = 0$ and letting the corresponding term appear explicitly in (1.7.7). Boundary values must be treated in a similar way.

This general framework can be adapted in various ways to the specific problem considered, using the peculiar structure of $\vec{j}$.

1.8. More remarks about diffusion

As we shall see in the next chapter (sect.2), the heat equation exhibits the property of *infinite speed of propagation* of disturbances, clashing with the relativity principle and suggesting that the heat conduction process is described by a law more complicated than Fourier's law and of hyperbolic rather than parabolic character. Such an alternative approach has been first proposed in[28] and[132] and it has been studied in a number of papers, also in connection with phase change. Nevertheless, the heat equation has an excellent experimental match in all practical cases.

The same kind of criticism can be put forward for Fick's law modelling diffusion, but in that case there are other aspects to be considered, which are far more important. First of all Fick's law is valid only for diluted solutions, otherwise the displacement of the solvent induced by the solute migration cannot be ignored, so that the system is more appropriately described as a mixture.[117] In addition to that, in multiphase systems the flux of each species may be influenced not only by the gradient of its own concentration, but also by the gradient of the concentration of other species, producing a complex mathematical structure. We quote[7] and,[129] where the derivation of the so-called *Stefan-Maxwell equations* for multicomponent diffusive system is presented. Surprisingly difficult features are found even for the diffusion of two species which have practically identical properties from the point of view of diffusion and are just distinguishable owing to minor physical properties (e.g. two isotopes: see the paper[20]).

Another important phenomenon that, in the presence of gravity, may deeply influence the thermal field (in the case of heat conduction in fluids) or the concentration field (in the case of diffusion) is *buoyancy*. For instance, it is well known that thermal inhomogeneities in a fluid can produce instabilities associated with thermal dilation, giving rise to convective motions. This phenomenon is known as the Rayleigh-Bénard instability.[12,118]

Chapter 2

Some basic facts about the heat equation

2.1. Main results on the model problems

In this section we summarize a few fundamental results, stated in their simplest form and referring to the most elementary model problems.

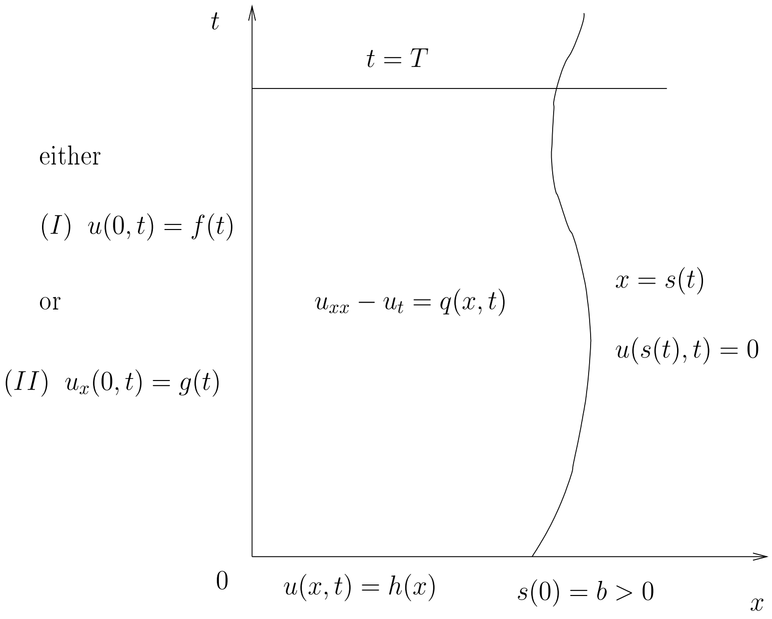


Figure 2.1.1. *Sketch of Dirichlet (I) and of Neumann (II) conditions.*

In Fig. 2.1.1 we sketch the typical Dirichlet (I) and Neumann (II) problem for the heat equation in one space dimension with a (prescribed) moving boundary $x = s(t)$.

Main assumptions on the data are:

- $s(t)$ Lipschitz, $\quad inf\, s(t) > 0$
- h, f, $[g]$ continuous and $h\,(0) = f\,(0)$, $h\,(b) = 0$ ($\Rightarrow u$ continuous in $\overline{Q}_T$)

Notation for norms on Q_T

$$\|f\| = \sup_{Q_T} |f| \quad \text{for } f \text{ continuous in } \overline{Q}_T \quad \left(f \in C\left(\overline{Q}_T\right)\right).$$

$C^{2,1}(Q_T)$ is the space of the functions u which are continuous in Q_T together with the derivatives u_x, u_{xx}, u_t.

To the Holder norm

$$|f|^{\alpha} = \|f\| + \sup_{x' \neq x''} \frac{|f(x',t) - f(x'',t)|}{|x' - x''|^{\alpha}} + \sup_{t' \neq t''} \frac{|f(x,t') - f(x,t'')|}{|t' - t''|^{\alpha/2}}$$

$$\alpha \in (0,1)$$

we associate the functional space denoted by $H^{\alpha,\alpha/2}(\overline{Q}_T)$.

Similarly we define

$$H^{1+\alpha,(1+\alpha)/2}\left(\overline{Q}_T\right)$$

as the space of functions having bounded norm

$$|f|^{(1+\alpha)} = \|f\| + |f_x|^{(\alpha)},$$

and the space $H^{2+\alpha,1+\frac{\alpha}{2}}\left(\overline{Q}_T\right)$ with norm

$$|f|^{(2+\alpha)} = \|f\| + |f_{xx}|^{(\alpha)} + |f_t|^{(\alpha)}.$$

Basic references are the classical books.[24,78,97]

More definitions:

- Definition of *parabolic boundary*

$$\partial_P Q_T = Cl\left\{\partial Q_T \cap \{t < T\}\right\}$$

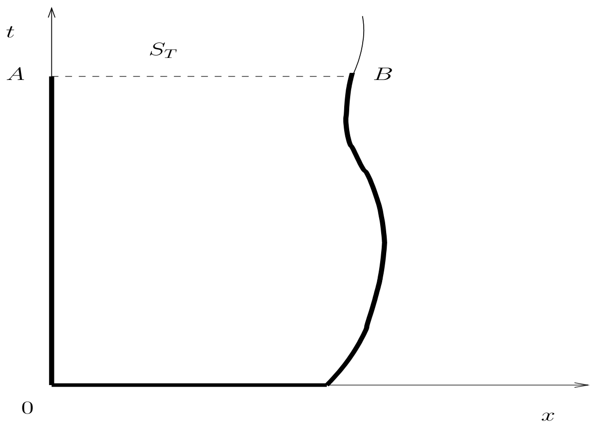


Figure 2.1.2. *The parabolic boundary.*

- Open segment $S_T = \{\overset{\circ}{\partial Q_T \cap \{t = T\}}\}$
- Spaces $H^{\alpha,\alpha/2}(Q_T)$, $H^{1+\alpha,(1+\alpha)/2}(Q_T)$, $H^{2+\alpha,1+\alpha/2}(Q_T)$:
  $f \in H^{\alpha,\alpha/2}(Q_T)$ if $|f|^{(\alpha)}_{Q'_T}$ is bounded for all domains Q'_T having positive distance from $\partial_P Q_T$.
  Similarly for the other Hölder spaces.

Now we are going to state some fundamental theorems.

Theorem 2.1.1. ***(Maximum principle (weak version))*** *Let* $u \in C^{2,1}(Q_T) \cap C(\bar{Q}_T)$ *be a solution of* $u_{xx} - u_t = q$ *in* Q_T *and let* Q_T *be bounded. Then if* $q \geq 0 \quad [\leq 0]$ u *takes its maximum [minimum] on the parabolic boundary* $\partial_P Q_T$. $\square$

The weak maximum principle does not forbid that $\max u$ $[\min u]$ is assumed somewhere in Q_T also. The strong maximum principle (valid also for Q_T not bounded) examines precisely this situation. Its general statement is rather complicated, but it is greatly simplified if the boundary $\partial_P Q_T$ has an interval on $t = 0$ and is completed laterally by one or two continuous curves along which time increases, as we are supposing.

Theorem 2.1.2. ***(Maximum principle (strong version))*** *Let* $u \in C^{2,1}(Q_T) \cap C(\bar{Q}_T)$ *be a solution of* $u_{xx} - u_t = q$ *in* Q_T*,with* Q_T *as in Fig. 2.1.2. Suppose* $q \geq 0 \quad [\leq 0]$*. If* u *has a maximum [minimum] on* S_T*, then* u *is constant in* $\bar{Q}_T$. $\square$

An immediate corollary is the uniqueness for the Dirichlet problem (I).

Again we state the following theorem for the particular boundary we have chosen.

Theorem 2.1.3. ***(Boundary point principle)****(Friedman (1958),*[77] *Vyborny (1957),*[135] *also known as* parabolic version of Hopf's theorem *for the elliptic case (1952)*[90] *). Let* $u \in C^{2,1}(Q_T) \cap C(\bar{Q}_T)$ *be a solution of* $u_{xx} - u_t = q$ *and* $q \geq 0$ $[\leq 0]$*. Suppose that at a boundary point* (x_0, t_0) *(either* $x_0 = 0$*, or* $x_0 = s(t_0)$*), with* $t_0 > 0$*,* u *attains a maximum [minimum] strictly larger [smaller] than the values taken in the intersection of* Q_T *with some half circle* $(x - x_0)^2 + (t - t_0)^2 < R^2$*,* $t \leq t_0$*. For any unit vector* $\vec{e}$ *pointing in the above neighborhood consider the points* $(x_\delta, t_\delta) = (x_0, t_0) + \delta\vec{e}$*, with* $\delta > 0$ *sufficiently small, and take the directional difference quotient* $\chi(\delta, \vec{e}) = \dfrac{u(x_\delta, t_\delta) - u(x_0, t_0)}{\delta}$.

Then $\limsup\limits_{\delta \to 0^+} \chi(\delta, \vec{e}) < 0 \quad \left[\liminf\limits_{\delta \to 0^+} \chi(\delta, \vec{e}) > 0\right]$ *for all* $\vec{e}$ *in the specified set.* $\square$

Hence if $u_x(x_0, t_0)$ exists, then $u_x(x_0, t_0) \begin{cases} < 0\,[< 0], & x_0 = 0 \\ > 0\,[> 0], & x_0 = s(t_0) \end{cases}$

As a corollary, uniqueness for the Neumann problem (II) follows.

Remark 2.1.1. For more general equations or more general domains (non-Lipschitz, or in more than one space dimension) additional requirements are needed on the coefficients and on the boundary. We just remark that if in place of $u_{xx} - u_t = q$ one considers the equation $a(x,t)u_{xx} + b(x,t)u_x + c(x,t)u - u_t = 0$, then $a \geq 0$ is a minimal requirement, the presence of the term bu_x is immaterial for the theorems above, while the condition $c \leq 0$ is important: if $c \neq 0$ and $c \leq 0$, in all statements the words *maximum* and *minimum* must be replaced by *positive maximum* and *negative minimum.* □

Besides the already quoted books on parabolic equations, for the specific topic of the maximum principle see also[107] and the book[115] .

Let us state some existence theorems for the initial-boundary-value problems (I), (II).

Existence for the Dirichlet problem.

Theorem 2.1.4. *If the chain of data on* $\partial_P Q_T$ *is continuous, problem (I) is solvable in* $H^{2+\alpha,1+\alpha/2}\left(Q_T\right)$*, provided* $q \in H^{\alpha,\alpha/2}\left(\overline{Q}_T\right)$.

Remark 2.1.2. Inside Q_T the regularity of the solution is determined by q. For the sake of simplicity the theorem is *not* stated in its most general form, particularly because of the strong assumptions made on the lateral boundary of $\partial_P Q_T$ and on the free term. □

Theorem 2.1.5. *If* $q \in H^{\alpha,\alpha/2}\left(\overline{Q}_T\right)$ *and there exists a function* $\psi \in H^{2+\alpha,1+\alpha/2}\left(\overline{Q}_T\right)$ *coinciding with the data on* $\partial_P Q$*, and if* $\dot{f}\,(0) = h''\,(0) - q\,(0,0)$, $h'\,(b)\,\dot{s}\,(0) + h''\,(b) = q\,(b,0)$*, with* $\dot{s}$ *in a Hölder class (exp.* $\dfrac{\alpha}{2}$*), then the problem (I) is solvable in* $H^{2+\alpha,1+\alpha/2}\left(\overline{Q}_T\right)$.

Existence for the Neumann problem.

We deal just with the smooth case:

Theorem 2.1.6. *Let* $q \in H^{\alpha,\alpha/2}\left(\overline{Q}_T\right)$ *and suppose there exists a function* $\psi \in H^{2+\alpha,1+\alpha/2}\left(\overline{Q}_T\right)$ *such that* $\psi_x = g$ *for* $x = 0$ *and* ψ *equals the data on the rest of* $\partial_P Q_T$*, with compatibility conditions satisfied at the corners* $(0,0)$, $(b,0)$*. Then problem (II) is solvable in* $H^{2+\alpha,1+\alpha/2}\left(\overline{Q}_T\right)$.

2.2. Fundamental solution of the heat equation

The function

$$\Gamma\left(x,t;\xi,\tau\right) = \frac{1}{2\sqrt{\pi\left(t-\tau\right)}} \exp\left[-\frac{\left(x-\xi\right)^2}{4\left(t-\tau\right)}\right], \qquad t > \tau \tag{2.2.1}$$

is called the *fundamental solution* of the one-dimensional heat equation. It is easy to check that (for $t > \tau$)

$$\Gamma_{xx} - \Gamma_t = 0, \qquad \Gamma_{\xi\xi} + \Gamma_\tau = 0 \ (\textit{adjoint equation}). \tag{2.2.2}$$

The basic property:

$$\lim_{t-\tau \downarrow 0} \int_{-\infty}^{+\infty} \varphi\left(\xi\right) \Gamma\left(x,t;\xi,\tau\right) d\xi = \varphi\left(x\right) \tag{2.2.3}$$

at all points of continuity of φ, provided the integral exists, can be demonstrated performing the limit with some care.

With the help of (2.2.3) we can study the *Cauchy problem*

$$u_{xx} - u_t = 0, \quad -\infty < x < +\infty, \quad t > 0, \tag{2.2.4}$$

$$u\,(x,0) = \varphi\,(x)\,, \quad -\infty < x < +\infty, \tag{2.2.5}$$

with $\varphi\,(x)$ continuous and such that $|\varphi\,(x)| < ce^{\alpha^2 x^2}$.

The unique solution (in the same class characterized by the growth restriction imposed on φ) of (2.2.4), (2.2.5) has the explicit representation

$$u\,(x,t) = \int_{-\infty}^{+\infty} \varphi\,(\xi)\,\Gamma\,(x,t;\xi,0)\,d\xi \quad \text{for } 0 < t < \frac{1}{4\alpha^2}. \tag{2.2.6}$$

Remark 2.2.1. It is very easy to calculate

$$\int_{-\infty}^{+\infty} \Gamma\,(x,t;\xi,\tau)\,d\xi = 1, \tag{2.2.7}$$

whose meaning is heat conservation. □

Remark 2.2.2. If x_0 is a point of discontinuity of $\varphi\,(x)$ (and defining in an appropriate way the solution of (2.2.4), (2.2.5)), then (2.2.6) is still the solution of the Cauchy problem, provided φ has the left and the right limit in x_0 (resp. φ_0^-, φ_0^+).

In such a case (2.2.3) is modified to

$$\lim_{t\to 0^+} \int_{-\infty}^{+\infty} \varphi\,(\xi)\,\Gamma\,(x,t;\xi,0)\,d\xi = \frac{\varphi_0^+ + \varphi_0^-}{2}. \quad \square \tag{2.2.8}$$

Remark 2.2.3. Equation (2.2.6) shows very clearly that the heat equation forces disturbances on the initial data to propagate at *infinite speed.* See the comments at the end of the previous chapter. □

The Cauchy problem for the non-homogeneuous equation

$$u_{xx} - u_t = q\,(x,t) \tag{2.2.9}$$

with q locally Hölder continuous w.r.t. x, uniformly in t, and with the same growth condition as the initial data $\varphi\,(x)$, is solved by

$$u\,(x,t) = \int_{-\infty}^{+\infty} \varphi\,(\xi)\,\Gamma\,(x,t;\xi,\tau)\,d\xi - \int_0^t \int_{-\infty}^{+\infty} \Gamma\,(x,t;\xi,\tau)\,q\,(\xi,\tau)\,d\xi d\tau. \tag{2.2.10}$$

The last term is called a *volume potential.*

Clearly, if $q =$ *constant* the volume potential is simply $-qt$.

Let us define two more heat potentials. In the following $x = s(t)$ is supposed (for simplicity) to be a Lipschitz continuous curve.

Simple layer potential ($\forall$ continuous function ψ)

$$\Psi_1(x,t) = \int_0^t \psi(\tau)\,\Gamma(x,t;s(\tau),\tau)\,d\tau. \tag{2.2.11}$$

Ψ_1 solves the heat equation for $t > 0$, $x \neq s(t)$ and is continuous across the curve $x = s(t)$.

Double layer potential ($\forall$ continuous function ψ)

$$\Psi_2(x,t) = \int_0^t \psi(\tau)\,\Gamma_x(x,t;s(\tau),\tau)\,d\tau. \tag{2.2.12}$$

Note that

$$\Gamma_x(x,t;\xi,\tau) = -\frac{x-\xi}{4\sqrt{\pi}\,(t-\tau)^{\frac{3}{2}}}\exp\left[-\frac{(x-\xi)^2}{4(t-\tau)}\right],$$

so for $x = s(t)$, $\xi = s(\tau)$ it behaves like $(t-\tau)^{-\frac{1}{2}}$ (remember we are considering Lipschitz curves).

Ψ_2 solves the heat equation for $t > 0$, $x \neq s(t)$ and satisfies the *jump relation*

$$\lim_{x \to s(t)\pm} \Psi_2(x,t) = \mp\frac{1}{2}\psi(t) + \int_0^t \psi(\tau)\,\Gamma_x(s(t),t;s(\tau),\tau)\,d\tau. \tag{2.2.13}$$

Example 2.2.1. For $s = s_0$, constant

$$\lim_{x \to s_0\pm} \Psi_2(x,t) = \mp\frac{1}{2}\psi(t).$$

Remark 2.2.4. For linear parabolic operators more complicated than the heat operator a fundamental solutions can still be found (under suitable conditions for the coefficients in the operator) using the so-called *parametrix method* (see[78]). For the heat operator in n space dimensions the fundamental solution is

$$\Gamma(\vec{x},t;\vec{\xi},\tau) = 2^{-n}[\pi(t-\tau)]^{-n/2}\exp\left[-\frac{-|\vec{x}-\vec{\xi}|^2}{4(t-\tau)}\right].$$

□

2.3. Representation formulas

As an application of heat potentials we can get representation formulas for various typical problems.

Problem 1 (see fig. 2.3.1).

f_1, f_2 continuous
h continuous
f_i, h matching at corners,

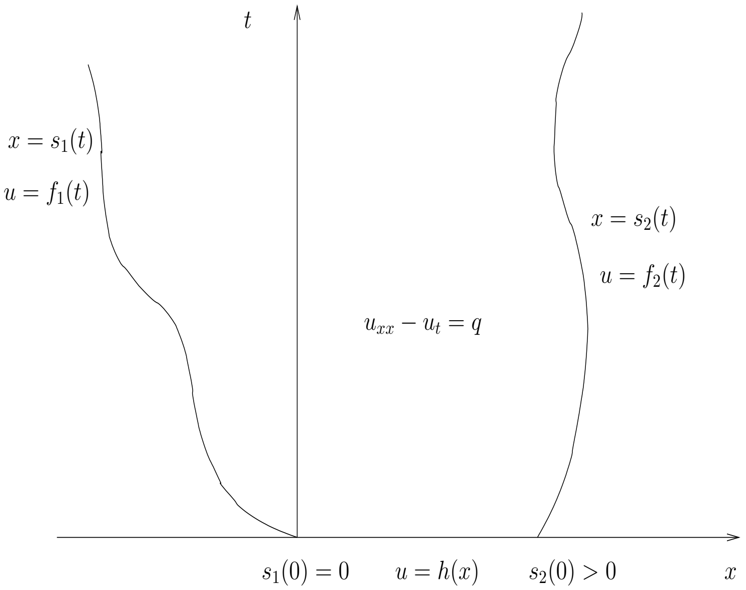


Figure 2.3.1. *Sketch of Problem 1*

s_i Lipschitz, $|s_1 - s_2| \geq \gamma > 0$.

We split u into the sum $w + v$, with

$$w_{xx} - w_t = q, \quad w\left(x,0\right) = h\left(x\right), \quad -\infty < x < +\infty \text{ (already solved)},$$

with arbitrary continuation of h and q (e.g. bounded).

Then $v\left(x,t\right)$ solves

$$v_{xx} - v_t = 0,$$

$$v\left(s_i\left(t\right),t\right) = f_i - w\left(s_i\left(t\right),t\right) = \varphi_i\left(t\right),$$

$$v\left(x,0\right) = 0,$$

and has the representation

$$v\left(x,t\right) = -\int_0^t \Gamma_x\left(x,t;s_1\left(\tau\right),\tau\right)\mu_1\left(\tau\right)d\tau + \int_0^t \Gamma_x\left(x,t;s_2\left(\tau\right),\tau\right)\mu_2\left(\tau\right)d\tau, \tag{2.3.1}$$

with μ_1, μ_2 solving a system of two Volterra integral equations of the second kind with weakly singular kernels:

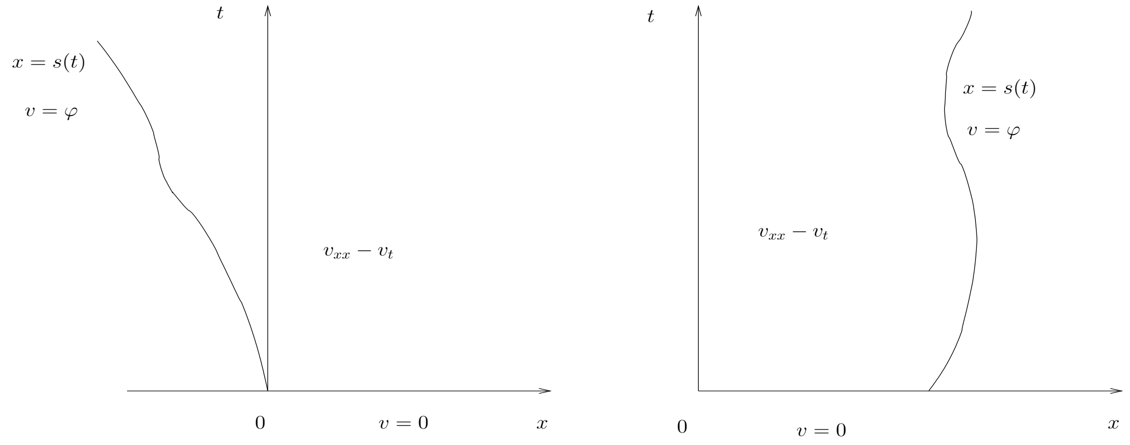
$$\begin{aligned}\varphi_1\left(t\right) = \frac{1}{2}\mu_1\left(t\right) &- \int_0^t \Gamma_x\left(s_1\left(t\right),t;s_1\left(\tau\right),\tau\right)\mu_1\left(\tau\right)d\tau \\ &+ \int_0^t \Gamma_x\left(s_1\left(t\right),t;s_2\left(\tau\right),\tau\right)\mu_2\left(\tau\right)d\tau,\end{aligned} \tag{2.3.2}$$

$$\begin{aligned}\varphi_2\left(t\right) = \frac{1}{2}\mu_2\left(t\right) &- \int_0^t \Gamma_x\left(s_2\left(t\right),t;s_1\left(\tau\right),\tau\right)\mu_1\left(\tau\right)d\tau \\ &+ \int_0^t \Gamma_x\left(s_2\left(t\right),t;s_2\left(\tau\right),\tau\right)\mu_2\left(\tau\right)d\tau,\end{aligned}$$

having a continuous unique solution (μ_1, μ_2).[a]

Problem 2.

Instead of the domain $s_1(t) < x < s_2(t)$, $t > 0$ consider the unbounded domain $x > s_1(t)$, $t > 0$ (or $x < s_2(t)$, $t > 0$) and drop the index 1 (or 2). Of course a growth condition must be imposed on h (as we have seen for the Cauchy problem). Using the same procedure as above we are led to consider one of the following problems.



(a) (b)

Figure 2.3.2. *Problem 2 with $x > s(t)$ (a), or $x < s(t)$ (b).*

For (a), (b) we can write

$$v(x,t) = \mp \int_0^t \Gamma_x(x,t;s(\tau),\tau)\,\mu(\tau)\,d\tau \tag{2.3.3}$$

with μ satisfying

$$\varphi(t) = \frac{1}{2}\mu(t) \mp \int_0^t \Gamma_x(s(t),t;s(\tau),\tau)\,\mu(\tau)\,d\tau \tag{2.3.4}$$

where "$-$" corresponds to (a) and "$+$" to (b).

Note that when s_1 or s_2 (or both) are constant, then the corresponding otherwise singular kernel in eq. (2.3.2) or (2.3.4) vanishes identically.

For instance, the solution of the first i.b.v. problem in the quarter plane $x > 0$, $t > 0$ with data $v(x,0) = 0$, $v(0,t) = \varphi(t)$ is given by

$$v(x,t) = -\int_0^t \Gamma_x(x,t;0,\tau)\,\mu(\tau)\,d\tau$$

$$\varphi(t) = \frac{1}{2}\mu(\tau),$$

i.e.

$$v(x,t) = -2\int_0^t \Gamma_x(x,t;0,\tau)\,\varphi(\tau)\,d\tau = \frac{1}{2\sqrt{\pi}}x\int_0^t \frac{\varphi(\tau)}{(t-\tau)^{\frac{3}{2}}}\exp\left[-\frac{x^2}{4(t-\tau)}\right]d\tau. \tag{2.3.5}$$

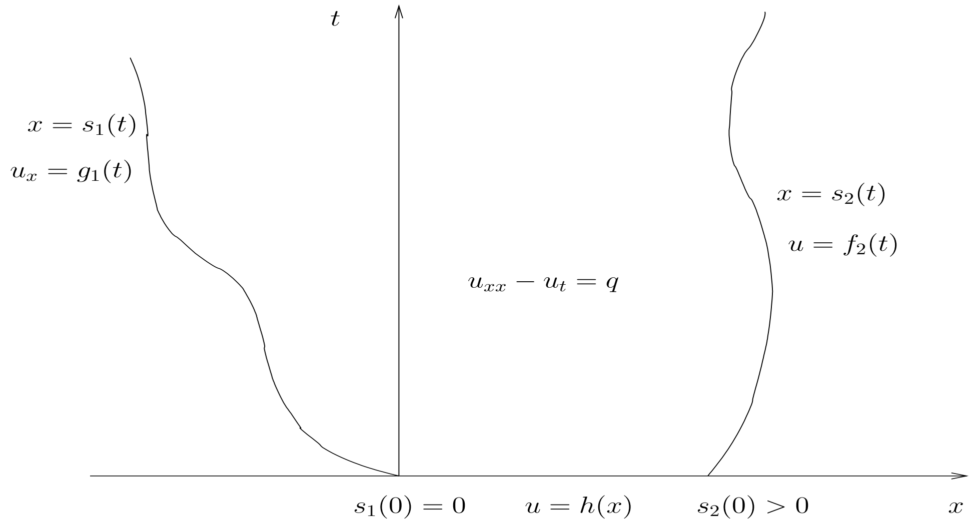


Figure 2.3.3. *Sketch of Problem 3.*

Problem 3.

With the same procedure used for Problem 1 we arrive at considering the problem

$$v_{xx} - v_t = 0,$$

$$v_x\left(s_1\left(t\right), t\right) = \psi_1\left(t\right), v\left(s_2\left(t\right), t\right) = \varphi_2\left(t\right)$$

$$v\left(x, 0\right) = 0,$$

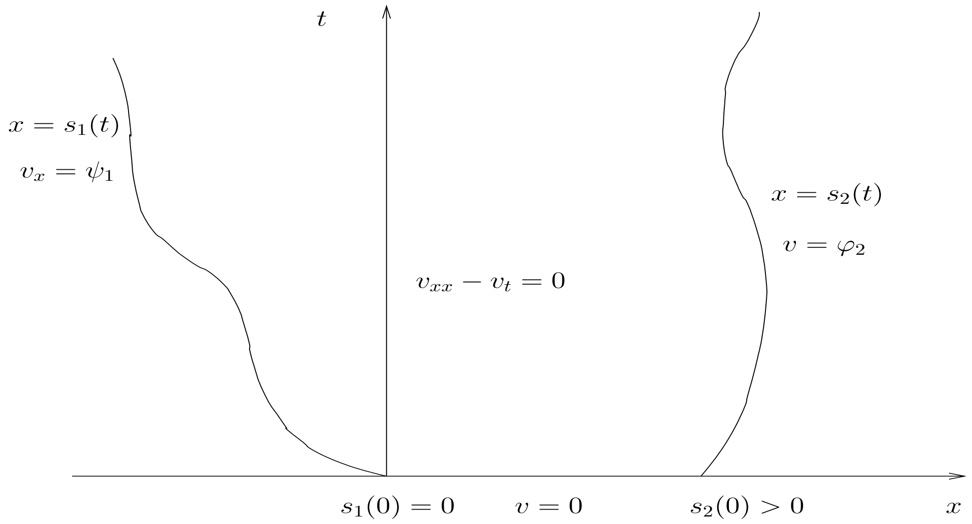


Figure 2.3.4. *Reduction of Problem 3 to homogeneous initial data and zero source.*

with φ_2 defined as before and $\psi_1 = g_1 - w_x\left(s_1\left(t\right), t\right)$.

---

[a] See e.g.[36] .

The representation formula (2.3.1) is modified replacing the double layer potential on $x = s_1(t)$ by a simple layer potential:

$$v(x,t) = -\int_0^t \Gamma(x,t;s_1(\tau),\tau)\,\nu_1(\tau)\,d\tau + \int_0^t \Gamma_x(x,t;s_2(\tau),\tau)\,\mu_2(\tau)\,d\tau. \tag{2.3.6}$$

The associated system of Volterra integral equations is:

$$\begin{aligned}\psi_1(t) &= \frac{1}{2}\nu_1(t) - \int_0^t \Gamma_x(s_1(t),t;s_1(\tau),\tau)\,\nu_1(\tau)\,d\tau + \\ &+ \int_0^t \Gamma_{xx}(s_1(t),t;s_2(\tau),\tau)\,\mu_2(\tau)\,d\tau, \\ \varphi_2(t) &= \frac{1}{2}\mu_2(t) - \int_0^t \Gamma(s_2(t),t;s_1(\tau),\tau)\,\nu_1(\tau)\,d\tau + \\ &+ \int_0^t \Gamma_x(s_2(t),t;s_2(\tau),\tau)\,\mu_2(\tau)\,d\tau.\end{aligned} \tag{2.3.7}$$

Note that the kernel $\Gamma_{xx}(s_1(t),t;s_2(\tau),\tau)$ is not singular because of the condition that the two boundaries stay at a positive distance from each other.

Moving the right boundary to $+\infty$ leads to the problem illustrated in the next figure.

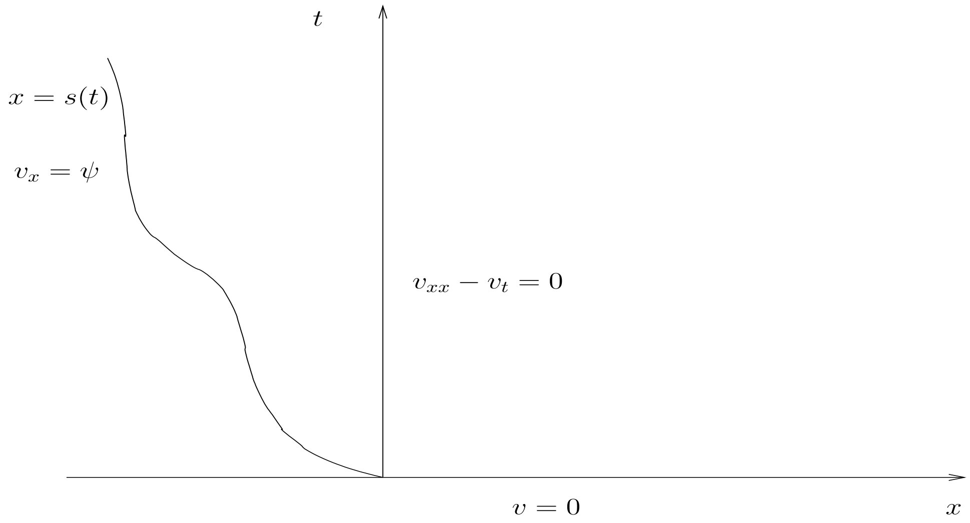


Figure 2.3.5. *Neumann Problem for* $x > s(t)$.

We call it problem (α) and we also consider problem (β), formulated on the left of $x = s(t)$. The corresponding solutions are

$$v(x,t) = \mp \int_0^t \Gamma(x,t;s(\tau),\tau)\,\nu(\tau)\,d\tau \tag{2.3.8}$$

with

$$\psi(t) = \frac{1}{2}\nu(t) \mp \int_0^t \Gamma_x(s(t),t;s(\tau),\tau)\,\nu(\tau)\,d\tau, \tag{2.3.9}$$

where $\mp$ corresponds to (α), (β), respectively.

When $s = s_0$, constant, we simply have $\nu(t) = 2\psi(t)$ and (2.3.8) reduces to

$$v(x,t) = \mp 2 \int_0^t \Gamma(x,t;s_0,\tau)\,\psi(\tau)\,d\tau. \tag{2.3.10}$$

2.4. The Green and Neumann functions for the quarter plane

We have already solved the Dirichlet and the Neumann problem in the quarter plane with no source and zero initial data by means of (2.3.5), (2.3.10).

We know how to modify the respective data $\varphi(t)$, $\psi(t)$ so to take care of the source term $q(x,t)$ and of the initial data $h(x)$, via the splitting $u = w + v$, like in Problem 1.

If we take $q = 0$, we may continue $h(x)$ for $x < 0$ in such a way that $w = 0$ or $w_x = 0$ on $x = 0$, so that φ, ψ coincide with the original data.

For the Dirichlet problem the obvious continuation is $h(x) = -h(-x)$, while we take $h(x) = h(-x)$ for the Neumann problem.

In the first case the solution of the associated Cauchy problem is

$$w(x,t) = \int_0^{+\infty} h(\xi)\left[\Gamma(x,t;\xi,0) - \Gamma(x,t;-\xi,0)\right] d\xi, \tag{2.4.1}$$

and in the second case

$$w(x,t) = \int_0^{+\infty} h(\xi)\left[\Gamma(x,t;\xi,0) + \Gamma(x,t;-\xi,0)\right] d\xi. \tag{2.4.2}$$

The functions

$$G(x,t;\xi,\tau) = \Gamma(x,t;\xi,\tau) - \Gamma(x,t;-\xi,\tau) \tag{2.4.3}$$

$$N(x,t;\xi,\tau) = \Gamma(x,t;\xi,\tau) + \Gamma(x,t;-\xi,\tau) \tag{2.4.4}$$

are the Green and Neumann function (respectively) for the quarter plane.

Thus we are able to write down the explicit solution of the problem in fig. 2.4.1

$$u(x,t) = \int_0^{+\infty} h(\xi)\,G(x,t;\xi,0)\,d\xi + \frac{1}{2\sqrt{\pi}}x \int_0^t \frac{f(\tau)}{(t-\tau)^{\frac{3}{2}}} \exp\left[-\frac{x^2}{4(t-\tau)}\right] d\tau \tag{2.4.5}$$

and of the problem in fig. 2.4.2

$$u(x,t) = \int_0^{+\infty} h(\xi)\,N(x,t;\xi,0)\,d\xi - \frac{1}{\sqrt{\pi}} \int_0^t \frac{g(\tau)}{\sqrt{t-\tau}} \exp\left[-\frac{x^2}{4(t-\tau)}\right] d\tau. \tag{2.4.6}$$

We note that the functions G, N have some of the properties of Γ, namely:

$$G_{xx} - G_t = 0, \qquad G_{\xi\xi} + G_\tau = 0, \tag{2.4.7}$$

$$N_{xx} - N_t = 0, \qquad N_{\xi\xi} + N_\tau = 0, \tag{2.4.8}$$

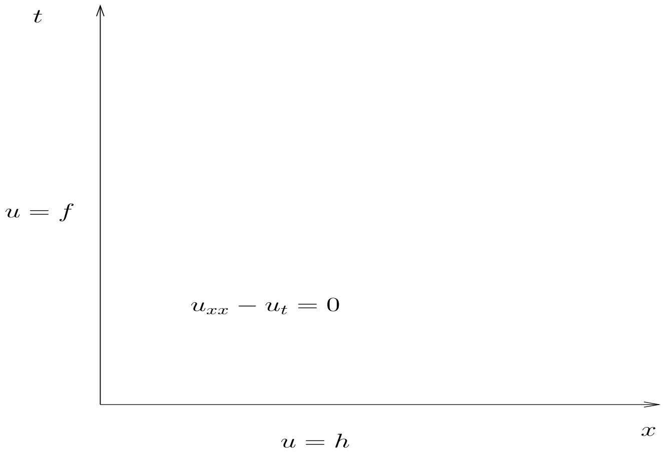


Figure 2.4.1. *Dirichlet i.b.v. problem in the quarter plane.*

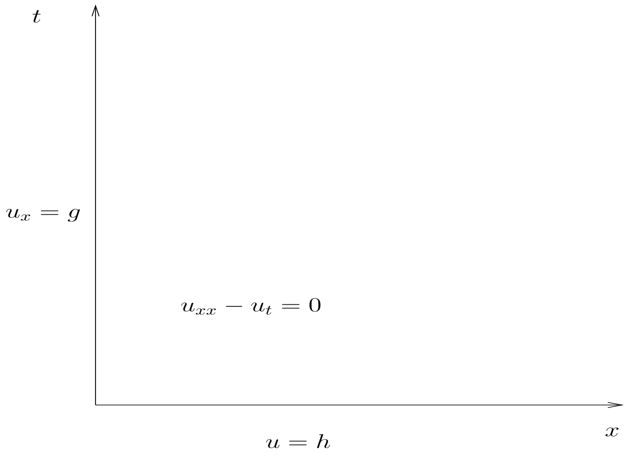


Figure 2.4.2. *Neumann i.b.v. problem in the quarter plane.*

$$\lim_{t\downarrow\tau}\int_{-\infty}^{+\infty}\varphi(\xi)\,G(x,t;\xi,\tau)\,d\xi=\varphi(x)\,, \tag{2.4.9}$$

$$\lim_{t\downarrow\tau}\int_{-\infty}^{+\infty}\varphi(\xi)\,N(x,t;\xi,\tau)\,d\xi=\varphi(x)\,, \tag{2.4.10}$$

at points of continuity of φ (fulfilling the usual growth condition at infinity).

In addition

$$G(0,t;\xi,\tau)=0, \tag{2.4.11}$$

$$N_x(0,t;\xi,\tau)=0, \tag{2.4.12}$$

and

$$G_x=-N_\xi, \qquad G_\xi=-N_x. \tag{2.4.13}$$

It is convenient to have the explicit expressions of the x-derivatives

$$G_x\left(x,t;\xi,\tau\right)= \\ =\frac{1}{4\sqrt{\pi}\left(t-\tau\right)^{\frac{3}{2}}}\left\{-\left(x-\xi\right)\exp\left[-\frac{\left(x-\xi\right)^2}{4\left(t-\tau\right)}\right]+\left(x+\xi\right)\exp\left[-\frac{\left(x+\xi\right)^2}{4\left(t-\tau\right)}\right]\right\} \quad (2.4.14)$$

$$N_x\left(x,t;\xi,\tau\right)= \\ =\frac{1}{4\sqrt{\pi}\left(t-\tau\right)^{\frac{3}{2}}}\left\{-\left(x-\xi\right)\exp\left[-\frac{\left(x-\xi\right)^2}{4\left(t-\tau\right)}\right]-\left(x+\xi\right)\exp\left[-\frac{\left(x+\xi\right)^2}{4\left(t-\tau\right)}\right]\right\} \quad (2.4.15)$$

2.5. A simplified version of Gronwall's lemma

Lemma 2.5.1. *If a continuous function* $y\left(t\right)$ *satisfies the integral inequality*

$$0\leqslant y\left(t\right)\leqslant c+\int_0^t\lambda\left(\tau\right)y\left(\tau\right)d\tau, \quad (2.5.1)$$

for some constant $c\geq 0$ *and a summable non-negative kernel* λ*, then*

$$0\leqslant y\left(t\right)\leqslant c\exp\left(\int_0^t\lambda\left(\tau\right)d\tau\right). \quad (2.5.2)$$

Proof.

Set $\Lambda\left(t\right)=\exp\left(-\int_0^t\lambda\left(\tau\right)d\tau\right)$ and multiply (2.5.1) by $\lambda\Lambda=-\dot{\Lambda}$, obtaining

$$y\lambda\Lambda+\dot{\Lambda}\int_0^t\lambda y d\tau\leqslant -c\dot{\Lambda} \quad (2.5.3)$$

i.e.

$$\frac{d}{dt}\left[\Lambda\int_0^t\lambda y\,d\tau\right]\leqslant -c\dot{\Lambda} \quad (2.5.4)$$

from which

$$\int_0^t\lambda y\,d\tau\leqslant c\left(\Lambda^{-1}-1\right), \quad (2.5.5)$$

providing the estimate of the r.h.s. of (2.5.1) leading to (2.5.2) □.

A slightly more general version of Gronwall's inequality is

$$0\leqslant y\left(t\right)\leqslant c+c_1\int_0^t\frac{y\left(\tau\right)}{\sqrt{t-\tau}}d\tau, \quad (2.5.6)$$

(the kernel is now of Abel type). Using the same technique employed for solving Abel's integral equation, one arrives at the following result ([24] , Lemma 17.7.1)

$$0\leqslant y\left(t\right)\leqslant c\left(1+2c_1\sqrt{T}\right)e^{\pi c_1^2 T}. \quad (2.5.7)$$

2.6. Computing the temperature gradient at the boundary

In many applications it is important to calculate the heat flux at a boundary where temperature is specified and to investigate its behaviour when $t \downarrow 0$ (i.e. at a corner point of the parabolic boundary). If the data match at that point and the boundary is not singular, then the flux will be continuous. We want to show this in a particularly simple case.

We consider the following model problem in a wedge:

Problem A.

$$u_{xx} - u_t = 0, \quad \alpha t < x, \quad 0 < t,$$
$$u(x,0) = -\beta x, \quad 0 < x,$$
$$u(\alpha t, t) = 0, \quad 0 < t,$$

where α, β are constants. Our aim is to compute $u_x(\alpha t, t)$. Dealing with more general data and a more general boundary (provided they are sufficiently regular) requires some more complicated calculations, but the procedure is the same. In particular we want to show that u_x is continuous at the corner:

$$\lim_{t\to 0} u_x(\alpha t, t) = -\beta. \tag{2.6.1}$$

Instead of Problem A, we consider

Problem B.

$$v_{xx} - v_t = 0, \quad \alpha t < x, \quad 0 < t,$$
$$v(x,0) = 0, \quad 0 < x,$$
$$v(\alpha t, t) = \alpha\beta t, \quad 0 < t,$$

having in mind the decomposition

$$u(x,t) = -\beta x + v(x,t). \tag{2.6.2}$$

Clearly (2.6.1) is equivalent to

$$\lim_{t\to 0} v_x(\alpha t, t) = 0. \tag{2.6.3}$$

We use the double layer potential (2.2.12) to represent the solution

$$v(x,t) = \int_0^t \mu(\tau)\Gamma_x(x,t;\alpha\tau,\tau)d\tau \tag{2.6.4}$$

and the jump relation (2.2.13) to obtain the integral equation for μ:

$$\alpha\beta t = -\frac{1}{2}\mu(t) - \frac{\alpha}{4\sqrt{\pi}}\int_0^t \frac{\mu(\tau)}{\sqrt{t-\tau}} e^{-\frac{\alpha^2}{4}(t-\tau)} d\tau. \tag{2.6.5}$$

We use this same equation to compute

$$\int_0^t \frac{\mu(\tau)}{\sqrt{t-\tau}} e^{-\frac{\alpha^2}{4}(t-\tau)} d\tau = -2\alpha\beta \int_0^t \frac{\tau}{\sqrt{t-\tau}} e^{-\frac{\alpha^2}{4}(t-\tau)} d\tau +$$
$$-\frac{\alpha}{2\sqrt{\pi}} \int_0^t\int_0^\tau \frac{\mu(\eta)}{\sqrt{(t-\tau)(\tau-\eta)}} e^{-\frac{\alpha^2}{4}(t-\eta)} d\eta d\tau. \tag{2.6.6}$$

We may interchange τ and $t-\tau$ in the first integral on the r.h.s. and exchange the integration order in the second integral, obtaining

$$\int_0^t \frac{\mu(\tau)}{\sqrt{t-\tau}} e^{-\frac{\alpha^2}{4}(t-\tau)} d\tau =$$
$$= -2\alpha\beta \int_0^t \frac{t-\tau}{\sqrt{\tau}} e^{-\frac{\alpha^2}{4}\tau} d\tau - \frac{\alpha\sqrt{\pi}}{2} \int_0^t \mu(\eta) e^{-\frac{\alpha^2}{4}(t-\eta)} d\eta. \tag{2.6.7}$$

Inserting (2.6.7) in (2.6.5), the latter becomes

$$\mu(t) = F(t) + \frac{\alpha^2}{4} \int_0^t \mu(\eta) e^{-\frac{\alpha^2}{4}(t-\eta)} d\eta, \tag{2.6.8}$$

with

$$F(t) = -2\alpha\beta t + \frac{\alpha^2\beta}{\sqrt{\pi}} \int_0^t \frac{t-\tau}{\sqrt{\tau}} e^{-\frac{\alpha^2}{4}\tau} d\tau, \tag{2.6.9}$$

which tends to zero (as expected) if $\alpha\beta \to 0$, and is simply proportional to β.
The last integral can be calculated by means of the transformation $\frac{\alpha}{2}\sqrt{\tau} = \vartheta$ and the result is:

$$F(t) = 2\beta\sqrt{t}\Big\{ -\alpha\sqrt{t} + 2\Big[\frac{1}{\sqrt{\pi}} e^{-\frac{\alpha^2}{4}t} +$$
$$+ erf\Big(\frac{\alpha\sqrt{t}}{2}\Big)\Big(\frac{\alpha\sqrt{t}}{2} - \frac{1}{\alpha\sqrt{t}}\Big)\Big]\Big\}. \tag{2.6.10}$$

This way of writing $F(t)$ emphasizes that α and β always multiply $\sqrt{t}$.
We can easily compute

$$\dot{F}(t) = -2\alpha\beta\Big[1 - erf\Big(\frac{\alpha}{2}\sqrt{t}\Big)\Big]. \tag{2.6.11}$$

Now we differentiate (2.6.8), getting the simple expression

$$\dot{\mu}(t) = \dot{F}(t) + \frac{\alpha^2}{4} F(t). \tag{2.6.12}$$

Since we know from (2.6.8) that $\mu(0) = 0$, we obtain the integral

$$\mu(t) = F(t) + \frac{\alpha^2}{4} \int_0^t F(\tau) d\tau. \tag{2.6.13}$$

Using (2.6.4) we compute

$$v_x(x,t) = \int_0^t \mu(\tau)\Gamma_{xx}(x,t;\alpha\tau,\tau)d\tau = -\int_0^t \mu(\tau)\Gamma_\tau(x,t;\alpha\tau,\tau)d\tau. \tag{2.6.14}$$

Noting that

$$\Gamma_\tau(x,t;\alpha\tau,\tau) = \frac{d}{d\tau}\Gamma(x,t;\alpha\tau,\tau) - \alpha\Gamma_\xi(x,t;\alpha\tau,\tau) =$$
$$= \frac{d}{d\tau}\Gamma(x,t;\alpha\tau,\tau) + \alpha\Gamma_x(x,t;\alpha\tau,\tau), \tag{2.6.15}$$

from (2.6.14) we get

$$\begin{aligned} v_x(x,t) &= \mu(\tau)\Gamma(x,t;\alpha\tau,\tau)|_0^t + \\ &+ \int_0^t \dot{\mu}(\tau)\Gamma(x,t;\alpha\tau,\tau)d\tau - \alpha\int_0^t \mu(\tau)\Gamma_x(x,t;\alpha\tau,\tau)d\tau. \end{aligned} \tag{2.6.16}$$

The first term is zero for all $x \neq \alpha t$.

Now we take the limit $x \to \alpha t+$. We know already that $\mu(t)$ has been constructed in such a way that the last term tends to $-\alpha^2\beta t$. In order to compute the integral containing $\dot{\mu}$ we use (2.6.12), obtaining the final expression

$$\begin{aligned} v_x(\alpha t,t) &= -\alpha^2\beta t - \frac{\alpha\beta}{2\sqrt{\pi}}\int_0^t \frac{1}{\sqrt{t-\tau}} e^{-\frac{\alpha^2}{4}(t-\tau)} \\ &\Big\{2\Big(1+\frac{\alpha^2\tau}{4}\Big)\Big[1-erf\Big(\frac{\alpha}{2}\sqrt{\tau}\Big)\Big] + \\ &+ \Big[erf\Big(\frac{\alpha}{2}\sqrt{\tau}\Big) - \frac{\alpha\sqrt{\tau}}{\sqrt{\pi}} e^{-\frac{\alpha^2}{4}\tau}\Big]\Big\}d\tau, \end{aligned} \tag{2.6.17}$$

evidently satisfying (2.6.3) for any α and β. Again we point out that $v_x(\alpha t,t)$ is proportional to β and vanishes as α tends to zero.

Bibliographical remarks.

There are many methods to compute solutions of initial-boundary-value problems for the heat equation (expansions in series of the eigenfunctions of the specific problem, Laplace or Fourier transforms, etc.) A very useful and classical book mainly devoted to that scope is[27] .

Chapter 3

The Stefan problem. Classical solutions

3.1. Self-similar solutions

(a) Self-similar solutions for the heat equation.

We look for a pair of functions $f(\xi)$, $\gamma(t)$ such that

$$u(x,t) = f(\gamma(t)\,x)$$

satisfies $u_{xx} = u_t$. Thus, excluding the trivial case $f = \textit{constant}$, we impose $\gamma^2 f'' = \dot{\gamma}\, x f'$, and we separate the variables

$$\frac{f''}{\xi f'} = \frac{\dot{\gamma}}{\gamma^3} \Rightarrow \frac{\dot{\gamma}}{\gamma^3} = -\lambda^2,\ \frac{f''}{f'} = -\lambda^2 \xi$$

with $\lambda \in \mathbb{R}$. From the first equation we obtain

$$\gamma(t) = \lambda^{-1}\left[2(t-t_0)\right]^{-\frac{1}{2}}, \qquad t > t_o. \tag{3.1.1}$$

The second equation leads to

$$f(\xi) = A\left[erf\left(\frac{\lambda\xi}{\sqrt{2}}\right) - erf\left(\frac{\lambda\xi_0}{\sqrt{2}}\right)\right]$$

with A, ξ_0 integration constants and

$$erf(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\,dy \qquad \left(\lim_{z\to\pm\infty} erf(z) = \pm 1\right). \tag{3.1.2}$$

Noting that $\lambda\xi = \lambda\gamma x = \dfrac{x}{\sqrt{2(t-t_0)}}$, we realise that the constant λ has no role and we can define the desired class of self-similar solutions:

$$u(x,t) = A\left\{erf\left(\frac{x}{2\sqrt{t-t_0}}\right) - erf(z_0)\right\} \tag{3.1.3}$$

depending on the three parameters A, t_0, z_0.

(b) Self-similar solutions to the one-phase Stefan problem.

We look for a pair (s,u) with u of the form (3.1.3), satisfying

$$u(s(t),t) = 0, \tag{3.1.4}$$

$$\left.\frac{\partial u}{\partial x}\right|_{x=s(t)} = -\dot{s}\,(t)\,, \qquad \text{(the limit is taken for } x \uparrow s\,(t)\text{)}\,. \tag{3.1.5}$$

The choice of the sign in (3.1.5) is compatible with the fact that the heat conducting phase is liquid, while the solid is uniformly at the phase change temperature (namely zero).

We set $t_0 = 0$ and we remark that all the level curves of (3.1.3) are parabolas in the (x, t) plane. Therefore we must seek $s\,(t)$ in the form $s = 2\alpha\sqrt{t}$. Imposing (3.1.5), since $\frac{\partial u}{\partial x} = A\frac{1}{\sqrt{\pi t}}e^{-\frac{x^2}{4t}}$, $\dot{s} = \frac{\alpha}{\sqrt{t}}$, we find

$$A = -\sqrt{\pi}\alpha e^{\alpha^2}$$

and we obtain a one parameter family of self-similar solutions:

$$u\,(x,t) = \sqrt{\pi}\alpha e^{\alpha^2}\left\{erf\,(\alpha) - erf\left(\frac{x}{2\sqrt{t}}\right)\right\} = 2\alpha e^{\alpha^2}\int_{\frac{x}{2\sqrt{t}}}^{\alpha} e^{-\eta^2}d\eta, \tag{3.1.6}$$

$$s\,(t) = 2\alpha\sqrt{t}. \tag{3.1.7}$$

The pair (3.1.6), (3.1.7) is sometimes referred to as Neumann's solution. Let us compute the limits for $t \downarrow 0$ and for $x \to 0$. Before doing that we remark that we can interpret (3.1.6), (3.1.7) in one of the following ways (see fig. 3.1.1):

(i) $\alpha > 0$, $x < 2\alpha\sqrt{t}$
Cauchy problem
($u > 0$)
(ii) $\alpha > 0$, $0 < x < 2\alpha\sqrt{t}$
($u > 0$) boundary value problem
(iii) $\alpha < 0$, $x < 2\alpha\sqrt{t}$
($u < 0$: supercooled liquid)

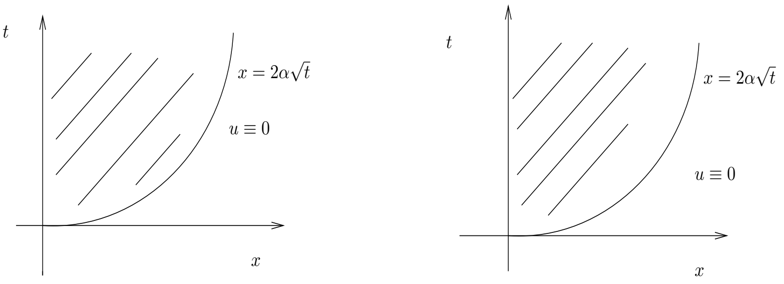
We also have the symmetric cases (the heat conducting phase is the solid)
(iv) $\alpha < 0$, $x > 2\alpha\sqrt{t}$
Cauchy problem
($u < 0$)
(v) $\alpha < 0$, $2\alpha\sqrt{t} < x < 0$
($u < 0$): boundary value problem
(vi) $\alpha > 0$, $x > 2\alpha\sqrt{t}$
($u > 0$: superheated solid)

We confine our attention to cases (i), (ii), (iii).

Case (i): $\alpha > 0$, $x < 2\alpha\sqrt{t}$

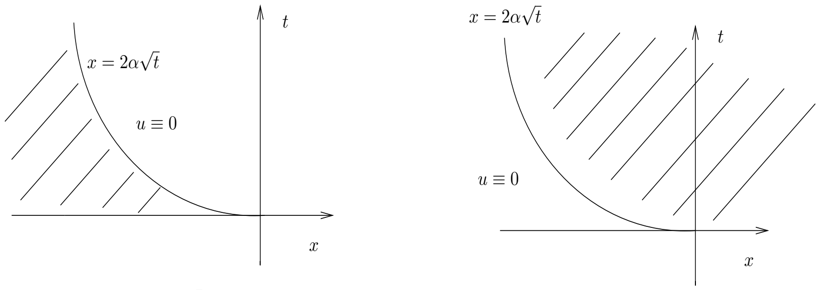
$$\lim_{t\downarrow 0} u\,(x,t) = 2\alpha e^{\alpha^2}\int_{-\infty}^{\alpha} e^{-\eta^2}d\eta \equiv u_0\,(\alpha)\,, \qquad \forall x < 0. \tag{3.1.8}$$

Thus for any $\alpha > 0$ (3.1.6), (3.1.7) solve the Cauchy problem with initial value $u\,(x,0) = u_0\,(\alpha)$ defined by (3.1.8) for $x < 0$.



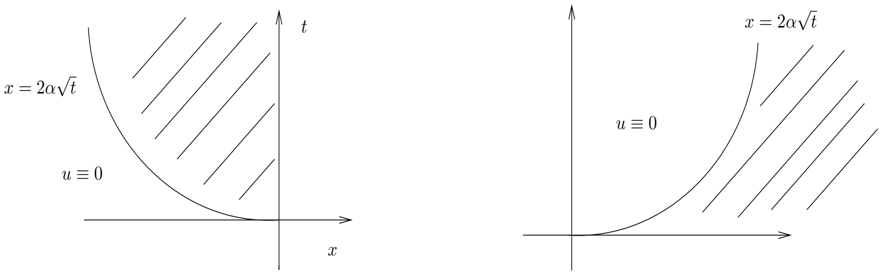
(i): $\alpha > 0,\ x < 2\alpha\sqrt{t}$
$(u > 0)$, Cauchy Problem

(ii): $\alpha > 0,\ 0 < x < 2\alpha\sqrt{t}$
$(u > 0)$, Boundary value problem



(iii): $\alpha < 0,\ x < 2\alpha\sqrt{t}$
$(u < 0)$, Supercooled liquid

(iv): $\alpha < 0,\ x > 2\alpha\sqrt{t}$
$(u < 0)$, Cauchy problem



(v): $\alpha < 0,\ 2\alpha\sqrt{t} < x < 0$
$(u < 0)$, Boundary value Problem

(vi): $\alpha > 0,\ x > 2\alpha\sqrt{t}$
$(u > 0)$, Superheated solid

Figure 3.1.1. *Self-similar solutions for melting (i), (ii); solidification of a supercooled liquid (iii); solidification (iv), (v); melting of a superheated solid (vi).*

Note that u is discontinuous at the origin (requiring some care in the definition of solution) and $\dot{s}$ is singular $\left(\dot{s} = \dfrac{\alpha}{\sqrt{t}}\right)$.

Case (ii): $\alpha > 0,\ 0 < x < 2\alpha\sqrt{t}$

$$\lim_{x \downarrow 0} u\,(0,t) = 2\alpha e^{\alpha^2} \int_0^{\alpha} e^{-\eta^2} d\eta \equiv u_1\,(\alpha) > 0. \tag{3.1.9}$$

Note that $u_1\,(\alpha) = u_0\,(\alpha) - \sqrt{\pi}\alpha e^{\alpha^2}$ and again $\dot{s}(t)$ has a singular behaviour at the origin.

Case (iii): $\alpha < 0,\ x < 2\alpha\sqrt{t}$

The limit of u for $t \downarrow 0,\ x < 0$ is the same function $u_0\,(\alpha)$ defined by (3.1.8), but this time $u_0\,(\alpha) < 0$.

Now we want to solve the *inverse problems*:

Problem (i):
Given $U_0 \geq 0$, find α such that $u_0(\alpha) = U_0$.

Problem (ii):
Given $U_1 \geq 0$, find α such that $u_1(\alpha) = U_1$.

Problem (iii):
Given $U_0 < 0$, find α such that $u_0(\alpha) = U_0$.
Let us anticipate the conclusion:

Theorem 3.1.1. *Problems (i), (ii) have one unique solution* $(\alpha \geq 0)$ *for any choice of* $U_0 \geq 0$, $U_1 \geq 0$. *Problem (iii) has one and only one solution* $(\alpha < 0)$ *if* $U_0 \in (-1, 0)$ *and no solutions for* $U_0 \leq -1$.

Proof.
Recalling the definition (3.1.8) of $u_0(\alpha)$ we have to study the equation

$$u_0(\alpha) = 2\alpha e^{\alpha^2} \int_{-\infty}^{\alpha} e^{-\eta^2} d\eta = \sqrt{\pi}\alpha e^{\alpha^2}(1 + uf\alpha) = U_0. \tag{3.1.10}$$

We have

$$u_0'(\alpha) = 2e^{\alpha^2}\left(1 + 2\alpha^2\right) \int_{-\infty}^{\alpha} e^{-\eta^2} d\eta + 2\alpha, \tag{3.1.11}$$

$$u_0''(\alpha) = 4\alpha e^{\alpha^2}\left(3 + 2\alpha^2\right) \int_{-\infty}^{\alpha} e^{-\eta^2} d\eta + 2(1 + 2\alpha^2) + 2 \tag{3.1.12}$$

and we realize that all the derivatives of $u_0(\alpha)$ are positive for $\alpha > 0$. Clearly $\lim\limits_{\alpha \to +\infty} u_0(\alpha) = +\infty$ and therefore the equation $u_0(\alpha) = U_0$ is uniquely solvable for any $U_0 \geq 0$ (of course $U_0 = 0$ corresponds to the trivial solution $u = 0$, $s = 0$).

The same analysis and the same conclusion hold for Problem (ii).

Solving (3.1.10) for $U_0 < 0$ is not equally easy (Problem (iii)).

From (3.1.11) and (3.1.12) we see that $u_0'(0) = \sqrt{\pi}$, $u_0''(0) = 4$, but the behaviour of $u_0'(\alpha)$, $u_0''(\alpha)$ is not immediately evident for $\alpha < 0$ (clearly all possible solutions of (3.1.10) for $U_0 < 0$ are negative, since $u_0(\alpha)$ has the same sign as α).

However we can establish that $u_0(\alpha)$ has the graph shown in fig. 3.1.2.

Let us first compute the limit

$$\lim_{\alpha \to -\infty} u_0(\alpha) = \lim_{\alpha \to -\infty} 2\frac{\int_{-\infty}^{\alpha} e^{-\eta^2} d\eta}{\frac{e^{-\alpha^2}}{\alpha}} = \lim_{\alpha \to -\infty} 2\frac{1}{-2 - \frac{1}{\alpha^2}} = -1. \tag{3.1.13}$$

Next we rewrite (3.1.11) as

$$u_0'(\alpha) = u_0\frac{1}{\alpha}\left(1 + 2\alpha^2\right) + 2\alpha \tag{3.1.14}$$

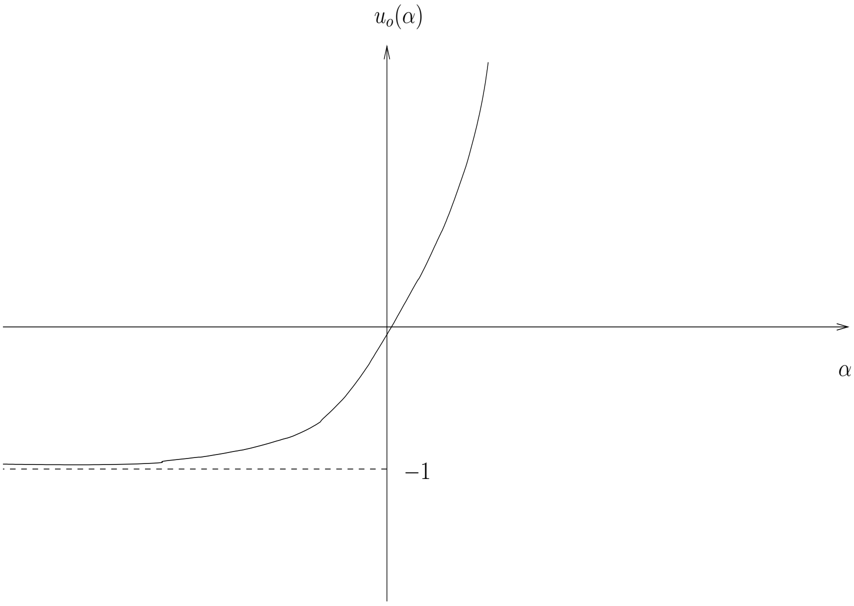


Figure 3.1.2. *Graph of the function* $u_0(\alpha)$ *in (3.1.10).*

and (3.1.12) as

$$u_0''(\alpha) = u_0' \frac{1}{\alpha}\left(1 + 2\alpha^2\right) + u_0 \frac{2\alpha^2 - 1}{\alpha^2} + 2 \tag{3.1.15}$$

If u_0' can vanish for some $\hat{\alpha} < 0$, then

$$u_0\left(\hat{\alpha}\right) = -\frac{2\,\hat{\alpha}^2}{1 + 2\,\hat{\alpha}^2} \in (-1, 0)$$

and consequently

$$u_0''\left(\hat{\alpha}\right) = \frac{4}{1 + 2\,\hat{\alpha}^2} > 0.$$

Therefore $u_0\left(\hat{\alpha}\right)$ can only be a minimum, thus contradicting (3.1.13). We conclude that $u_0'(\alpha) > 0$ also for $\alpha < 0$, which completes the proof of the theorem. □

As an exercise rewrite (3.1.12) in the form $u_0''(\alpha) = 4\alpha^2(u_0 + 1) + 6u_0 + 4$ and show that $u_0''(\alpha)$ tends to zero as $\alpha \to -\infty$.

The physical interpretation of Theorem 3.1.1 is easy. While melting of ice due to a given positive initial temperature of the confining liquid (Problem (i)) or to a prescribed positive temperature on the surface $x = 0$ (Problem (ii)) is always possible, the conversion of a supercooled liquid at a given initial negative temperature into ice at zero temperature proceeds with a parabolic interface only if the supercooled liquid is not “too cold”.

There is a large literature devoted to various types of supercooling.

We just quote[49] for a survey.

3.2. The one-dimensional one-phase Stefan problem

(a) Statement of the problem

Problem 2.1.

Find a pair (s,u) such that, for some $T>0$, $s\in C\,[0,T]\cap C^1\,[0,T]$, $u\in C\left(\overline{Q}_T\right)$, $u\in C^{2,1}\left(Q_T\right)$, $\dfrac{\partial u}{\partial x}$ continuous up to $x=s\,(t)$, $t\in[0,T]$, satisfying

$$u_{xx}-u_t=0,\quad \text{in } Q_T=\left\{(x,t)\in\mathbb{R}^2/0<x<s\,(t)\,,0<t<T\right\} \tag{3.2.1}$$

$$s\,(0)=b>0, \tag{3.2.2}$$

$$u\,(x,0)=h\,(x)\,,\ 0<x<b, \tag{3.2.3}$$

$$u\,(0,t)=f\,(t)\,,\ 0<t<T, \tag{3.2.4}$$

$$u\,(s\,(t)\,,t)=0,\ 0<t<T, \tag{3.2.5}$$

$$u_x\,(s\,(t)\,,t)=-\,\dot{s}\,(t)\,,\ 0<t<T. \tag{3.2.6}$$

Condition (3.2.4) may be replaced e.g. by

$$u_x\,(0,t)=g\,(t) \tag{3.2.7}$$

We will also consider the case $s\,(0)=b=0$, thus dropping the initial condition (3.2.3).

There are two main classes of problems:

Problem 2.1A

with sign restrictions on the data ($h\geq 0$, $f\geq 0$ or $g\leq 0$).

Problem 2.1B

with no sign restrictions.

In the framework of phase change we can say that if we do not impose the "correct" sign of the data, we allow supercooling.

However Problem 2.1B makes sense in a variety of cases, since, as we shall see, free boundary problems in areas quite far from thermodynamics can be given the form (3.2.1)-(3.2.6), even if we cannot attach a physical meaning to the sign of the data.

We anticipate that there is a fundamental difference between Problem 2.1A and Problem 2.1B: the former is solvable globally in time, the latter can develop various kinds of singularities in a finite time (or it can have a solution for all $T>0$, or it can have no solution at all).

A final remark concerns the condition $u \in C\left(\overline{Q}_T\right)$, that implies matching conditions for the data, but can be relaxed in many ways.

(b) Global heat balance (a weaker version of Stefan's condition).

Multiply equation (3.2.1) by x and for any $t \in (0,T)$ integrate over the domain Q_t. Using the identity $xu_{xx} = (xu_x - u)_x$, we can say that

$$0 = \int_{Q_t} x\left(u_{xx} - u_t\right)\, dx d\tau = \oint_{\partial Q_t} \left[\left(xu_x - u\right)\, d\tau + xu\, dx\right]$$

Hence

$$\int_0^{s(t)} xu\left(x,t\right)\, dx = \int_0^b xh\left(x\right)\, dx + \int_0^t f\left(\tau\right)\, d\tau - \frac{1}{2}\left(s^2\left(t\right) - b^2\right). \tag{3.2.8}$$

If condition (3.2.7) is prescribed instead of (3.2.4), we integrate directly (3.2.1) and obtain

$$\int_0^{s(t)} u\left(x,t\right)\, dx = \int_0^b h\left(x\right)\, dx - \int_0^t g\left(\tau\right)\, d\tau - \frac{1}{2}\left(s\left(t\right) - b\right) \tag{3.2.9}$$

which is clearly readable in terms of heat balance: the heat stored in the phase at time t is the one at time $t = 0$ plus the heat that entered the system through $x = 0$ in the time interval $(0,t)$ and minus the latent heat needed to produce phase change in the layer of thickness $s\left(t\right) - b$.

Equation (3.2.8) is also a kind of balance formulated in terms of weighted averages.

Both (3.2.8) and (3.2.9) are weaker form of the Stefan condition, because they do not involve $\dot{s}$ nor $u_x\left(s\left(t\right), t\right)$.

However, if we know that $s\left(t\right)$ is Lipschitz continuous, then $u_x\left(s\left(t\right), t\right)$ is continuous and from (3.2.8) or (3.2.9) we may compute the limit of the difference quotient of $s\left(t\right)$, proving that $\dot{s} = -u_x\left(s\left(t\right), t\right)$ and therefore that s is C^1. Thus (3.2.8), (3.2.9) are actually *equivalent* to the Stefan condition, provided we add the requirement of Lipschitz continuity of s.

Remark 3.2.1. We have not used the condition $b > 0$. □

(c) Stefan Problem 2.1A (melting with no undercooling): existence

For the time being we refer to the case

$$s\left(0\right) = b > 0 \tag{3.2.10}$$

and we assume that $f\left(t\right)$, $h\left(x\right)$ are continuous and nonnegative, and

$$0 \leq h\left(x\right) \leq H\left(b - x\right) \tag{3.2.11}$$

for some constant $H \geq 0$.

A minor assumption is $f\left(0\right) = h\left(0\right)$.

A first a-priori result is

Proposition 3.1. *For any solution of Problem 2.1A we have $u \geq 0$, $\dot{s} \geq 0$. If h or f are not identically zero in a neighborhood of* t $= 0$*, then $u > 0$ in Q_T and $\dot{s} > 0$ for $t > 0$.*

Proof.

A simple consequence of Theorems 2.1.2 and 2.1.3. □

Now we prove existence.

Theorem 3.2.1. *Under the assumptions (3.2.10), (3.2.11) Problem 2.1A has at least one solution.*

Proof.

For any given $T > 0$ we consider the set

$$\Sigma(A) = \left\{ s \in C[0,T] \mid s(0) = b,\ 0 \leq \frac{s(t') - s(t'')}{t' - t''} \leq A,\ 0 \leq t' < t'' \leq T \right\}. \tag{3.2.12}$$

If s is *prescribed* in $\Sigma(A)$ the problem (3.2.1), (3.2.3), (3.2.4), (3.2.5) is uniquely solvable (Thm. 2.1.4), Chapt.2 and $u_x(s(t), t)$ exists continuous. Thus we can define the mapping $\tau : s \in \Sigma(A) \to \sigma$ by means of

$$\dot{\sigma} = -u_x(s(t), t), \quad \sigma(0) = b. \tag{3.2.13}$$

Note that if s is a fixed point of τ (i.e. $s = \tau s$), then (3.2.6) is satisfied and the pair (s, u) is a solution of Problem 2.1A. Thus we look for the fixed points of τ. The plan is to show that for a suitable choice of A

(i) $\tau\Sigma(A) \subset \Sigma(A)$,

(ii) τ is completely continuous, i.e. it is continuous and $\overline{\tau\Sigma(A)}$ is compact in the selected topology.

Since $\Sigma(A)$ is compact, it will be enough to show continuity. Then the existence of at least one fixed point in $\Sigma(A)$ will be guaranteed by Schauder's theorem.

The first target is easy: we need an estimate for $u_x(s(t), t)$.

From (Thm. 2.1.3), Chapt.2 we can immediately see that

$$u \geq 0, \quad u_x(s(t), t) \leq 0 \Rightarrow \dot{\sigma}(t) \geq 0. \tag{3.2.14}$$

In order to get a lower estimate for $u_x(s(t), t)$ we use the so-called technique of *barriers.* Take t_0 arbitrarily in $(0, T]$ and compare the solution u of (3.2.1), (3.2.3), (3.2.4), (3.2.5) with the linear function

$$v(x, t_0) = -A(x - s(t_0)) \tag{3.2.15}$$

which is also a solution of (3.2.1). We choose A in such way that $v(x, t_0) \geq u(x, t)$ in Q_{t_0} (by construction $v(s(t_0), t_0) = u(s(t_0), t_0)$ and for this reason the comparison function v is called a *barrier* for u).

Since $s(t) \leq s(t_0)$ in $(0, t_0)$, we have $v(s(t), t_0) \geq 0 = u(s(t), t)$.

If we take $A \geq H$ in (3.2.11), then $v(x, t_0) \geq H(b - x) \geq u(x, 0)$.

Finally, if $bA \geq \sup\limits_{t \in (0,T)} f(t) = F(t)$, then we have also $v(0, t_0) \geq u(0, t)$ in $(0, t_0)$. Therefore the inequality $v(x, t_0) \geq u(x, t)$ in Q_{t_0} is a trivial consequence of the maximum principle. Note the use of the assumption $b > 0$.

At this point we use the coincidence of v and u in $(s(t_0), t_0)$ to infer that

$$-A = v_x \le u_x(s(t_0), t_0). \tag{3.2.16}$$

Recalling that t_0 is arbitrary, we conclude that for all t in $(0, T]$ we have

$$A(s(t) - x) \ge u(x,t) \ge 0, \quad 0 \le x \le s(t), \tag{3.2.17}$$

$$-A \le u_x(s(t), t) \Rightarrow \dot{\sigma}(t) \le A, \tag{3.2.18}$$

with

$$A = \max\left(H, \frac{1}{b} \sup_{t\in(0,T)} f(t)\right). \tag{3.2.19}$$

Thus we have proved (i) with A given by (3.2.19).

In order to prove the continuity of the mapping τ, we start from the identity

$$\oint\limits_{\partial Q_t} [(xu_x - u)\, d\tau + xu\, dx] = 0 \tag{3.2.20}$$

(already introduced in (b)), in connection with $u_x(s(t), t) = -\dot{\sigma}(t)$.

For a pair of functions s_1, s_2 taken in $\Sigma(A)$ we consider the corresponding functions $u_1(x,t)$, $u_2(x,t)$ and for each of them we write (3.2.20), namely

$$\int_0^t s_i(\tau)\, \dot{\sigma_i}(\tau)\, d\tau - \int_0^{s_i(t)} u_i(x,t)\, dx + \int_0^b xh(x)\, dx - \int_0^t f(\tau)\, d\tau = 0, \quad i = 1, 2 \tag{3.2.21}$$

and by substraction we get

$$\int_0^t s_1(\tau)(\dot{\sigma_1}(\tau) - \dot{\sigma_2}(\tau))\, d\tau + \int_0^t (s_1(\tau) - s_2(\tau))\, \dot{\sigma_2}(\tau)\, d\tau = \tag{3.2.22}$$

$$= \int_0^{\alpha(t)} (u_1(x,t) - u_2(x,t))\, dx + (-1)^{j+1} \int_{\alpha(t)}^{\beta(t)} u_j(x,t)\, dx,$$

where $\alpha(t) = \min(s_1(\tau), s_2(\tau))$, $\beta(t) = \max(s_1(\tau), s_2(\tau))$, and $j = 1$ if $\beta = s_1$, $j = 2$ if $\beta = s_2$.

Our aim is to arrive at an inequality of the type

$$\|\sigma_1 - \sigma_2\| \le C\, \|s_1 - s_2\| \tag{3.2.23}$$

with $\|\cdot\|$ denoting the norm of $C[0,T]$ and C being a positive constant depending on A, T, and on $b > 0$.

Clearly the most delicate term in (3.2.22) is the first one. We can approach our target with an integration by parts replacing that term with

$$s_1(t)[\sigma_1(t) - \sigma_2(t)] - \int_0^t \dot{s}_1(\tau)[\sigma_1(\tau) - \sigma_2(\tau)]\, d\tau \tag{3.2.24}$$

(recall that $\dot{s}_1 \in L^\infty$ with $\|\dot{s}_1\|_{L^\infty} \le A$).

Next we have to estimate the difference $u_1 - u_2$ in the domain $0 < x < \alpha(t)$, $0 < t < T$. The difference of the data is zero for $t = 0$ and $x = 0$. For $x = \alpha(t)$ we have $u_i(\alpha(t), t) = 0$ if $s_i(t) = \alpha(t)$ and $u_j(\alpha(t), t) \le A(\beta(t) - \alpha(t))$ for $j \ne i$, because of (3.2.17). The maximum principle provides the desired inequality:

$$|u_1(x,t) - u_2(x,t)| \le A \|s_1 - s_2\|_t , \tag{3.2.25}$$

where $\|\cdot\|_t$ denotes the sup in $(0,t)$.

For u_j in (α, β) we use again (3.2.17). Passing to the absolute values in (3.2.22), and recalling (3.2.24) , (3.2.25), we obtain the inequality

$$s_1(t)\,|\sigma_1(t) - \sigma_2(t)| \le A \int_0^t |\sigma_1(\tau) - \sigma_2(\tau)|\, d\tau +$$

$$A \int_0^t |s_1(\tau) - s_2(\tau)|\, d\tau + \alpha(t)\, \|s_1 - s_2\|_t + \frac{1}{2} A \left|s_1^2(t) - s_2^2(t)\right| . \tag{3.2.26}$$

Now we can use (once more in a crucial way) assumption (3.2.10) ($b > 0$) and we note that $\alpha(t) \le b + AT$, $\frac{1}{2}(s_1(t) + s_2(t)) \le b + AT$, obtaining

$$|\sigma_1(t) - \sigma_2(t)| \le \frac{A}{b} \int_0^t |\sigma_1(\tau) - \sigma_2(\tau)|\, d\tau + \tag{3.2.27}$$

$$+\frac{1}{b}\left[AT + b + AT + A(b + AT)\right] \|s_1 - s_2\|_t .$$

Gronwall's inequality leads eventually to (3.2.23) and at the same time to the conclusion of the existence proof. □

Exercise 2.1.

Prove the analogous theorem with (3.2.7) replacing (3.2.4).

(d) Stefan problem 2.1A: continuous, monotone dependence and uniqueness

Theorem 3.2.2. ***(monotone dependence on the data).*** *Let (b_1, h_1, f_1), (b_2, h_2, f_2) be a pair of data satisfying the assumption of Theorem 3.2.1 and such that*

$$b_1 \le b_2 \tag{3.2.28}$$

$$h_1(x) \le h_2(x) \qquad in\ \ (0, b_1) \tag{3.2.29}$$

$$f_1(t) \le f_2(t) . \tag{3.2.30}$$

Then

$$s_1(t) \le s_2(t) , \tag{3.2.31}$$

$$u_1(x,t) \le u_2(x,t) \qquad in\ 0 < x < s_1(t),\ t > 0. \tag{3.2.32}$$

Moreover, if

$$b_1 < b_2 \tag{3.2.33}$$

then

$$s_1(t) < s_2(t). \tag{3.2.34}$$

Proof.

Let us first consider the stronger version of the theorem, i.e. (3.2.33). As a preliminary we examine the trivial case $h_1 = h_2 = f_1 = f_2 = 0$. If the initial and boundary data are zero, since the value of u on the free boundary is also zero, the maximum principle forces u to be identically zero with the obvious consequence that s is constant. Thus $(b, 0)$ is the only solution to the trivial case and comparing trivial solutions is also trivial.

Now we may suppose that the set of larger data do not produce a trivial solution: this implies that $\dot{s_2} > 0$ for $t > 0$, and $u_2 > 0$ at inner points. We know that $\dot{s_1}$, $\dot{s}_2$ are both bounded in $[0, A]$ and therefore there is a time interval $(0, t^*)$ in wich $s_1(t) < s_2(t)$, with $t^* \geq \dfrac{b_2 - b_1}{A}$ (note that, since at least h_2 or f_2 are not identically zero, A has to be positive).

Suppose that for some finite t^* the two boundaries intersect each other for the first time and compare u_1, u_2 in the smaller domain.

By assumption $u_1 - u_2 \leq 0$ for $t = 0$ in $(0, b_1)$, $u_1 - u_2 \leq 0$ for $x = 0$ in $(0, t^*)$ and $u_1 - u_2 = -u_2 < 0$ on $x = s(t)$ in $(0, t^*)$.

The intersection point $(s(t^*), t^*)$ is such that we may apply Theorem 2.1.3, Chapt.2 concluding that $(u_{1x} - u_{2x})(s(t^*), t^*) > 0$, implying that $\dot{s}_2(t^*) > \dot{s}_1(t^*)$. Such inequality is not compatible with the assumption that t^* is a point of absolute minimum for $s_2 - s_1$ in $[0, t^*]$. Thus (3.2.34) is proved and (3.2.32) follows at once.

The above argument fails if $b_1 = b_2$, because the starting point of both boundaries could be an accumulation point of intersections.

If $b_1 = b_2 = b > 0$, we construct a sequence of dominating solutions $\left(s^\delta, u^\delta\right)$ corresponding to the data

$$b^\delta = b + \delta, \quad h^\delta(x) = \begin{cases} h_2(x), & x \in [0, b] \\ 0, & x \in [b, b + \delta] \end{cases}, \qquad f^\delta(t) = f_2(t). \tag{3.2.35}$$

We know that for each $\delta > 0$ at least one solution $\left(s^\delta, u^\delta\right)$ of Problem 2.1A exists. From the previous monotonicity result we conclude that

$$s_1 < s^\delta, \qquad s_2 < s^\delta, \qquad u_1 \leq u^\delta, \qquad u_2 \leq u^\delta. \tag{3.2.36}$$

Now we write equation (3.2.8) for the pairs $\left(s^\delta, u^\delta\right)$, (s_2, u_2) and take the difference, obtaining

$$\frac{1}{2}\left(s^\delta(t) - s_2(t)\right)\left(s^\delta(t) + s_2(t)\right) =$$

$$= \frac{1}{2}\delta(2b + \delta) - \int_0^{s_2(t)} x\left(u^\delta(x,t) - u_2(x,t)\right) dx - \int_{s_2(t)}^{s^\delta(t)} x\, u^\delta(x,t)\, dx \leq$$

$$\leq \frac{1}{2}\delta(2b + \delta). \tag{3.2.37}$$

Since $s^{\delta}(t) + s_2(t) \geq 2b + \delta$ we conclude that

$$s_1(t) < s^{\delta}(t) \leq s_2(t) + \delta \tag{3.2.38}$$

and letting δ tend to zero we complete the proof. □

Corollary 3.2.1. ***Uniqueness.*** *The same assumptions of the existence theorem (Theorem 3.2.1) guarantee uniqueness.*

Exercise 2.2.

Study Problem 2.1A with Neumann data for $x = 0$.

Remark 3.2.2. Theorem 3.2.2 extends to the case $b_1 = 0$ (and possibly $b_2 = 0$) and in such a case we must consider it (at this stage of our exposition) an a-priori result. As a matter of fact, in the proof we have used (3.2.8) (valid also for $b = 0$) and we have applied the existence theorem only for the dominating solutions $\left(s^{\delta}, u^{\delta}\right)$, having in any case $s^{\delta}(0) \geq \delta > 0$. □

Theorem 3.2.3. ***(Continuous dependence).*** *Let (s_1, u_1), (s_2, u_2) be the solutions of Problem 2.1A corresponding to the respective sets of data (b_1, h_1, f_1), (b_2, h_2, f_2) both satisfying the assumption of Theorem 3.2.1. Let $b = \min(b_1, b_2)$, $A = \max(A_1, A_2)$, with A_1, A_2 defined as in (3.2.19). Then there exists a constant $C = C(b, T, A)$ such that*

$$\|s_1 - s_2\| \leq C(\|h_1 - h_2\| + |b_1 - b_2| + \|f_1 - f_2\|),$$

$$\|u_1 - u_2\| \leq C(\|h_1 - h_2\| + |b_1 - b_2| + \|f_1 - f_2\|).$$

When computing $\|h_1 - h_2\|$ the functions h_1, h_2 are given zero extension beyond b_1, b_2 if necessary.

The result is valid also when Dirichlet data are replaced by Neumann data.

Proof.

We sketch the proof for the Dirichlet data. We have to start from (3.2.8), from which we immediately deduce the inequality

$$b\|s_1 - s_2\|_t \leq C[|b_1 - b_2| + \|h_1 - h_2\| + \|f_1 - f_2\|] + \int_0^{\alpha(t)} x|u_1(x,t) - u_2(x,t)|dx + \int_{\alpha(t)}^{\beta(t)} x u_j dx,$$

where α, β, j have the same meaning as in the proof of Theorem 3.2.2 and from now on C denotes a constant depending on b, T, A.

Let us estimate the last two terms, exploiting the information

$$|u_1(\alpha(t),t) - u_2(\alpha(t),t)| \leq A(\beta - \alpha).$$

Setting $v(x,t) = u_1(x,t) - u_2(x,t)$ we use the inequality

$$|v| \leq v_1 + v_2,$$

where v_1 solves the heat equation with data

$$v_1(0,t) = |f_1(t) - f_2(t)|, \quad v_1(x,0) = |h_1(x) - h_2(x)| \text{for } x \in (0,b),$$

$$v_1(\alpha(t), t) = 0,$$

and v_2 is the solution of the heat equation with data on $t = 0$ and on $x = 0$, and such that $v_2(\alpha(t), t) = A(\beta - \alpha)$.

The function v_1 is easily estimated by means of the maximum principle.

In turn v_2 is dominated by the solution v_3 of the initial boundary-value problem in the unbounded domain $-\infty < x < \alpha(t)$, $t \in (0, T)$ with the data $A\|\beta - \alpha\|_t$ on $x = \alpha(t)$ and vanishing for $t = 0$. We recall that $\alpha(t)$ is Lipschitz (with a Lipschitz constant not greater than A), thus we may use the representation

$$v_3(x, t) = \int_0^t \mu(\tau)\Gamma_x(x, t; \alpha(\tau), \tau)d\tau,$$

with μ solving the integral equation

$$A\|\beta - \alpha\|_t = \frac{1}{2}\mu(t) + \int_0^t \mu(\tau)\Gamma_x(\alpha(t), t; \alpha(\tau), \tau)d\tau.$$

Recalling (2.5.6), we deduce

$$\|\mu\| \le C\|\beta - \alpha\|_t$$

and consequently

$$\int_{-\infty}^{\alpha(t)} v_3(x, t) \le C\int_0^t \frac{\|\beta - \alpha\|_\tau}{\sqrt{t - \tau}}d\tau.$$

Thus the term $\int_0^{\alpha(t)} x|u_1 - u_2|dx$ has the estimate

$$\int_0^{\alpha(t)} x|u_1 - u_2|dx \le C\Big[|b_1 - b_2| + \|h_1 - h_2\| + \|f_1 - f_2\| + \int_0^t \frac{\|\beta - \alpha\|_\tau}{\sqrt{t - \tau}}d\tau\Big].$$

Similarly we can say that $u_j(x, t)$ for $x \in (\alpha, \beta)$ is majorized by $\|h_1 - h_2\| + v_4$, where v_4 solves the heat equation for $x > \alpha(t)$, $t > 0$ with data $A\|\beta - \alpha\|_t$ on $x = \alpha(t)$ and vanishing for $t = 0$. Hence we get for v_4 precisely the same estimate as v_3.

Putting all these elements together we arrive at the inequality

$$\|s_1 - s_2\|_t \le C\Big[|b_1 - b_2| + \|h_1 - h_2\| + \|f_1 - f_2\| + \int_0^t \frac{\|s_1 - s_2\|_\tau}{\sqrt{t - \tau}}d\tau\Big],$$

again of the type (2.5.6) and yielding the desired continuous dependence result. The similar inequality for $\|u_1 - u_2\|$ is now trivial. □

(e) Stefan problem 2.1A: appearance of a phase ($b = 0$)

When the thickness of the conducting phase is initially zero of course we drop the initial condition (3.2.3).

The assumptions we make on f, besides $f \ge 0$ are

$$f \in C\,[0, T]\,, \quad f \text{ not identically zero in a neighbourhood of } t = 0. \tag{3.2.39}$$

Remark 3.2.3. Differentiating (3.2.5) and using (3.2.6)we deduce that at regular points of the free boundary

$$u_t\,(s\,(t)\,, t) = -\dot{s}^2\,(t)\,. \tag{3.2.40}$$

Thus we expect that $\dot{s}(0)$ will exist if $f \in C^1[0,\tau]$ and $f(0) = 0$. Since (3.2.39) is quite general, the free boundary is likely to be singular at the origin. We may have singularities for $t = 0$ also when $b > 0$ but condition (3.2.11) is violated, a case we have not treated. $\square$

Remark 3.2.4. Uniqueness is guaranteed a-priori by the monotone dependence on f, which applies also in this case (Remark (3.2.2)). $\square$

Now we want to prove existence.

First of all we deduce an a-priori lower bound for $s(t)$.

Lemma 3.2.1. *Let* (s,u) *be a solution of Problem 2.1A with* $b \geq 0$ *and* $h(x) \equiv 0$ *if* $b > 0$. *Then*

$$s(t) > \rho(t) = \left\{ \frac{2}{1 + \|f\|_t} \int_0^t f(\tau)\, d\tau \right\}^{\frac{1}{2}}. \tag{3.2.41}$$

Proof.

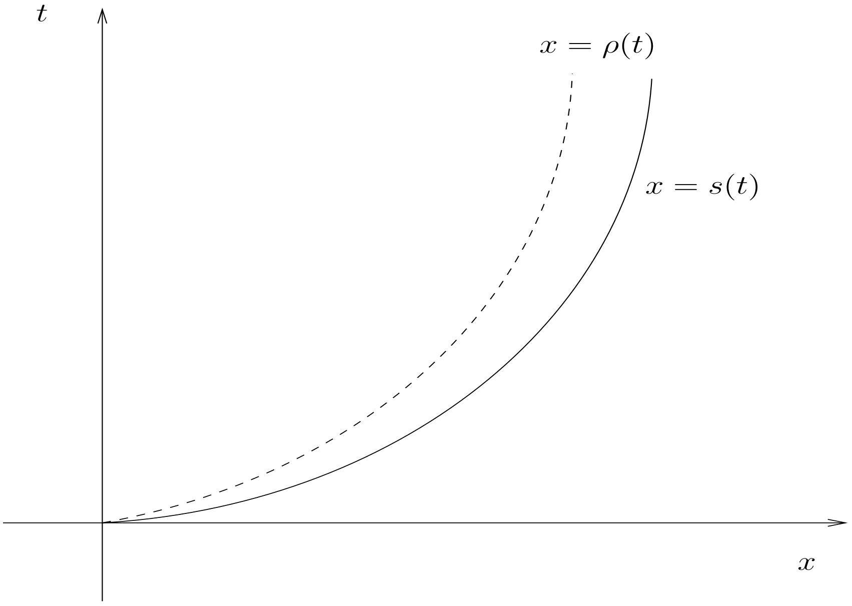


Figure 3.2.1. *Lower bound for the free boundary.*

We start from (3.2.8), now reduced to

$$\frac{1}{2}s^2(t) = \frac{1}{2}b^2 + \int_0^t f(\tau)\, d\tau - \int_0^{s(t)} x\, u(x,t)\, dx, \tag{3.2.42}$$

and we use the obvious estimate (recall (3.2.39) and the maximum principle)

$$0 < u(x,t) < \|f\|_t, \qquad 0 < x < s(t), \qquad t > 0$$

to obtain

$$\frac{1}{2}(1 + \|f\|_t)\, s^2(t) > \int_0^t f(\tau)\, d\tau. \quad \square \tag{3.2.43}$$

In order to prove existence it will be enough to show existence for a sufficiently small time interval, because, once we have reached a time $\tau_0 > 0$, it will be clear that $u(x, \tau_0)$ satisfies (3.2.11) in $(0, s(\tau_0))$ and we are back to the previous case.

We split the existence proof in two parts.

Theorem 3.2.4. ***(First case of existence).*** *Suppose (3.2.39) and*

$$\frac{\|f\|_t}{\rho(t)} \quad \textit{bounded in } (0, T). \tag{3.2.44}$$

Then Problem 2.1A with $b = 0$ has a solution and moreover

$$0 < \dot{s}(t) \leq \sup_{t\in(0,T)} \frac{\|f\|_t}{\rho(t)}. \tag{3.2.45}$$

Proof.

Take a sequence $\{b_n\}$ strictly decreasing to zero. For each b_n we can find the solution of the problem in fig. 3.2.2

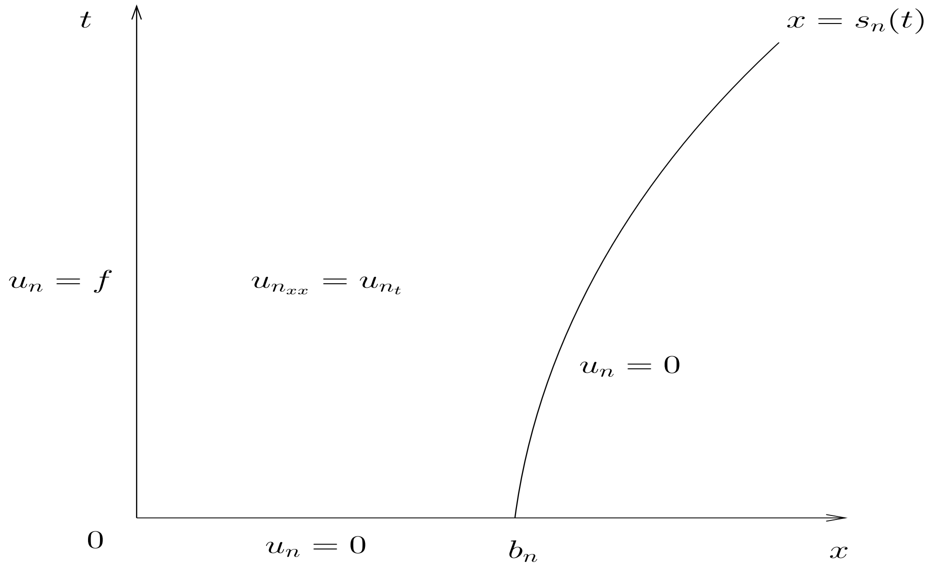


Figure 3.2.2. *Construction of a comparison function.*

We know that the pairs (s_n, u_n) depend monotonically on n, and we also know from 3.2.1 that the sequence $\{s_n\}$ is bounded from below by $\rho(t) > 0$. In order to get some information on the limit, for any $t^* \in (0, T)$ and each n we look for a linear barrier of the form

$$v_n(x, t^*) = \kappa(s_n(t^*) - x). \tag{3.2.46}$$

The condition guaranteeing that $v_n(x, t^*)$ is a barrier for u_n is

$$v_n(0, t^*) = \kappa\, s_n(t^*) \geq \|f\|_{t^*}. \tag{3.2.47}$$

Thanks to 3.2.1 we can say that (3.2.47) holds, provided that

$$\kappa = \sup_{t\in(0,T)} \frac{\|f\|_t}{\rho(t)} \tag{3.2.48}$$

which leads to the uniform estimate

$$0 < \dot{s}_n(t) \leq \kappa \quad \text{in } (0,T). \tag{3.2.49}$$

Hence $\{s_n\}$ decreases to a Lipschitz continuous function $s(t)$, such that $s(0)=0$, $s(t) > \rho(t)$. If $u(x,t)$ denotes the solution of the problem in fig. 3.2.3

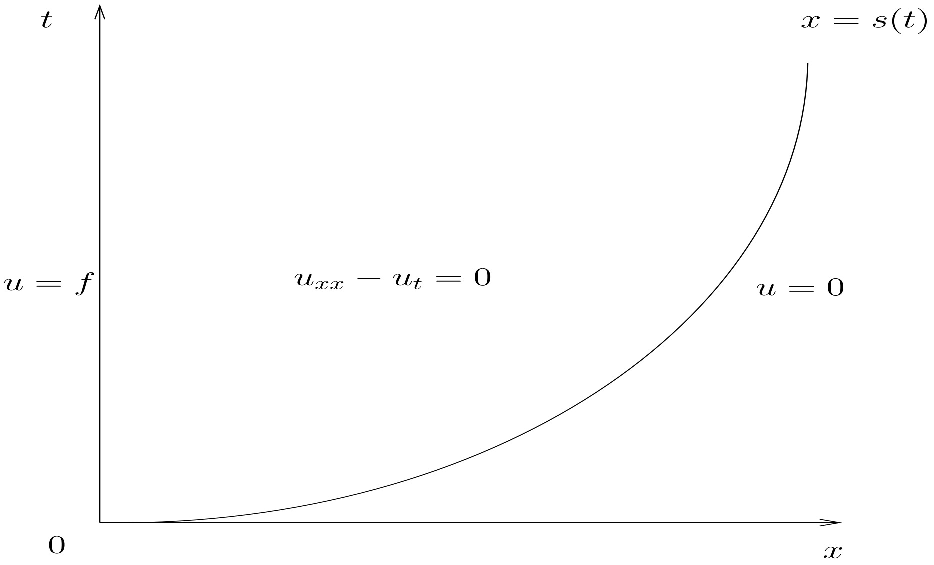


Figure 3.2.3. *Performing the limit.*

it is easy to see that $\{u_n\} \to u$ uniformly in $0 < x < s(t)$, $0 < t < T$.

Now we write (3.2.42) for each pair (s_n, u_n):

$$\frac{1}{2}s_n^2(t) = \frac{1}{2}b_n^2 + \int_0^t f(\tau)\, d\tau - \int_0^{s_n(t)} x\, u_n(x,t)\, dx \tag{3.2.50}$$

and we pass to the limit, obtaining

$$\frac{1}{2}s^2(t) = \int_0^t f(\tau)\, d\tau - \int_0^{s(t)} x\, u(x,t)\, dx. \tag{3.2.51}$$

We know that (3.2.51) together with the Lipschitz continuity of $s(t)$ is equivalent to the Stefan condition $u_x = -\dot{s}$ and therefore (s,u) is the solution of Problem 2.1A. □

Remark 3.2.5. If $f(t)$ behaves like ct^α near $t=0$, assumption (3.2.44) is verified for $\alpha \geq 1$ (in agreement with Remark 2.3). □

We are left with the case opposite to (3.2.44), i.e.

$$\frac{\|f\|_t}{\rho(t)} \quad \text{is not bounded near } t = 0. \tag{3.2.52}$$

This time we need a finer comparison theorem for the increments of $s(t)$.

Lemma 3.2.2. *Consider the pair of problems illustrated in fig. 3.2.4*

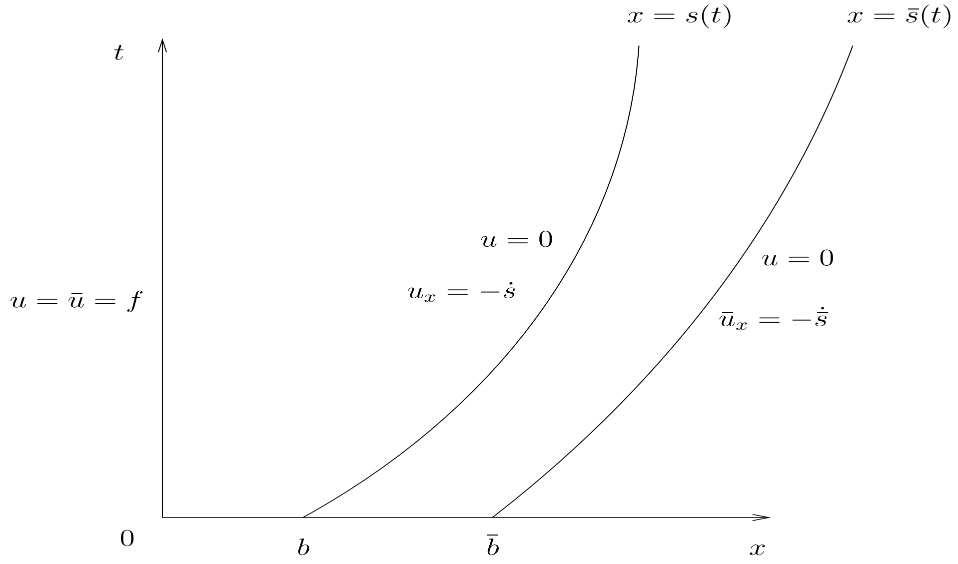


Figure 3.2.4. *Approximating sequence.*

differing only for $s\,(0) = b < \overline{b} = \overline{s}\ (0)$*. For any* $t > 0$ *we have*

$$s^2\,(t) - b^2 > \overline{s}^2\ (t) - \overline{b}^2\ . \tag{3.2.53}$$

Proof.

We write (3.2.42) for the pairs (s, u), $\left(\overline{s}, \overline{u}\right)$ and by substraction we get

$$\frac{1}{2}\left[s^2\,(t) - b^2\right] - \frac{1}{2}\left[\overline{s}^2\ (t) - \overline{b}^2\right] = \tag{3.2.54}$$

$$= -\int_0^{s(t)} x\ \left[u\,(x,t) - \overline{u}\ (x,t)\right]\ dx + \int_{s(t)}^{\overline{s}(t)} x\ \overline{u}\ (x,t)\ dx,$$

where we have used $\overline{s}\ (t) > s\,(t)$. We also know that $0 < u < \overline{u}\ (x,t)$ and therefore the r.h.s. of (3.2.54) is strictly positive. □

Now we prove:

Theorem 3.2.5. *(complementary to Theorem 3.2.4). If in Theorem 3.2.4 we replace (3.2.44) with the opposite condition (3.2.52) we still have existence.*

Proof.

Again we work with the sequence $\{(s_n, u_n)\}$. Of course we cannot obtain a uniform estimate for $\dot{s}_n$ in $(0, T)$, as in (3.2.49). Instead we look for bounds in intervals separated from $t = 0$. With this aim in mind we fix $\tau \in (0, T)$ and define the domains

$$Q^{\tau}_{n,t^*} = \left\{(x,t) \in \mathbb{R}^2 /\, 0 < x < s_n\,(t)\,,\ \tau < t < t^*\right\}$$

for any $t^* \in (\tau, T)$. We want to construct a linear barrier in Q^{τ}_{n,t^*} of the type

$$v_n\,(x, \tau, t^*) = \kappa\ (\tau, t^*)\ (s_n\,(t^*) - x)\,. \tag{3.2.55}$$

Not only we need

$$v_n(0,\tau,t^*) \geq \|f\|_{t^*}, \tag{3.2.56}$$

but also

$$v_n(x,\tau,t^*) \geq u_n(x,\tau), \quad 0<x<s_n(\tau). \tag{3.2.57}$$

The difficulty comes from the absence of uniform bounds on $u_n(x,\tau)$ more precise than $0 \leq u_n(x,\tau) < \|f\|_\tau$. Therefore the only thing we can do in order to ensure (3.2.57) is to impose that

$$v_n(s_n(\tau),\tau,t^*) \geq \|f\|_{t^*}, \tag{3.2.58}$$

which also implies (3.2.56). Thus $\kappa(\tau,t^*)$ must be defined so that

$$\kappa(\tau,t^*)\,(s_n(t^*)-s_n(\tau)) \geq \|f\|_{t^*}, \tag{3.2.59}$$

which leads us to the necessity of a uniform lower bound of the increment $s_n(t^*)-s_n(\tau)$. Here Lemma 3.2.2 comes into play.

First we construct the solution (s_n^τ, u_n^τ) of the Stefan problem for $t>\tau$ with data $u_n^\tau(0,t)=f(t)$, $u_n^\tau(x,\tau)=0$ for $0<x<s_n(\tau)$, $s_n^\tau(\tau)=s_n(\tau)$.

Since $u_n^\tau \leq u_n$ and in particular $u_n^\tau(x,t)<u_n(x,\tau)$ for $0<x<s_n(\tau)$, we have $s_n^\tau(t)<s_n(t)$ (Theorem 3.2.2). Next, we construct a supersolution for the latter problem. We have learned how to obtain the self-similar solution of the problem in fig. 3.2.5

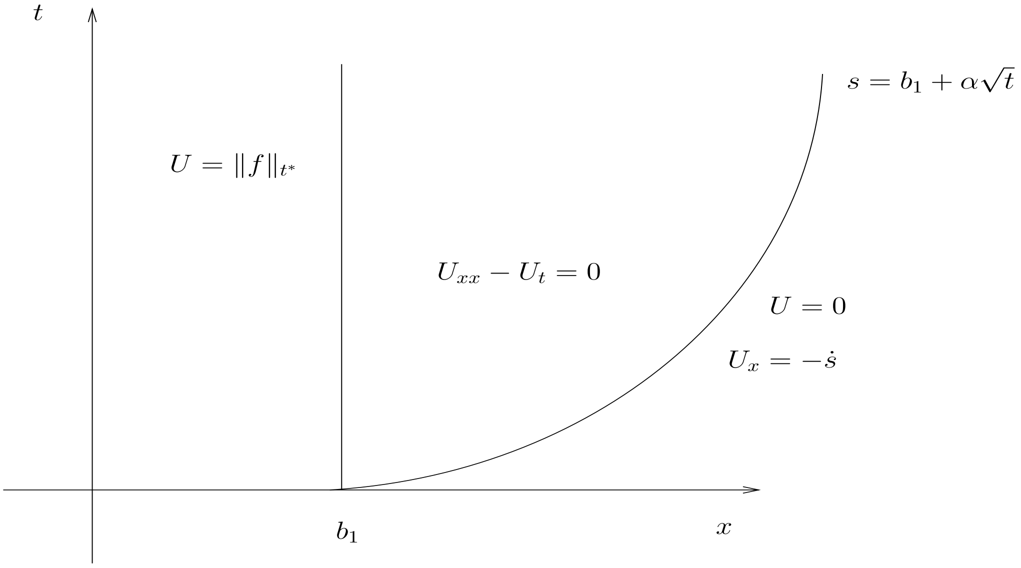


Figure 3.2.5. *The dominating solution*

i.e. how to find α in terms of $\|f\|_{t^*}$. Here b_1 is the first element in the sequence $\{b_n\}$. From Theorem 3.2.2 we have obviously

$$s_n(t) < b_1 + \alpha\sqrt{t}, \quad \forall n.$$

Therefore we can say that the solution $(\sigma^\tau,\omega^\tau)$ of the Stefan problem for $t>\tau$ with data $\omega^\tau(0,t)=f(t)$, $\omega^\tau(x,0)=0$ for $0<x<b_1+\alpha\sqrt{t}$, and $\sigma^\tau(\tau)=b_1+\alpha\sqrt{t}$, dominates the solutions (s_n^τ,u_n^τ).

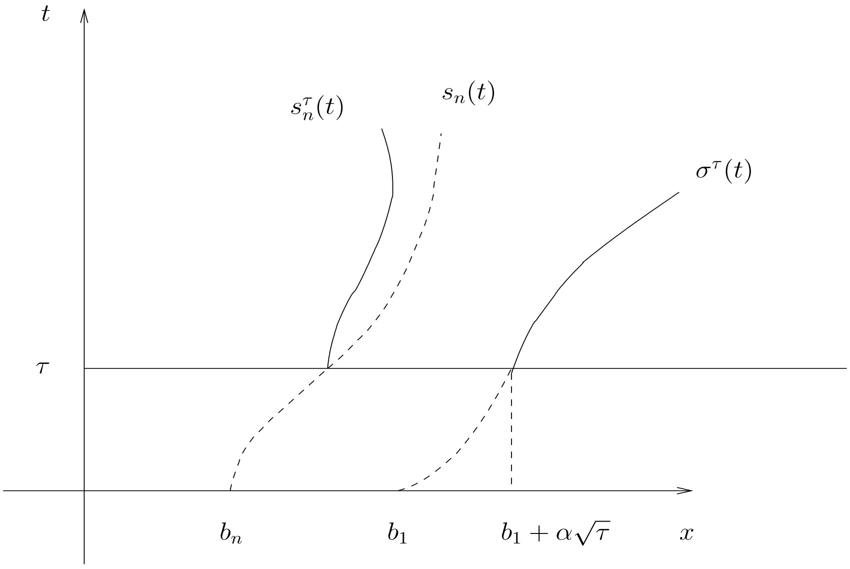


Figure 3.2.6. *The increment $s^2 - b^2$ decreases with b.*

At this point we apply Lemma 3.2.2 to the pairs (s_n^τ, u_n^τ), $(\sigma^\tau, \omega^\tau)$, concluding that

$$s_n^2\,(t) - s_n^2\,(\tau) > \left(s_n^\tau\,(t)\right)^2 - s_n^2\,(t) > \left(\sigma^\tau\,(t)\right)^2 - \left(\sigma^\tau\,(\tau)\right)^2, \tag{3.2.60}$$

and consequently

$$s_n\,(t) - s_n\,(\tau) > \frac{\left(\sigma^\tau\,(t)\right)^2 - \left(\sigma^\tau\,(\tau)\right)^2}{s_n\,(t) + s_n\,(\tau)} > \sigma^\tau\,(t) - \sigma^\tau\,(\tau)\,. \tag{3.2.61}$$

Now we come back to (3.2.59) and we realize that it is satisfied for all n if we take

$$\kappa\,(\tau, t^*) = \frac{\|f\|_{t^*}}{\sigma^\tau\,(t^*) - \sigma^\tau\,(\tau)}. \tag{3.2.62}$$

With the help of the linear barrier (3.2.55) we can say that $\kappa\,(\tau, t^*)$ is a uniform bound for $\dot{s}_n\,(t)$ in the interval (τ, t^*), implying the uniform convergence of $\{s_n\}$ in (τ, T) to a Lipschitz continuous function $s\,(t) > \rho\,(t)$ (Lemma 3.2.1). Of course the Lipschitz constant goes to infinity as $\tau \to 0$. However we can say that the convergence of s_n is anyway uniform in $(0, T)$. Indeed, chosen $\varepsilon > 0$, we select $\tau_0\,(\varepsilon)$, $n_0\,(\varepsilon)$, so that $0 \le s_n\,(t) - s\,(t) \le s_n\,(t) < b_n + \alpha\sqrt{\tau_0} < \varepsilon$ for $n > n_0$ and $t \in (0, \tau_0)$ (α is the same as in the self-similar solution used above, but with $\|f\|_{t^*}$ replaced by $\|f\|_T$), and we already know that the convergence is uniform in (τ_0, T).

From now on the proof is identical to the one of Theorem 3.2.4. $\square$

3.3. Stefan problem with no sign specification

When we say that in a one-phase melting problem the conducting phase is not necessarily at a non-negative temperature, the main information we lose is the monotonicity of the free boundary. The possibility of using the technique of linear barriers in the existence proof of Problem 2.1A was strictly linked to the fact that in that case the conducting phase is expanding. This is a deep difference between the two classes of problems, which is not reflected just in the technical details of the existence proof, but has also more substantial consequences: for instance the solutions of Problem 2.1B (if they exist) may blow up in finite time.

As a matter of fact, the general existence theorem we are going to prove refers only to a sufficiently small time interval.

A remarkable feature of this class of problems is that, since monotonicity of the free boundary is ignored, there is no basic difference between one-phase and two-phase problems.

We confine our analysis to the case (3.2.10) ($b > 0$) and we keep the continuity assumption on the data h, f and the matching conditions at the corners $(0, 0)$, $(b, 0)$. Condition (3.2.12) is naturally replaced by

$$|h(x)| \leq H(b - x), \quad 0 < x < b. \tag{3.3.1}$$

Theorem 3.3.1. ***(Existence.)*** *Under the assumptions cited above Problem 2.1B has at least one solution in a sufficiently small time interval* $(0, T)$.

Proof.

We argue as in the proof of Theorem 3.2.1, studying exactly the same mapping $\tau : \sigma \to \sigma$. However, we have a remarkable difference right from the starting point: instead of the set (3.2.12) we take now

$$\Sigma(A, T, c) = \Big\{ s \in C[0, T] \,|\, s(0) = b, \ \frac{|s(t') - s(t'')|}{|t' - t''|} \leq A, \tag{3.3.2}$$
$$0 \leq t' < t'' \leq T, \ s(t) \geq c > 0 \text{ for some } c < b \Big\}$$

where we have eliminated monotonicity of s, and T can no longer be arbitrary. For s in $\Sigma(A, T, c)$ we solve (3.2.1), (3.2.3), (3.2.4), (3.2.5) and we consider the mapping (3.2.13).

Clearly we must look for a bound on $|u_x(s(t), t)|$. A very natural comparison function (actually a barrier for each point of the boundary $x = s(t)$) is the solution of the problem

$$v_{xx} - v_t = 0, \quad 0 < x < s(t), \quad 0 < t < T, \tag{3.3.3}$$

$$v(s(t), t) = 0, \quad 0 < t < T, \tag{3.3.4}$$

$$v(x, 0) = \kappa(b - x), \quad 0 < x < b, \tag{3.3.5}$$

$$v(0, t) = \kappa b, \quad 0 < t < T, \tag{3.3.6}$$

where

$$\kappa = \frac{1}{b} \max(Hb, \|f\|_T). \tag{3.3.7}$$

The inequality

$$|u(x, t)| \leq v(x, t) \tag{3.3.8}$$

follows immediately from the maximum principle, implying

$$|u_x(s(t), t)| \leq |v_x(s(t), t)|. \tag{3.3.9}$$

In order to estimate the latter quantity we use a representation formula for $v\left(x,t\right)$. For fixed t we consider the variables $\left(\xi,\tau\right)$ in the domain $0<\xi<s\left(\tau\right)$, $0<\tau<t$, and we introduce the operator

$$\mathcal{L}=\frac{\partial^2}{\partial\xi^2}-\frac{\partial}{\partial\tau}$$

and its adjoint

$$\mathcal{L}^*=\frac{\partial^2}{\partial\xi^2}+\frac{\partial}{\partial\tau}.$$

We recall from Section 4.II that $\mathcal{L}^*G\left(x,t;\xi,\tau\right)=0$, G being the Green function for the quarter plane.

From the identity

$$0=v\,\mathcal{L}^*G-G\,\mathcal{L}v=\left(vG_\xi-Gv_\xi\right)_\xi+\left(vG\right)_\tau,$$

integrating over the domain $Q_{t-\varepsilon}=\left\{\left(\xi,\tau\right)\in\mathbb{R}^2\,/\,0<\xi<s\left(\tau\right),\ 0<\tau<t-\varepsilon\right\}$, $\varepsilon>0$, we get

$$0=\oint\limits_{\partial Q_{t-\varepsilon}}\left[\left(vG_\xi-Gv_\xi\right)\,d\tau+vG\,d\xi\right]$$

$$=\int_0^{s(t-\varepsilon)}v\left(\xi,t-\varepsilon\right)G\left(x,t;\xi,t-\varepsilon\right)\,d\xi-\int_0^b\kappa\left(b-\xi\right)G\left(x,t;\xi,0\right)\,d\xi$$
$$-\int_0^{t-\varepsilon}\kappa b\,G_\xi\left(x,t;0,\tau\right)\,d\tau-\int_0^{t-\varepsilon}G\left(x,t;s\left(\tau\right),\tau\right)\,v_\xi\left(s\left(\tau\right),\tau\right)\,d\tau,$$

where we have used $G|_{\xi=0}=0$.

Letting $\varepsilon\downarrow0$, we use the fundamental property (2.2.3) (obviously valid for G as well as for Γ, to obtain

$$v\left(x,t\right)=\int_0^b\kappa\left(b-\xi\right)G\left(x,t;\xi,0\right)\,d\xi+\kappa b\int_0^tG_\xi\left(x,t;0,\tau\right)\,d\tau$$
$$+\int_0^tG\left(x,t;s\left(\tau\right),\tau\right)\,v_\xi\left(s\left(\tau\right),\tau\right)\,d\tau.\tag{3.3.10}$$

Then we compute $v_x\left(x,t\right)$:

$$v_x\left(x,t\right)=-\int_0^b\kappa\left(b-\xi\right)N_\xi\left(x,t;\xi,0\right)\,d\xi$$

$$+\kappa b\int_0^tN_\tau\left(x,t;0,\tau\right)\,d\tau+\int_0^tG_x\left(x,t;s\left(\tau\right),\tau\right)\,v_\xi\left(s\left(\tau\right),\tau\right)\,d\tau\tag{3.3.11}$$
$$=-\kappa\int_0^bN\left(x,t;\xi,0\right)\,d\xi+\int_0^tG_x\left(x,t;s\left(\tau\right),\tau\right)\,v_\xi\left(s\left(\tau\right),\tau\right)\,d\tau$$

(recalling (2.4.13), $G_{\xi x}=-N_{\xi\xi}=N_\tau$).

We pass to the limit $x\to s\left(t\right)^-$, using the jump relation of the double layer potential (2.4.13), obtaining for $v_x\left(s\left(t\right),t\right)$ the following Volterra equation with weakly singular kernel

$$\frac{1}{2}\left|v_x\left(s\left(t\right),t\right)\right|=-\kappa\int_0^bN\left(s\left(t\right),t;\xi,0\right)\,d\xi+\int_0^tG_x\left(s\left(t\right),t;s\left(\tau\right),\tau\right)\,v_x\left(s\left(\tau\right),\tau\right)\,d\tau.\tag{3.3.12}$$

The kernel is

$$G_x\left(s\left(t\right),t;s\left(\tau\right),\tau\right)=-\frac{s\left(t\right)-s\left(\tau\right)}{4\sqrt{\pi}\left(t-\tau\right)^{\frac{3}{2}}}\exp\left\{-\frac{\left[s\left(t\right)-s\left(\tau\right)\right]^2}{4\left(t-\tau\right)}\right\} \tag{3.3.13}$$

$$+\frac{s\left(t\right)+s\left(\tau\right)}{4\sqrt{\pi}\left(t-\tau\right)^{\frac{3}{2}}}\exp\left\{-\frac{\left[s\left(t\right)+s\left(\tau\right)\right]^2}{4\left(t-\tau\right)}\right\}$$

and since $s\in\Sigma\left(A,T\right)$ we have the estimate

$$\left|G_x\left(s\left(t\right),t;s\left(\tau\right),\tau\right)\right|\leq\frac{A}{4\sqrt{\pi\left(t-\tau\right)}}+\frac{AT+b}{2\sqrt{\pi}\left(t-\tau\right)^{\frac{3}{2}}}\exp\left\{-\frac{c^2}{t-\tau}\right\}$$

$$=\frac{A}{4\sqrt{\pi\left(t-\tau\right)}}\left(1+\frac{2\left(T+\frac{b}{A}\right)}{t-\tau}\exp\left\{-\frac{c^2}{t-\tau}\right\}\right) \tag{3.3.14}$$

$$\leq\frac{A}{4\sqrt{\pi\left(t-\tau\right)}}\left(1+\frac{2}{ec^2}\left(T+\frac{b}{A}\right)\right)=\frac{1}{4\sqrt{\pi\left(t-\tau\right)}}\left\{A\left(1+\frac{2T}{ec^2}\right)+\frac{2b}{ec^2}\right\}$$

where we just used $ye^{-y}\leq\frac{1}{e}$.

Let us estimate the two terms in the first integral of (3.3.12).

$$\frac{1}{2\sqrt{\pi t}}\int_0^b\exp\left\{-\frac{\left[s\left(t\right)-\xi\right]^2}{4t}\right\}d\xi=\frac{1}{\sqrt{\pi}}\int_{\frac{s(t)-b}{2\sqrt{t}}}^{\frac{s(t)}{2\sqrt{t}}}e^{-\eta^2}\,d\eta<1, \tag{3.3.15}$$

$$\frac{1}{2\sqrt{\pi t}}\int_0^b\exp\left\{-\frac{\left[s\left(t\right)+\xi\right]^2}{4t}\right\}d\xi=\frac{1}{\sqrt{\pi}}\int_{\frac{s(t)}{2\sqrt{t}}}^{\frac{s(t)+b}{2\sqrt{t}}}e^{-\eta^2}\,d\eta<\frac{1}{2}. \tag{3.3.16}$$

Thus we deduce the inequality

$$\left|v_x\left(s\left(t\right),t\right)\right|\leq 3\kappa+\frac{1}{4\sqrt{\pi}}\left\{A\left(1+\frac{2T}{ec^2}\right)+\frac{2b}{ec^2}\right\}\int_0^t\frac{\left|v_x\left(s\left(\tau\right),\tau\right)\right|}{\sqrt{t-\tau}}\,d\tau \tag{3.3.17}$$

which is of type (2.5.6), yielding the estimate

$$\left|v_x\left(s\left(t\right),t\right)\right|\leq 3\kappa\,F\left(T,A,c\right), \tag{3.3.18}$$

with

$$F\left(T,A,c\right)=\left(1+2C_1\left(T,A,c\right)T^{\frac{1}{2}}\right)\exp\left(\pi C_1^2\left(T,A,c\right)T\right), \tag{3.3.19}$$

$$C_1\left(T,A,c\right)=\frac{1}{2\sqrt{\pi}}\left\{A\left(1+\frac{2T}{ec^2}\right)+\frac{2b}{ec^2}\right\}.$$

For $T=0$, $F\equiv 1$. For $T>0$ we have $\frac{\partial^n F}{\partial A^n}>0$, $\forall n$.

Thus A_c, T_c are uniquely defined, such that

$$3\kappa\,F\left(T_c,A_c,c\right)=A_c. \tag{3.3.20}$$

For all $T\in\left(0,T_c\right)$ we have

$$3\kappa\,F\left(T,A,c\right)<A \tag{3.3.21}$$

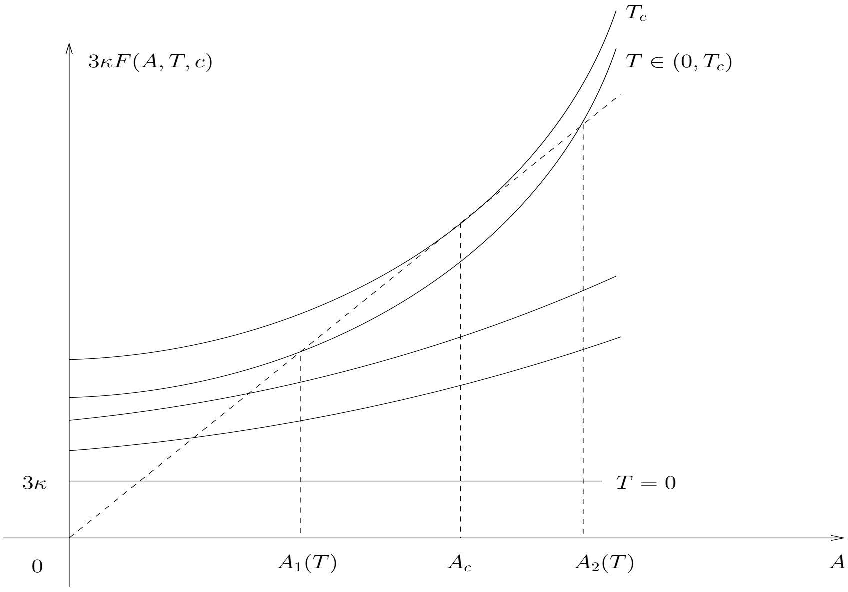


Figure 3.3.1. *Investigating the inequality (3.3.21).*

for A in an interval $(A_1(T), A_2(T))$.

From (3.3.18), (3.3.21), (3.3.9) and the definition of σ we conclude that for $T \in (0, T_c)$ and $A \in (A_1(T), A_2(T))$

$$\dot{\sigma} \le A. \tag{3.3.22}$$

However (3.3.22) alone is not enough to say that $\sigma \in \sum(A, T, c)$, because the condition $\sigma \ge c$ must also be satisfied. On the basis of (3.3.22) we must possibly reduce T in such a way that

$$b - AT \ge c. \tag{3.3.23}$$

It is immediately realized that (3.3.21) and (3.3.23) are compatible. Just remark that A_c is always an admissible choice for A, since it belongs to $(A_1(T), A_2(T))$ for all $T \in (0, T_c)$. Then an appropriate choice for T fulfilling both (3.3.21) and (3.3.23) is

$$T_c^* = \min\left(T_c, \frac{b-c}{A_c}\right). \tag{3.3.24}$$

Thus the set $\sum(A_c, T_c^*, c)$ is mapped into itself by the operator $\mathcal{T} : s \to \sigma$. In view of (3.3.24) we can optimize the choice of c so to maximize T_c^*.

As for the case of Problem 2.1A, also in the present situation the existence proof is now reduced to showing the continuity of $\mathcal{T}$, i.e. the existence of a constant C such that

$$\|\mathcal{T}_{s_1} - \mathcal{T}_{s_2}\| \le C \|s_1 - s_2\| \tag{3.3.25}$$

for any choice of s_1, $s_2 \in \sum(A_c, T_c^*)$. It is easily seen that (3.3.25) can be obtained through the same procedure as in the previous proof, using the inequality

$$|u(x,t)| \le v(x,t) \le \|v_x\| \, (s(t) - x). \tag{3.3.26}$$

All we have to do is to provide an estimate of $\|v_x\|$ independent of the choice of s in $\sum(A_c, T_c^*)$.

The function v_x satisfies the heat equation and on the parabolic boundary it satisfies the following conditions

$$v_x(x,0) = \kappa, \quad v_{xx}(0,t) = 0, \quad |v_x(s(t),t)| \le A_c. \tag{3.3.27}$$

From Theorems 2.1.1, 2.1.3 we deduce

$$\|v_x\| \le A_c, \tag{3.3.28}$$

which is the last step of the proof. □

We have already stressed that the solution may not exist in the large.

Theorem 3.3.2. *The solution found in Theorem 3.3.1 ceases to exist in a finite time θ if (at least) one of the following facts occurs*

$$\lim_{t\uparrow\theta} s(t) = 0 \tag{3.3.29}$$

or

$$\lim_{t\uparrow\theta} \dot{s}(t) = \infty. \tag{3.3.30}$$

Proof.

It is possible to continue the solution beyond T_c^*, since the pair $(s(T_c^*), u(x, T_c^*))$ satisfies the assumptions of Theorem 3.3.1, owing to (3.3.26).

Looking at (3.3.19) we realize that $c > 0$ is an essential condition in the deduction of (3.3.20), therefore if (after repeated continuations) $s(t)$ approaches zero in a finite time, the continuation procedure comes to a stop.

Also we have to notice that $A_c > 3\kappa$ (see fig. 3.3.1), so going through a chain of continuations it may happen that $\dot{s}$ blows up in a finite time. □

Examples of (3.3.29) and (3.3.30) can be provided.

The analysis of blowing up solutions and of possible further continuation is extremely delicate, and here we will not deal with it. This study has been performed at a deep level and singularities have been classified ([3]).

We still have to prove uniqueness. This time we cannot rely on a monotone dependence result and therefore we study the continuous dependence on the data. The following theorem extends Theorem 3.2.4.

Theorem 3.3.3. ***(Continuous dependence.)*** *Consider a pair of data (b_1, h_1, f_1), (b_2, h_2, f_2) satisfying the assumptions of Theorem 3.1 and let (s_1, u_1), (s_2, u_2) be corresponding solutions of Problem 2.1B. If e.g. $b_2 > b_1$ we continue h_1 for $b > b_1$ as $h_1 = 0$.*

Suppose $(0,T)$ is a time interval in which for both solutions the bound $\left|\dot{s}_i\right| \le A$, $i = 1, 2$, is available as well as $s_i \ge c > 0$, $i = 1, 2$. Then, in the same time interval

$$\|s_1 - s_2\| < \tag{3.3.31}$$

$$< C\left(|b_1 - b_2| + \int_0^{\max(b_1,b_2)} x\,|h_1(x) - h_2(x)|\,dx + \int_0^T |f_1(\tau) - f_2(\tau)|\,d\tau\right)$$

where C depends on T, A and on c. A similar bound for $\|u_1 - u_2\|$ in the common domain of definition is easily obtained.

Proof.

As a preliminary we remark that T, A can indeed be found in terms of the data, following the proof of Theorem 3.3.1.

We start from

$$\frac{1}{2}\left|s_1^2 - s_2^2\right| \le \frac{1}{2}\left|b_1^2 - b_2^2\right| + \int_0^{\max(b_1,b_2)} x\,|h_1(x) - h_2(x)|\,dx \tag{3.3.32}$$

$$+\int_0^t |f_1(\tau) - f_2(\tau)|\,d\tau + \int_0^{\alpha(t)} x\,|u_1(x,t) - u_2(x,t)|\,dx + \int_{\beta(t)}^{\alpha(t)} x\,|u_j(x,t)|\,dx,$$

where, as in the proof of Theorem 3.2.2, we define

$$\alpha(t) = \min(s_1(t), s_2(t)), \quad \beta(t) = \max(s_1(t), s_2(t))$$

and $j = 1$ if $s_1 > s_2$, $j = 2$ if $s_1 < s_2$.

We must estimate the last two integrals.

(I) Estimate of $\int_0^{\alpha(t)} x\,|u_1(x,t) - u_2(x,t)|\,dx$.

Observing that

$$|u_j(\alpha(t), t)| \le A\,|s_1(t) - s_2(t)|, \tag{3.3.33}$$

we can use the maximum principle to say that

$$|u_1 - u_2| \le W + Z \tag{3.3.34}$$

with W, Z solving the following initial-boundary value problems for the heat equation:

$$W(0,t) = |f_1(t) - f_2(t)|, \tag{3.3.35}$$

$$W(x,0) = \begin{cases} |h_1(x) - h_2(x)|, & 0 < x < \max(b_1,b_2) \\ 0, & x > \max(b_1,b_2) \end{cases}$$

(problem in the quarter plane),

$$Z(0,t) = 0, \tag{3.3.36}$$

$$Z(x,0) = 0, \quad 0 < x < \min(b_1,b_2)$$

$$Z(\alpha(t), t) = A\,|s_1(t) - s_2(t)|.$$

Recalling (2.4.5) we have

$$W(x,t) = \int_0^{\max(b_1,b_2)} |h_1(x) - h_2(x)|\,G(x,t;\xi,0)\,dx \tag{3.3.37}$$

$$+\frac{x}{2\sqrt{\pi}}\int_0^t \frac{f(\tau)}{(t-\tau)^{\frac{3}{2}}}\exp\left[-\frac{x^2}{4(t-\tau)}\right]d\tau$$

and it is not difficult to check that both $x\,W(x,t)$ and $x\,W_x(x,t)$ tend to zero as $x \to \infty$ uniformly for t in compact sets.

If we take a rectangle $R = (0,X)\times(0,t)$ in the (x,τ)-plane and we integrate over R the equation $W_{xx} - W_t = 0$, we find, for X large enough,

$$\int_0^X x\,W(x,t)\,dx = \int_0^{\max(b_1,b_2)} x\,|h_1(x) - h_2(x)|\,dx + \int_0^t |f_1(\tau) - f_2(\tau)|\,d\tau \tag{3.3.38}$$

$$+\int_0^t (x\,W_x - W)|_{x=X}\,d\tau.$$

Letting $X \to +\infty$ we get the final expression

$$\int_0^\infty x\,W(x,t)\,dx = \int_0^{\max(b_1,b_2)} x\,|h_1(x) - h_2(x)|\,dx + \int_0^t |f_1(\tau) - f_2(\tau)|\,d\tau. \tag{3.3.39}$$

The function $Z(x,t)$ can be represented as a double layer potential:

$$Z(x,t) = \int_0^t \mu(\tau)\,N_x(x,t;\alpha(\tau),\tau)\,d\tau \tag{3.3.40}$$

(remember that $N_x(0,t;\xi,\tau) = 0$: see (2.4.13)) with μ solving the Volterra equation

$$A\,|s_1(t) - s_2(t)| = \frac{1}{2}\mu(t) + \int_0^t \mu(\tau)\,N_x(\alpha(t),t;\alpha(\tau),\tau)\,d\tau \tag{3.3.41}$$

from which, by means of Gronwall's lemma, we have an estimate of the type

$$|\mu(t)| \le C(t)\,\|s_1 - s_2\|_t \tag{3.3.42}$$

with $C(t)$ depending on A, c and being an increasing function of t.

We need an estimate of

$$\int_0^{\alpha(t)} x\,Z(x,t)\,dx = \int_0^t\int_0^{\alpha(t)} x\,\mu(\tau)\,N_x(x,t;\alpha(\tau),\tau)\,dxd\tau. \tag{3.3.43}$$

First we compute

$$\int_0^{\alpha(t)} x\,N_x(x,t;\alpha(\tau),\tau)\,dx = \alpha(t)\,N(\alpha(t),t;\alpha(\tau),\tau)$$

$$-\int_0^{\alpha(t)} N(x,t;\alpha(\tau),\tau)\,dx.$$

A rough upper estimate of the latter integral is 1. Moreover $c \le \alpha(t) \le AT + \min(b_1,b_2)$ and $0 < N(\alpha(t),t;\alpha(\tau),\tau) < \dfrac{1}{\sqrt{\pi}\,(t-\tau)}$. Thus using (3.3.42),

$$0 < \int_0^{\alpha(t)} x\,Z(x,t)\,dx \le C_1\int_0^t \frac{\|s_1 - s_2\|_\tau}{\sqrt{t-\tau}}\,d\tau + C_2\int_0^t \|s_1 - s_2\|_\tau\,d\tau \tag{3.3.44}$$

$$\le C_3\int_0^t \frac{\|s_1 - s_2\|_\tau}{\sqrt{t-\tau}}\,d\tau, \quad C_3 = C_1 + \sqrt{t}C_2.$$

Collecting (3.3.39), (3.3.44) we have the desired estimate

$$\int_0^{\alpha(t)} x\left|u_1(x,t)-u_2(x,t)\right|dx \tag{3.3.45}$$

$$\leq \int_0^{\max(b_1,b_2)} x\left|h_1(x)-h_2(x)\right|dx+\int_0^t\left|f_1(\tau)-f_2(\tau)\right|d\tau+C_3\int_0^t\frac{\|s_1-s_2\|_\tau}{\sqrt{t-\tau}}\,d\tau.$$

(II) Estimate of $\int_{\beta(t)}^{\alpha(t)} x\left|u_j\right|dx$.
Of course we are assuming $\alpha(t)<\beta(t)$. We distinguish two cases

(i) in $[0,t)$ $\alpha(t)<\beta(t)$ (no intersections)

(ii) there is at least one intersection in $[0,t)$.

Case (i). $|u_j|\leq Y_1+Y_2$ with Y_1, Y_2 solving the following initial-boundary-value problems for the heat equation

$$\begin{gathered} Y_{1xx}-Y_{1t}=0,\quad x>\alpha(t),\quad t>0, \\ Y_1(x,0)=0,\quad x>\alpha(0), \\ Y_1(\alpha(t),t)=A\left|s_1(t)-s_2(t)\right|, \end{gathered} \tag{3.3.46}$$

$$\begin{gathered} Y_{2xx}-Y_{2t}=0,\quad \alpha(t)<x<\beta(t),\quad t>0, \\ Y_2(x,0)=\left|h_j(x)\right|,\quad \alpha(0)<x<\beta(0), \\ Y_2(\alpha(t),t)=Y_2(\beta(t),t)=0. \end{gathered} \tag{3.3.47}$$

We know that

$$Y_1(x,t)=\int_0^t\mu_1(\tau)\,\Gamma_x(x,t;\alpha(\tau),\tau)\,d\tau \tag{3.3.48}$$

with

$$A\left|s_1(t)-s_2(t)\right|=-\frac{1}{2}\mu_1+\int_0^t\mu_1(\tau)\,\Gamma_x(\alpha(t),t;\alpha(\tau),\tau)\,d\tau \tag{3.3.49}$$

and again

$$|\mu(t)|\leq C(t)\,\|s_1-s_2\|_t\,. \tag{3.3.50}$$

Thus

$$\int_{\alpha(t)}^{\beta(t)} x\,Y_1(x,t)\,dx\leq\int_{\beta(t)}^{+\infty} x\,Y_1(x,t)\,dx \tag{3.3.51}$$

$$=\int_0^t\mu_1(\tau)\left\{-\alpha(t)\,\Gamma(\alpha(t),t;\alpha(\tau),\tau)-\int_{\alpha(t)}^{+\infty}\Gamma(x,t;\alpha(\tau),\tau)\,dx\right\}d\tau.$$

The integral of Γ is less than 1, and therefore

$$0\leq\int_{\alpha(t)}^{\beta(t)} x\,Y_1(x,t)\,dx\leq C_4\int_0^t\frac{\|s_1-s_2\|_\tau}{\sqrt{t-\tau}}\,d\tau, \tag{3.3.52}$$

thanks to (3.3.50).

Passing to Y_2, integrating the identity $(xY_{2x} - Y_2)_x - (xY_2)_t = 0$ we find immediately

$$\int_{\alpha(t)}^{\beta(t)} x\, Y_2\left(x,t\right)\, dx = \int_{\alpha(0)}^{\beta(0)} x\, \left|h_j\left(x\right)\right|\, dx + \int_0^t \beta\left(\tau\right)\, Y_{2x}\left(\beta\left(\tau\right),\tau\right)\, d\tau \tag{3.3.53}$$

$$- \int_0^t \alpha\left(\tau\right)\, Y_{2x}\left(\alpha\left(\tau\right),\tau\right)\, d\tau.$$

Observing that Y_2 is minimum on the lateral boundaries we see that $Y_{2x}\left(\beta\left(\tau\right),\tau\right) \leq 0$, $Y_{2x}\left(\alpha\left(\tau\right),\tau\right) \geq 0$, so that

$$0 \leq \int_{\alpha(t)}^{\beta(t)} x\, Y_2\left(x,t\right)\, dx \leq \int_{\alpha(0)}^{\beta(0)} x\, \left|h_j\left(x\right)\right|\, dx. \tag{3.3.54}$$

Hence

$$\int_{\alpha(t)}^{\beta(t)} x\left|u_j\left(x,t\right)\right|\, dx \leq C_4 \int_0^t \frac{\left\|s_1 - s_2\right\|_\tau}{\sqrt{t-\tau}}\, d\tau + \int_{\alpha(0)}^{\beta(0)} x\left|h_j\left(x\right)\right|\, dx. \tag{3.3.55}$$

Case (ii). Let t^* be such that $\alpha\left(t^*\right) = \beta\left(t^*\right)$ and $\alpha\left(\tau\right) < \beta\left(\tau\right)$ for $\tau \in \left(t^*, t\right)$.

Now $\left|u_j\left(x,t\right)\right|$ is less than the solution of

$$Y_{xx} - Y_t = 0, \quad x > \alpha\left(t\right), \quad t > t^*, \tag{3.3.56}$$

$$Y\left(x,t^*\right) = 0, \quad x > \alpha\left(t^*\right),$$

$$Y\left(\alpha\left(t\right),t\right) = A\left|s_1\left(t\right) - s_2\left(t\right)\right|, \quad t > t^*,$$

and all we have to do is to remark that $Y\left(x,t\right) < Y_1\left(x,t\right)$.

Therefore (3.3.52) is valid also for Y.

The conclusion of this discussion is that the desired estimate for $\int_{\beta(t)}^{\alpha(t)} x\left|u_j\left(x,t\right)\right|\, dx$ is again (3.3.55).

We can now revert to inequality (3.3.32), using (3.3.45), (3.3.55), and $s_1\left(t\right) + s_2\left(t\right) \geq 2c > 0$:

$$\left|s_1\left(t\right) - s_2\left(t\right)\right| \leq C \left\{ \left|b_1 - b_2\right| + \int_0^{\max(b_1,b_2)} x\left|h_1\left(x\right) - h_2\left(x\right)\right|\, dx \right. \tag{3.3.57}$$

$$\left. + \int_0^t \left|f_1\left(\tau\right) - f_2\left(\tau\right)\right|\, d\tau + \int_0^t \frac{\left\|s_1 - s_2\right\|_\tau}{\sqrt{t-\tau}}\, d\tau \right\}.$$

We observe that the integral $\displaystyle\int_0^t \frac{\varphi\left(\tau\right)}{\sqrt{t-\tau}} d\tau = \int_0^t \frac{\varphi\left(t-\tau\right)}{\sqrt{\tau}} d\tau$ is non-decreasing if φ is non-negative and non-decreasing.

Thus the r.h.s of (3.3.57) is non-decreasing and for this reason we may replace $\left|s_1\left(t\right) - s_2\left(t\right)\right|$ by $\left\|s_1 - s_2\right\|_t$ on the l.h.s.

In this way we have constructed an integral inequality for $\left\|s_1 - s_2\right\|$ of the type studied in Section 5, II, which leads precisely to (3.3.31). □

Bibliographical remarks.

After the early papers[99,126,127] , the first analytical investigation of the classical one-dimensional Stefan problem was due to L.I. Rubinstein (see the references in[119]). Important contributions came next from A. Friedman (see the references in[78,80]), J.R. Cannon and C.D. Hill (see the references in[24] and others). A systematic analysis of one-dimensional problems (including some singular case) was performed by A. Fasano, M. Primicerio in[62–64] , later extended to the case of nonlinear parabolic equations and nonlinear free boundary conditions .[65]

We cannot deal with the more recent and quite fundamental contributions by a number of important mathematicians who have developed an extremely rich theory (particularly for the multidimensional Stefan problem and other free boundary problems). As we said, this is far beyond our scopes and we refer once more to the books and surveys already quoted.

Another kind of approach not dealt with here consists in introducing a parameter ϕ varying e.g. in $(0,1)$, indicating the volume fraction of one of the phases, and evolving according to some differential law. In that case the interface is replaced by a transition zone of fast variation of ϕ. Models in this class are called *phase field models* and have been studied extensively by a number of authors (see e.g. Fife[75] and Caginalp[23]).

Numerical methods have been developed to a great extent and with different approaches. We cannot devote any space to this important topic. We just refer to[108,109,111,121] .

EXERCISES.

1. Show that repeated continuations of the solutions of Problem 2.1B by means of the technique of Theorem 3.1 may lead to blow-up in finite time. Hint: in the second step we may expect that $3A_c$ replaces 3κ. Varying κ the curves of the family $3\kappa F(A, T, c)$ change by a multiplying factor and by rescaling we conclude that A_c at the n-th iteration is larger than $3^n\kappa$ (going to infinity), while summing the extension times we get a convergent sequence.

2. Study the behaviour for large t of the solution of Problem 2.1A.

3. Extend the results of Section 3 to the two-phase problem.

4. Show that blow-up cannot occur for two-phase problems with no superheating or supercooling.

Chapter 4

The Stefan problem. Weak solutions.

4.1. General concepts and weak formulation

The weak formulation allows to deal with multidimensional problems and at the same time gives a better understanding of the mathematical structure of the problem. Another significant advantage concerns the formulation of numerical methods.

It applies rigorously to the case of constant melting temperature and absence of supercooling or superheating. In the following we will use the symbols of Section 6, Chapt.1, and we keep the assumption of constant pressure.

For simplicity we suppose we may neglect convection (other than the one generated by $\rho\,(T)$), which is not always permitted, although there is no difficulty in dealing with the general case (as long as the velocity field is prescribed).

In order to derive the weak formulation of the multidimensional two-phase Stefan problem we suppose we know a classical solution consisting of:

(i) the interface $\gamma\,(t)$, supposed to be a regular surface in $\mathbb{R}^n$

(ii) the thermal fields in the liquid and in the solid.

We try to write the whole problem, irrespectively of the phase partition, in the form

$$\rho\frac{\partial h}{\partial t} - div\,(\kappa\,\nabla T) + \rho\,\nabla h \cdot \vec{v} = 0 \tag{4.1.1}$$

interpreting the derivatives in the distributional sense. In such a way we have no separate equation for the evolution of the interface, which is incorporated in (4.1.1).

Before we proceed, let us briefly consider the relationship between h and T.

In Chapter 1 h was defined as a discontinuous function of T by (2.4.1), (2.4.2), the jump being the latent heat of the material. In Fig. 4.1.1 we use a schematic representation with c_s, c_l constant.

So far we have said nothing about h at $T = T_m$, because we have only considered situations in which the system can be either solid or liquid. But, even in this simple case, in regions of nonzero measure where $T = T_m$ we have to specify whether the system is solid or liquid. Thus the temperature alone cannot decsribe completely the thermodynamical state.

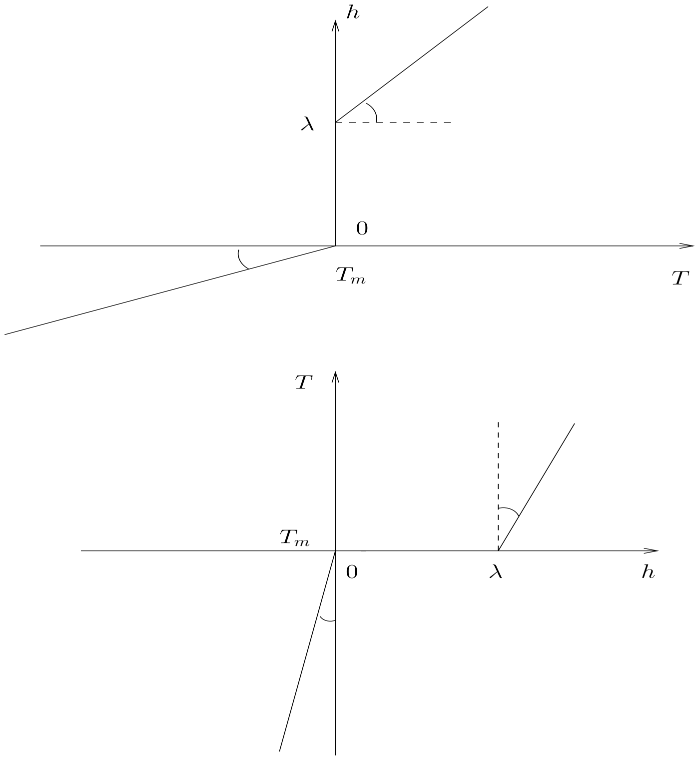


Figure 4.1.1. .

The variable that does the job is the specific enthalpy. Indeed, not only it specifies the phase but it determines T uniquely, since the inverse function $T(h)$ is Lipschitz continuous.

The latter emphasizes the role of the values of h in $[0,\lambda]$, all corresponding to $T=T_m$. What is the underlying physics?

Take a thermally insulated sample of copper and raise its temperature to T_m by Joule heating. If you keep supplying electric current phase change will not take place instantaneously because it needs a finite amount of heat, which only can be supplied in a finite time. Therefore temperature stays constant at T_m while h enters the interval $(0,\lambda)$ and melting will be completed when the value λ is reached. The intermediate states in which $h\in(0,\lambda)$ can be considered as a phase mixture and regions with such values of h are called *mushy regions*.

It is legitimate to expect the presence of mushy regions when solving (4.1.1) in the distributional sense. Also, the discussion above points out that at $t=0$ enthalpy (and not temperature) must be prescribed.

In view of the fact that h is the real unknown of the problem, we remark that the function

$$\theta=\begin{cases}\int_{T_m}^{T}\kappa_l(T')\,dT', & T\geq T_m\\ \int_{T_m}^{T}\kappa_s(T')\,dT', & T<T_m\end{cases}\tag{4.1.2}$$

can be regarded as a Lipschitz continuous function of h through $T=T(h)$.

Also ρ is more correctly described as a function of h: in the mushy region it is a linear interpolation between the values in the pure phases at $T=T_m$.

After this digression, let us resume our project of deriving the weak formulation from the classical statement including (i), (ii).
We rewrite the **field equation** (4.1.1) using (4.1.2) and referring for the moment to pure phases:

$$\rho(h)\,\frac{\partial h}{\partial t} + \rho(h)\,\nabla h \cdot \vec{v} - \Delta\theta = 0 \quad \text{in } Q_s \cup Q_l, \tag{4.1.3}$$

where Q_s, Q_l are subsets of $Q_T = \Omega \times (0,T)$. More precisely

$$Q_s = Q_T \cap \{h < 0\}, \quad Q_l = Q_T \cap \{h > \lambda\}.$$

To be specific we refer to Fig. 4.1.2 in which the external boundaries of the solid and of the liquid phase have no intersection, and where the following domains and boundaries are shown:

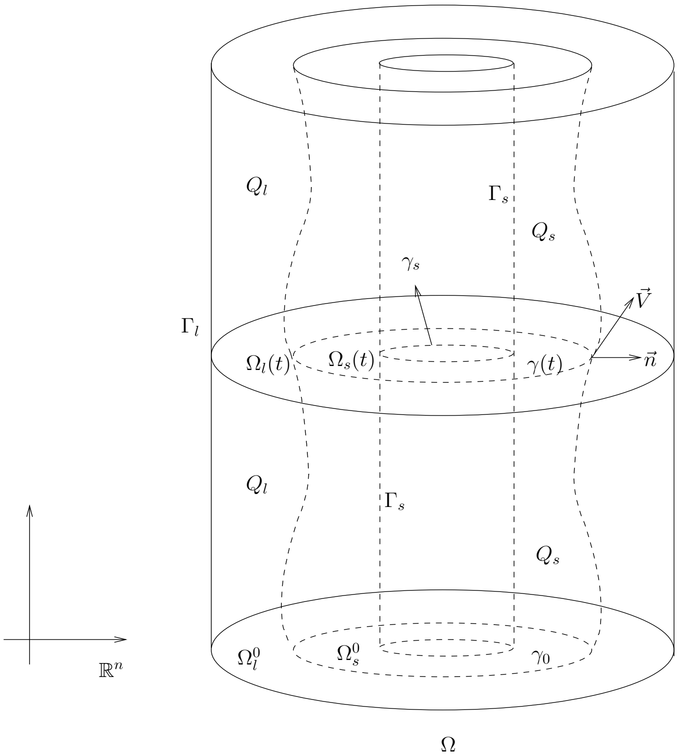


Figure 4.1.2. *Evolution of the interface in* $\mathbb{R}^{n+1}$.

$Q_l = Q_T \cap \{h > \lambda\}$
$Q_s = Q_T \cap \{h < 0\}$
$\Omega_l(t) = Q_l \cap \{t = const.\}$
$\Omega_s(t) = Q_s \cap \{t = const.\}$
Γ_l external boundary of Q_l
Γ_s external boundary of Q_s
Γ_0 interface in $\mathbb{R}^{n+1}$
$\gamma(t) = \Gamma_0 \cap \{t = const.\}$
$\vec{n}$ = normal to $\gamma(t)$ pointing towards $\Omega_l(t)$
$\gamma_s = \Gamma_s \cap \{t = const.\}$

$\gamma_l = \Gamma_l \cap \{t = const.\}$

Remark 4.1.1. Figure 4.1.2 refers to the case $\rho_l = \rho_s = const.$ For ρ_l, ρ_s variable and/or different we can take Γ_s fixed and let Γ_l move so to accommodate the total volume of the system at each time: a condition involving all the unknowns. □

Equation (4.1.13) is supplemented by

initial data

$$\gamma(0) = \gamma_0, \quad h(\vec{x}, 0) = h_0(\vec{x}) \text{ prescribed in } \overset{\circ}{\Omega}_l \cup \overset{\circ}{\Omega}_s \tag{4.1.4}$$

boundary data

$$T|_{\Gamma_l} = f_l(t) > T_m, \quad T|_{\Gamma_s} = f_s(t) < T_m \quad (\Rightarrow h \text{ is known}) \tag{4.1.5}$$

interface condition (we use (1.6.4))

$$\lambda\, \rho_l (\vec{v} - \vec{v}_l) \cdot \vec{n} = -\frac{\partial \theta_l}{\partial n} + \frac{\partial \theta_s}{\partial n}, \quad \rho_l = \rho(h = \lambda). \tag{4.1.6}$$

Now we introduce the set Φ of test functions

$$\Phi = \left\{ \varphi \in W^{2,1}(Q_T) \mid \varphi = 0 \text{ on } \Gamma_l \cup \Gamma_s \cup \Omega \times \{T\} \right\}. \tag{4.1.7}$$

We multiply (4.1.3) by $\varphi \in \Phi$ and integrate separately over Q_s and Q_l.
In order to compute $\int_{Q_s} \frac{\partial h}{\partial t} \varphi\, d\vec{x}dt$ we note that

$$\frac{d}{dt} \int_{\Omega_s(t)} \rho\, h\, \varphi\, d\vec{x} = \int_{\Omega_s(t)} \rho\, \frac{\partial h}{\partial t}\, \varphi\, d\vec{x} + \int_{\Omega_s(t)} \rho\, h\, \frac{\partial \varphi}{\partial t}\, d\vec{x} \tag{4.1.8}$$

$$- \int_{\Omega_s(t)} h\, div\,(\rho \vec{v})\, \varphi\, d\vec{x} + \int_{\gamma(t)^-} V_n\, \rho\, h\, \varphi\, d\sigma,$$

where we have used the properties of φ and the continuity equation. The last integral, in which V_n is the normal velocity of $\gamma(t)$, vanishes because $h = 0$ on $\gamma(t)^-$, i.e. on the side of the solid. Thus

$$\int_0^T \int_{\Omega_s(t)} \rho\, \frac{\partial h}{\partial t}\, \varphi\, d\vec{x}dt = - \int_0^T \int_{\Omega_s(t)} \rho\, h\, \frac{\partial \varphi}{\partial t}\, d\vec{x}dt \tag{4.1.9}$$

$$+ \int_0^T \int_{\Omega_s(t)} h\, div\,(\rho \vec{v})\, \varphi\, d\vec{x}dt - \int_{\overset{\circ}{\Omega}_s} \rho(h_0)\, h_0 \varphi(\vec{x}, t)\, d\vec{x}.$$

Next we calculate

$$\int_{\Omega_s(t)} \rho\, \nabla h \cdot \vec{v}\, \varphi\, d\vec{x} = \int_{\Omega_s(t)} div\,(\rho h \varphi \vec{v})\, d\vec{x} \tag{4.1.10}$$

$$- \int_{\Omega_s(t)} \left[\rho\, h\, \vec{v} \cdot \nabla \varphi + h\, \varphi\, div\,(\rho \vec{v})\right] d\vec{x}$$

that, using again $\varphi|_{\Gamma_s} = 0$, and $h|_{\gamma^-} = 0$, gives

$$\int_0^T \int_{\Omega_s(t)} \rho\, \nabla h \cdot \vec{v}\, \varphi\, d\vec{x} = - \int_0^T \int_{\Omega_s(t)} \left[\rho\, h\, \vec{v} \cdot \nabla \varphi + h\, \varphi\, div\,(\rho \vec{v})\right] d\vec{x}. \tag{4.1.11}$$

Finally, using the identity

$$-\varphi\Delta\theta = -\theta\Delta\varphi + div\left(\theta\nabla\varphi - \varphi\nabla\theta\right) \tag{4.1.12}$$

we have

$$-\int_{\Omega_s(t)} \varphi\Delta\theta\, d\vec{x} = -\int_{\Omega_s(t)} \theta\Delta\varphi\, d\vec{x} + \int_{\Gamma_s} \theta\left(f_s\right)\frac{\partial\varphi}{\partial n_s}\, d\sigma - \int_{\gamma(t)^-} \varphi\frac{\partial\theta_s}{\partial n}\, d\sigma \tag{4.1.13}$$

where we remark that the trace of $\nabla\varphi$ is defined on γ_s, γ_l, γ for a.e. t as a function in L^2, as well as on Γ_s, Γ_l, Γ_0.

Thus we may write

$$-\int_0^T \int_{\Omega_s(t)} \varphi\Delta\theta\, d\vec{x}dt = -\int_0^T \int_{\Omega_s(t)} \theta\Delta\varphi\, d\vec{x}dt + \tag{4.1.14}$$

$$+\int_{\Gamma_s} \theta\left(f_s\right)\frac{\partial\varphi}{\partial n_s}\, d\sigma dt - \int_0^T \int_{\gamma(t)^-} \varphi\frac{\partial\theta_s}{\partial n}\, d\sigma dt.$$

Summing (4.1.9), (4.1.11), (4.1.14),

$$\int_{Q_s} \left\{\rho\frac{\partial h}{\partial t} - \Delta\theta + \rho\nabla h\cdot\vec{v}\right\}\varphi\, d\vec{x}dt = \tag{4.1.15}$$

$$-\int_{Q_s} \left\{\rho h\frac{\partial\varphi}{\partial t} + \theta\Delta\varphi - \rho\, h\cdot\vec{v}\nabla\varphi\right\}\, d\vec{x}dt - \int_{\Omega_s(0)} \rho\left(h_0\right)h_0\varphi\left(\vec{x},0\right)\, d\vec{x}$$

$$+\int_{\Gamma_s} \theta\left(f_s\right)\frac{\partial\varphi}{\partial n_s}\, d\sigma dt - \int_0^T \int_{\gamma(t)^-} \varphi\frac{\partial\theta_s}{\partial n}\, d\sigma dt.$$

We proceed in a similar way in Q_l, obtaining

$$\int_{Q_l} \left\{\rho\frac{\partial h}{\partial t} - \Delta\theta + \rho\nabla h\cdot\vec{v}\right\}\varphi\, d\vec{x}dt = \tag{4.1.16}$$

$$-\int_{Q_l} \left\{\rho h\frac{\partial\varphi}{\partial t} + \theta\Delta\varphi - \rho\, h\,\vec{v}\cdot\nabla\varphi\right\}\, d\vec{x}dt - \int_{\Omega_l(0)} \rho\left(h_0\right)h_0\varphi\left(\vec{x},0\right)\, d\vec{x}$$

$$+\int_{\Gamma_l} \theta\left(f_l\right)\frac{\partial\varphi}{\partial n_l}\, d\sigma dt - \int_0^T \int_{\gamma(t)^+} \varphi\left[\frac{\partial\theta_l}{\partial n} + V_n\rho_l\lambda - \rho_l\lambda v_n\right]\, d\sigma dt.$$

Summing (4.1.15), (4.1.16) we see that the terms on the interface cancel out owing to (4.1.6) and we arrive at the equation

$$\int_{Q_T} \left\{\rho h\frac{\partial\varphi}{\partial t} + \theta\Delta\varphi - \rho h\,\vec{v}\cdot\nabla\varphi\right\}\, d\vec{x}dt = \tag{4.1.17}$$

$$= \int_{\Gamma_s} \theta\left(f_s\right)\frac{\partial\varphi}{\partial n_s}\, d\sigma dt + \int_{\Gamma_l} \theta\left(f_l\right)\frac{\partial\varphi}{\partial n_l}\, d\sigma dt - \int_{\Omega(0)} \rho\left(h_0\right)h_0\varphi\left(\vec{x},0\right)\, d\vec{x}.$$

Definition 4.1. A weak solution of the Stefan problem (4.1.3) − (4.1.6) is a function $h \in L^\infty\left(Q_T\right)$ satisfying (4.1.17) for all $\varphi \in \Phi$. □

Note that, since h is only required to be bounded and measurable, the data are not prescribed directly but appear in the equations as free terms.

It is important to underline that the velocity field $\vec{v}$ is generally unknown and, except the system has a particular symmetry, it cannot be deduced just from kinematic considerations. Therefore (4.1.17) should be coupled with the fluid dynamics of the melt, specifying the stress at the boundary. As we have observed, also the motion of the outer boundary is coupled in a nonlocal way to the evolution of the thermal field and of the interface.

For these reasons we leave aside the project of considering the full problem and from now on we take the basic approximation

$$\rho_l\left(T\right) = \rho_s\left(T\right) = const. = \rho \tag{4.1.18}$$

In the next section we shall study procedure for constructing an approximated sequence of classical problems whose limit is a weak solution of the Stefan problem.
Phase change problems with flow of the melt have been treated in several contexts (mould injection, continuous casting, etc.). As an example we quote the pioneering paper in that direction[25]
.

4.2. Existence theorem

We refer to the following simplified version of (4.1.17): find $h \in L^{\infty}\left(Q_T\right)$ such that

$$\int_{Q_T} \left\{\rho h \frac{\partial \varphi}{\partial t} + \theta \Delta \varphi\right\} d\vec{x}dt = \tag{4.2.1}$$

$$= \int_{\Gamma_s} \theta\left(f_s\right) \frac{\partial \varphi}{\partial n_s}\, d\sigma dt + \int_{\Gamma_l} \theta\left(f_l\right) \frac{\partial \varphi}{\partial n_l}\, d\sigma dt - \int_{\Omega(0)} \rho h_0 \varphi\left(\vec{x}, 0\right) d\vec{x},$$

with $\rho = const.$, $\forall \varphi \in \Phi$.

The domain Q_T is cylindrical in $\mathbb{R}^{n+1}$ and for simplicity we suppose that the boundary of $\Omega(0)$ (and consequently Γ_s, Γ_l) are smooth and that f_s, f_l are continuously differentiable and bounded away from zero in $\overline{\Gamma}_s$, $\overline{\Gamma}_l$ respectively. For $t = 0$ we suppose they match the initial data and that $h_0 \in C^1\left(\overline{\Omega}\right)$. These assumptions are redundant, but they simplify the existence proof to a large extent. With the same spirit we suppose that c_l, c_s, κ_l, κ_s are twice continuously differentiable.

Theorem 4.2.1. *Under the assumptions listed above, problem (4.2.1) has at least one solution.*

Proof.

In the previous section we have analyzed the relationship between h and T. Now we have to be more precise, saying that $h\left(T\right)$ is not just a discontinuous function, but a graph, setting $h\left(T_m\right) = [0, \lambda]$.

It is more convenient to consider the graph $h\left(\theta\right)$ (we keep the same symbol), what is clearly possible since $\theta\left(T\right)$ is invertible (see (1.2)). With h function of θ we have $h\left(0\right) = [0, \lambda]$ and for $\theta \neq 0$, $h\left(\theta\right)$ has two continuous and bounded derivatives. Moreover $h'\left(\theta\right)$ is strictly positive for $\theta \neq 0$: $h' \geq \omega > 0$.

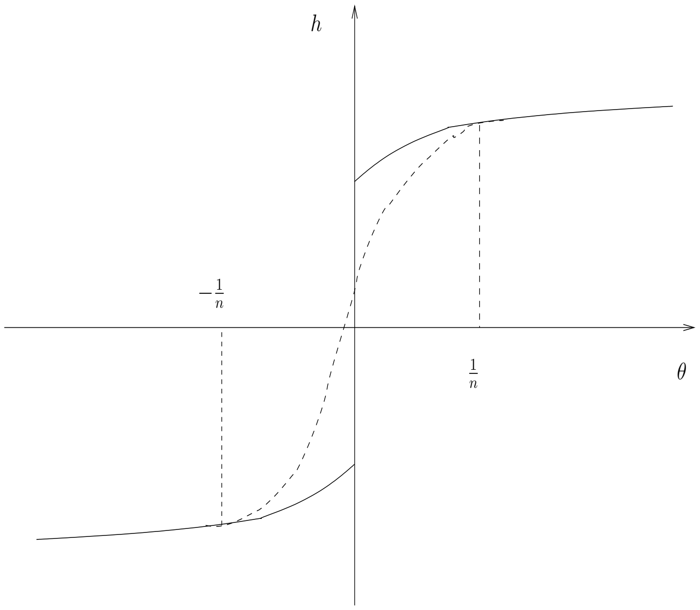


Figure 4.2.1. *Smooth approximation of the entalphy.*

We approximate $h(\theta)$ by the following sequence of functions

$$h_n(\theta) = \begin{cases} h(\theta) & \text{for} \quad |\theta| \geq \frac{1}{n} \\ \overset{\wedge}{h_n}(\theta) & \text{for} \quad |\theta| \geq \frac{1}{n} \end{cases}, n = 1, 2, ... \tag{4.2.2}$$

where $\overset{\wedge}{h_n}$ is smooth, matches h as smoothly as possible for $|\theta| = \dfrac{1}{n}$, and $\overset{\wedge}{h_n}' \geq \omega$.

Of course functions $h_n(\theta)$ are invertible: $\theta = \Theta_n(h)$, and $0 < \Theta_n' \leq \dfrac{1}{\omega}$.

We restrict our attention to the values of n which are large enough to satisfy $\theta(f_s) < -\dfrac{1}{n}$, $\theta(f_l) > \dfrac{1}{n}$ and we consider the family of problems

$$\rho h_n'(\theta_n) \frac{\partial \theta_n}{\partial t} - \Delta\theta_n = 0 \quad \text{in } Q_T, \tag{4.2.3}$$

$$\theta_n|_{\Gamma_s} = \theta(f_s), \quad \theta_n|_{\Gamma_l} = \theta(f_l), \tag{4.2.4}$$

$$\theta_n(\vec{x}, 0) = \Theta_n(h_0(\vec{x})) \tag{4.2.5}$$

Clearly, we look at (4.2.3) as an approximation to $\rho\dfrac{\partial h}{\partial t} - \Delta\theta = 0$ and in such a way we have a clear view of the nonlinearity and of the singularity of the problem: h_n' is nonlinear and not uniformly bounded.

Existence and uniqueness of the solution of (4.2.3) – (4.2.5) for each n are known from the classical literature. Also, in our simplifying assumptions we can find uniform bounds of the normal derivatives $\left.\dfrac{\partial \theta_n}{\partial n_s}\right|_{\Gamma_s}, \left.\dfrac{\partial \theta_n}{\partial n_l}\right|_{\Gamma l}$.

At this point we want to investigate the compactness properties of the sequence $\{\theta_n\}$. An easy result is that they are equibounded (maximum principle).

Next we prove the following

Lemma 4.2.1. *There exists a constant C, independent of n and determined by the data, such that*

$$\rho\omega\int_{Q_t}\left(\frac{\partial\theta_n}{\partial t}\right)^2 d\vec{x}d\tau+\int_{\Omega\times\{t\}}\frac{1}{2}\left|\nabla\theta_n\right|^2 d\vec{x}\leq C,\quad \forall t\in(0,T)\,. \tag{4.2.6}$$

Proof.

We multiply (4.2.3) by $\dfrac{\partial\theta_n}{\partial t}$ and integrate over Q_t. We remark that

$$\int_{Q_t}h'_n\left(\theta_n\right)\left(\frac{\partial\theta_n}{\partial t}\right)^2 d\vec{x}d\tau\geq\omega\int_{Q_t}\left(\frac{\partial\theta_n}{\partial t}\right)^2 d\vec{x}d\tau \tag{4.2.7}$$

and that

$$\begin{aligned}\int_{Q_t}\frac{\partial\theta_n}{\partial t}\Delta\theta_n\,d\vec{x}d\tau&=\int_{Q_t}div\left(\frac{\partial\theta_n}{\partial t}\nabla\theta_n\right)d\vec{x}d\tau \\ &-\int_{Q_t}\frac{1}{2}\frac{\partial}{\partial t}\left|\nabla\theta_n\right|^2 d\vec{x}d\tau= \\ &=\int_{\Gamma_{s,t}}\frac{\partial f_s}{\partial t}\frac{\partial\theta_n}{\partial n_s}d\sigma d\tau+\int_{\Gamma_{l,t}}\frac{\partial f_l}{\partial t}\frac{\partial\theta_n}{\partial n_l}d\sigma d\tau \\ &-\frac{1}{2}\int_{\Omega\times\{t\}}\left|\nabla\theta_n\right|^2 d\vec{x}+\frac{1}{2}\int_{\Omega_0}\left|\nabla\theta_n\left(\vec{x},0\right)\right|^2 d\vec{x}.\end{aligned} \tag{4.2.8}$$

Recalling that $\nabla\theta_n\left(\vec{x},0\right)=\Theta'_n\left(h_0\right)\nabla h_0$, using all our assumptions, from (4.2.7), (4.2.8) we deduce (4.2.6). □

An immediate consequence of (4.2.6) is that

(•) the sequence $\{\theta_n\}$ is weakly compact in $H^1\left(Q_T\right)$.

By Rellich's theorem we have

(••) there exists a subsequence $\{\theta_{n'}\}$ strongly convergent in $L^2\left(Q_T\right)$ to a function $\theta\in H^1\left(Q_T\right)$.

$\Rightarrow$

(•••) there exists a subsequence $\{\theta_{n''}\}$ converging a.e. to θ in Q_T.

$\Rightarrow$

(••••) there exists a subsequence $\{\theta_{n'''}\}$ converging almost uniformly to θ in Q_T.

Let us turn our attention to the sequence $\{h_{n'''}\left(\theta_{n'''}\right)\}$. We can select a subsequence which is weakly convergent in $L^2\left(Q_T\right)$ to a function $\tilde{h}\left(x,t\right)\in L^\infty$ (just use the fact that the elements are uniformly bounded). The key point in the existence proof is that we may interpret $\tilde{h}\left(x,t\right)$ as $h\left(\theta\left(x,t\right)\right)$ a.e. in Q_T. Let us show it.

For fixed $\varepsilon>0$ consider the sets Q_s^ε, Q_l^ε of the points of Q_T in which $\theta<-\varepsilon$, $\theta>\varepsilon$ respectively. Owing to the definition of h_n and to the almost uniform convergence of the selected sequence we can say that for n sufficiently large $h_n\left(\theta_n\right)=h\left(\theta_n\right)$ in $Q_s^\varepsilon\cup Q_l^\varepsilon$ (except from sets of arbitrarily small measure). Thus we can easily conclude that

$$\tilde{h}\left(x,t\right)=h\left(\theta\left(x,t\right)\right) \tag{4.2.9}$$

a.e. in the negativity set of θ, Q_s, and in the positivity set of θ, Q_l.

It remains to study $\tilde{h}(x,t)$ in the complement $Q_0 = Q_T \setminus \{Q_s \cup Q_l\}$ if its measure is positive. We want to show that $\tilde{h}(x,t) \in [0,\lambda]$ a.e. in Q_0.

Let us suppose for instance that exists a set $U \subset Q_0$ of positive measure in which $\tilde{h} < 0$, implying that $\int_U \tilde{h}\, d\vec{x}dt < 0$.

We are considering a sequence weakly convergent to $\tilde{h}$ in $L^2(Q_T)$ and therefore for all the elements h_κ in the sequence with a sufficiently large index we have $\int_U h_k\, d\vec{x}dt < -\sigma$ for some $\sigma > 0$.

Then for each of such κ it must exist a subset $U_\kappa \subset U$ in which $h_\kappa < -\sigma'$ for some $\sigma' > 0$ and $meas\,(U_\kappa)$ does not tend to zero. This fact is however not compatible with the fact that $\theta_\kappa \to 0$ in U almost uniformly.

The same argument proves that $\tilde{h}$ cannot exceed λ in a subset of Q_0 with positive measure.

Now we are ready to perform the last step.

Take the weak version of problem (4.2.3), (4.2.4), (4.2.5), namely

$$\int_{Q_T} \left\{ \rho h_n(\theta_n) \frac{\partial \varphi}{\partial t} + \theta_n \Delta\varphi \right\} d\vec{x}dt = \tag{4.2.10}$$

$$= \int_{\Gamma_s} \theta(f_s) \frac{\partial \varphi}{\partial n_s}\, d\sigma dt + \int_{\Gamma_l} \theta(f_l) \frac{\partial \varphi}{\partial n_l}\, d\sigma dt - \int_{\Omega(0)} \rho h_0 \varphi(\vec{x})\, d\vec{x}, \quad \forall \varphi \in \Phi.$$

We can exploit the limits $\theta_n \overset{L^2}{\to} \theta$, $h_n(\theta_n) \overset{L^2}{\rightharpoonup} \tilde{h}$ and the illustrated properties of $\tilde{h}$ to conclude that we have found a solution of (4.2.1). □

Remark 4.2.1. The solution we have just found satisfies the inequality (4.2.6). Therefore we can say that the weak formulation (4.2.1) is equivalent (once we know uniqueness) to the less weak formulation in which the boundary data are prescribed as traces and θ is allowed to belong to H^1 (accordingly, the space of test functions can be enlarged). It is also not difficult to see that in open sets with positive distance from Q_0 (i.e. at inner points of Q_l, Q_s) the differential equation.

$$\rho \frac{\partial h}{\partial t} - \Delta\theta = 0$$

is satisfied in the classical sense. □

Remark 4.2.2. The procedure used in proving existence is actually constructive (and can be used for numerical procedures), provided we show that the solution is unique. In fact uniqueness implies that the whole sequence of approximating solution is convergent.□

Remark 4.2.3. It has been proved that in the absence of mushy regions at $t = 0$, only pure phases will be present during the whole process, if there are no heat sources or sinks. However, mushy regions can be prescribed in the initial conditions. In such a case they are bound to disappear in a finite time. Mushy regions can be treated in the framework of a classical formulation. Much work has been done in this direction. We just quote the seminal paper[114] . See also the review paper[46] . □

4.3. Uniqueness

Theorem 4.3.1. *Problem (4.2.1) has at most one solution.* □

The proof of uniqueness of the weak solution is based on an argument whose key point is a clever choice of the test function (remember that (4.2.1) has to hold for any $\varphi \in \Phi$).

A basic step is a particular estimate for the Laplacian of the solutions of initial-boundary-value problems for degenerate parabolics equations.

Lemma 4.3.1. *Let* $u \in W^{2,1}(Q_T)$ *be a solution of*

$$\frac{\partial u}{\partial t} - \alpha(\vec{x},t)\,\Delta u = \psi(\vec{x},t)\,, \quad \text{in } Q_T = \Omega \times (0,T) \tag{4.3.1}$$

$$u|_{\partial_p Q_T} = 0 \tag{4.3.2}$$

with $\alpha(\vec{x},t) \geq 0$ *bounded in* $(0,A)$ *and* $\psi \in C_0^\infty(Q_T)$. *Then there exists* $C(T) > 0$, *independent of* α *and* ψ, *such that*

$$\int_{Q_T} \alpha\,(\Delta u)^2\, d\vec{x}dt \leq C(T)\,\|\nabla\psi\|^2_{L^2_{(Q_T)}}\,. \tag{4.3.3}$$

Proof.

Multiplying (4.3.1) by Δu and integrating over Q_t, $\forall t \in (0,T)$, we obtain (using (4.3.2))

$$\int_{Q_t} \frac{\partial u}{\partial t}\Delta u\, d\vec{x}d\tau = \int_{Q_t} div\left(\frac{\partial u}{\partial t}\nabla u\right) d\vec{x}d\tau - \frac{1}{2}\int_{Q_t} \frac{\partial}{\partial t}\left|\nabla u\right|^2 d\vec{x}d\tau \tag{4.3.4}$$

$$= -\frac{1}{2}\int_{\Omega\times\{t\}} \left|\nabla u\right|^2 d\vec{x}$$

and (using $\psi \in C_0^\infty$)

$$\int_{Q_t} \psi\Delta u\, d\vec{x}d\tau = \int_{Q_t} div\,(\psi\nabla u)\; d\vec{x}d\tau - \int_{Q_t} \nabla\psi\cdot\nabla u\, d\vec{x}d\tau = \tag{4.3.5}$$

$$-\int_{Q_t} \nabla\psi\cdot\nabla u\, d\vec{x}d\tau,$$

from which

$$\int_{Q_T} \alpha\,(\Delta u)^2\, d\vec{x}dt + \frac{1}{2}\int_{\Omega\times\{t\}} \left|\nabla u\right|^2 d\vec{x} = \int_{Q_t} \nabla\psi\cdot\nabla u\, d\vec{x}d\tau \tag{4.3.6}$$

$$\leq \frac{1}{2}\,\|\nabla\psi\|^2_{L^2_{(Q_T)}} + \frac{1}{2}\int_{Q_t} \left|\nabla u\right|^2 d\vec{x}d\tau.$$

Setting

$$F(t) = \int_{\Omega\times\{t\}} \frac{1}{2}\left|\nabla u\right|^2 d\vec{x},$$

from (4.3.6) we deduce the Gronwall's inequality

$$0 \leq F(t) \leq \frac{1}{2} \|\nabla \psi\|^2_{L^2_{(Q_T)}} + \int_0^t F(\tau)\, d\tau, \tag{4.3.7}$$

implying

$$F(t) \leq C(T) \|\nabla \psi\|^2_{L^2_{(Q_T)}}. \tag{4.3.8}$$

Going back to (4.3.6) we obtain the desired result. □

Proof of Thm. 4.3.1.

Let h_1, h_2 be solutions of (4.2.1), so that

$$\int_{Q_T} \left\{ \rho (h_1 - h_2) \frac{\partial \varphi}{\partial t} + [\Theta(h_1) - \Theta(h_2)] \Delta \varphi \right\} d\vec{x}dt = 0. \tag{4.3.9}$$

We recall that $\Theta(h)$ is the Lipschitz continuous function obtained by inverting the graph $h(\theta)$. Therefore, if we write

$$\Theta(h_1) - \Theta(h_2) = \beta(\vec{x}, t)(h_1 - h_2) \tag{4.3.10}$$

the function $\beta(\vec{x}, t)$ is well defined in the set $\{h_1 \neq h_2\}$ (the sign $\neq$ is meant in the sense of L^∞), where it satisfies a.e.

$$0 \leq \beta \leq \frac{1}{\omega}. \tag{4.3.11}$$

In the complement of the set $\{h_1 \neq h_2\}$ we may still define β arbitrarily as an L^∞ function satisfying (4.3.11).

Therefore (4.3.9) can be given in the form

$$\int_{Q_T} (h_1 - h_2) \left\{ \rho \frac{\partial \varphi}{\partial t} + \beta(\vec{x}, t) \Delta \varphi \right\} d\vec{x}dt = 0. \tag{4.3.12}$$

The basic idea is now the following: if for any $\psi \in C_0^\infty$ we may select $\varphi \in \Phi$ such that $\rho \frac{\partial \varphi}{\partial t} + \beta \Delta \varphi = \psi$, then (4.3.12) would immediately imply uniqueness (i.e. $h_1 = h_2$ a.e.).

However, finding such a φ is difficult for two reasons:

(i) the coefficient β is just in L^∞ and therefore it has not enough regularity,

(ii) β can approach zero, i.e. the (backward) parabolic operator $\rho \frac{\partial}{\partial t} + \beta \Delta$ is degenerate.

To overcome such difficulties, we take a sequence $\{\beta_n\}$ converging to β in $L^1(Q_T)$ with the properties

$$\beta_n \in C^\infty(Q_T), \quad \frac{1}{n} \leq \beta_n \leq \frac{2}{\omega} \tag{4.3.13}$$

and we solve the problems

$$\rho \frac{\partial \varphi_n}{\partial t} + (\beta_n + \varepsilon) \Delta \varphi_n = \psi, \tag{4.3.14}$$

$$\varphi_n = 0 \quad \text{on } \Gamma_s \cup \Gamma_l \cup \Omega \times \{T\} \tag{4.3.15}$$

(note that giving the "initial" condition for $t = T$ agrees with the fact that the equation is backward parabolic), with $\varepsilon > 0$. Note that $\varphi_n \in \Phi$.

To φ_n we may apply Lemma 4.3.1:

$$\left\| (\beta_n + \varepsilon)^{\frac{1}{2}} \Delta \varphi_n \right\|_{L^2_{(Q_T)}} \leq C \left\| \nabla \psi \right\|_{L^2_{(Q_T)}} \tag{4.3.16}$$

with C independent of n and ε.

Taking φ_n as test function in (4.3.12), we obtain

$$\int_{Q_T} (h_1 - h_2) \left\{ \psi + (\beta - \beta_n - \varepsilon) \Delta \varphi_n \right\} d\vec{x} dt = 0. \tag{4.3.17}$$

We know that h_1, h_2 are a-priori bounded in L^∞ and therefore

$$\left| \int_{Q_T} (h_1 - h_2) (\beta - \beta_n - \varepsilon) \Delta \varphi_n \, d\vec{x} dt \right| \tag{4.3.18}$$

$$\leq C \int_{Q_T} |\beta - \beta_n - \varepsilon| \, |\Delta \varphi_n| \, d\vec{x} dt.$$

Now we write $|\beta - \beta_n - \varepsilon| = |\beta - \beta_n - \varepsilon|^{\frac{1}{2}} \left| \dfrac{\beta}{\beta_n + \varepsilon} - 1 \right|^{\frac{1}{2}} |\beta_n + \varepsilon|^{\frac{1}{2}}$ and we divide Q_T into the subsets Q'_T in which $\dfrac{\beta}{\beta_n + \varepsilon} \leq 1$ and its complement Q''_T. By choosing a suitable subsequence, we can say that $\{\beta_n\}$ converges to β almost uniformly, so we can make the measure of Q''_T as small as we wish by taking n sufficiently large. We remark that in Q''_T we have at least the rough estimate $\dfrac{\beta}{\beta_n + \varepsilon} \leq \dfrac{1}{\omega \varepsilon}$, ε being fixed so far.

The integral on the r.h.s. of (4.3.18) can be estimated as follows

$$\int_{Q_T} |\beta - \beta_n - \varepsilon| \, |\Delta \varphi_n| \, d\vec{x} dt \leq \int_{Q'_T} |\beta - \beta_n - \varepsilon|^{\frac{1}{2}} \, |\beta_n + \varepsilon|^{\frac{1}{2}} \, |\Delta \varphi_n| \, d\vec{x} dt \tag{4.3.19}$$

$$+ \left(\frac{1}{\omega \varepsilon} \right) \int_{Q''_T} |\beta - \beta_n - \varepsilon|^{\frac{1}{2}} \, |\beta_n + \varepsilon|^{\frac{1}{2}} \, |\Delta \varphi_n| \, d\vec{x} dt.$$

Thanks to (4.3.16), we can say that as $meas\,(Q''_T) \to 0$ also $\int_{Q''_T} \to 0$, and that for $\int_{Q'_T}$ we have the inequality

$$\int_{Q_T} |\beta - \beta_n - \varepsilon|^{\frac{1}{2}} \, |\beta_n + \varepsilon|^{\frac{1}{2}} \, |\Delta \varphi_n| \, d\vec{x} dt \leq C \left\| \nabla \psi \right\|_{L^2_{(Q_T)}} \left\| \beta - \beta_n - \varepsilon \right\|^{\frac{1}{2}}_{L^2_{(Q_T)}} \tag{4.3.20}$$

(use Cauchy-Schwartz inequality).

For $n \to \infty$ we have $\left\| \beta - \beta_n - \varepsilon \right\|_{L^1} \leq \left\| \beta - \beta_n \right\|_{L^1} + \varepsilon \; meas\,(Q_T) \to \varepsilon \, meas\,(Q_T)\,.$

From (4.3.18), (4.3.19), (4.3.20), we conclude that

$$\left| \int_{Q_T} (h_1 - h_2) (\beta - \beta_n - \varepsilon) \Delta \varphi_n \, d\vec{x} dt \right|$$

can be made as small as desired. This means (see (4.3.17)) that

$$\int_{Q_T} (h_1 - h_2) \, \psi \, d\vec{x} dt = 0, \quad \forall \psi \in C_0^\infty (Q_T)\,, \tag{4.3.21}$$

hence uniqueness. □

Bibliographical remarks.

The existence of classical solutions to the multidimensional problem has been studied in several papers (the earliest contributions were.[85,103] For the 1-D case it has been proved that all weak solutions are classical.[68]

The first papers on weak solutions were by O.A. Oleinik,[110] S.L. Kamenomostskaja,[93] A. Friedman[79] .

The uniqueness proof written above is from[93] .

The variational formulation was given independently by M. Frémond[76] and by G. Duvaut,[40] introducing the so-called *freezing index.*

Chapter 5

Other free boundary problems for the heat equation

5.1. Reaction-diffusion processes with dead cores

Let $\hat{c}$ be the concentration of a substance diffusing in a medium with which it reacts chemically, according to some kinetics.

The process is governed by the equations ($T =$ absolute temperature)

$$\frac{\partial \hat{c}}{\partial t} - d\Delta \hat{c} = -A \hat{c}^{m} \exp\left(-\frac{E}{RT}\right) \tag{5.1.1}$$

$$\rho c \frac{\partial T}{\partial t} - \kappa \Delta T = QA \hat{c}^{m} \exp\left(-\frac{E}{RT}\right). \tag{5.1.2}$$

The symbols needing explanation are:

$A > 0$, constant, the so-called *pre-exponential factor*,

$m \geq 0$, the *order* of the reaction,

$E > 0$, *activation energy*,

$R =$universal gas constant,

$\exp\left(-\frac{E}{RT}\right)$is called the *Arrhenius factor*,

Q is the specific amount of heat produced (absorbed) in the reaction.

In the simplified case of isothermal reactions we only have to consider

$$\frac{\partial \hat{c}}{\partial t} - d\Delta \hat{c} = -\lambda \hat{c}^{m}, \quad \lambda > 0, \tag{5.1.3}$$

with appropriate initial and boundary conditions.

Of course (5.1.3) has to be solved in the set $\left\{\hat{c} > 0\right\}$. Indeed, the presence of the sink term $\lambda \hat{c}^{m}$ may produce regions in which the substance has been totally depleted. Such regions are called *dead cores* and their boundary is unknown. The free boundary conditions are of *Cauchy type*:

$$\hat{c} = 0, \quad \frac{\partial \hat{c}}{\partial n} = 0, \quad \vec{n} \text{ unit normal vector.} \tag{5.1.4}$$

A large literature has been devoted to such problems.

We just quote the Lecture Notes[87,124] .

In order to investigate the possible occurrence of a dead core, let us examine the stationary problem in one space dimension.

The physical domain is a slab $0 < x < a$ and we prescribe symmetric boundary data:

$$\hat{c}(0) = \hat{c}(a) = \hat{c}_0 \, . \tag{5.1.5}$$

Defining $u = \dfrac{\hat{c}}{\hat{c}_0}$ and using dimensionless variables, we reformulate the problem as follows: find $u \in C^2\,[0,1]$ such that

$$\frac{d^2u}{dx^2} = \lambda u^m \quad \text{in } \{0 < x < 1\} \cap \{u > 0\} \tag{5.1.6}$$

$$u\,(0) = u\,(1) = 1, \tag{5.1.7}$$

with conditions

$$u = u' = 0 \tag{5.1.8}$$

at interfaces with a possible dead core.

Due to the symmetry of the problem, we may replace $u\,(1) = 1$ with $\dfrac{du}{dx}\,|_{x=\frac{1}{2}} = 0$.

First of all we want to know for what values of λ, m we have a dead core.

Theorem 5.1.1. *Problem (5.1.6)−(5.1.8) has a dead core if and only if the following conditions are satisfied:*

$$0 \leq m < 1, \tag{5.1.9}$$

$$\left(2\frac{m+1}{\lambda}\right)^{\frac{1}{2}} < \frac{1}{2}\,(1-m)\,. \tag{5.1.10}$$

Proof.

Due to symmetry, if the dead core is present, the two "active" regions do not exchange information. Thus we may consider the reaction-diffusion problem e.g. in $0 < x < +\infty$ (see fig. 5.1.1).

Thus we integrate (5.1.6) imposing $u\,(0) = 1$ and $\lim\limits_{x \to +\infty} u\,(x) = 0$.

From (5.1.6) we deduce that $\dfrac{du}{dx}$ is monotone and therefore it has a limit as $x \to +\infty$, which is necessarily zero. Multiplying (5.1.6) by $\dfrac{du}{dx}$ and integrating we obtain

$$\frac{1}{2}\left[\left(\frac{du}{dx}\right)^2 - \gamma^2\right] = \frac{\lambda}{m+1}\left[(u\,(x))^{m+1} - 1\right], \tag{5.1.11}$$

where $\gamma = u'\,(0)$. Taking the limit $x \to +\infty$, we find

$$u'\,(0) = -\left(\frac{2\lambda}{m+1}\right)^{\frac{1}{2}}, \tag{5.1.12}$$

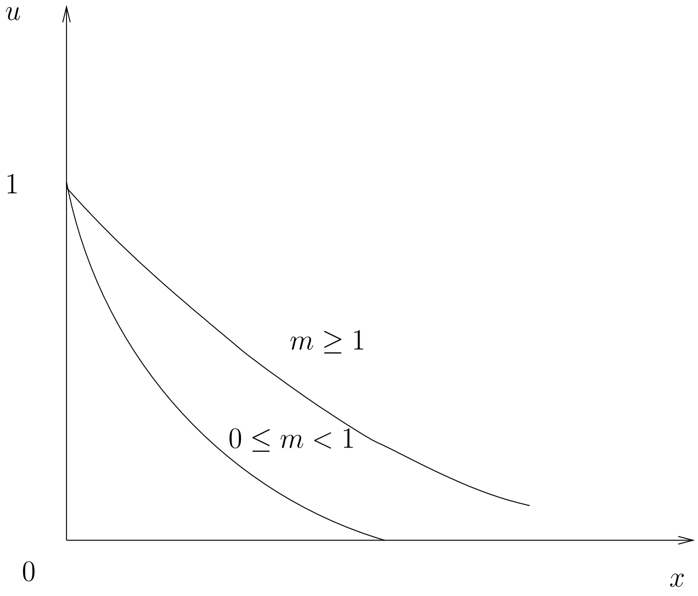


Figure 5.1.1. *The semi-infinite dead core problem.*

and the constant terms in (5.1.11) cancel out, yielding

$$\frac{du}{dx} = -\left(\frac{2\lambda}{m+1}\right)^{\frac{1}{2}} u^{\frac{m+1}{2}}. \tag{5.1.13}$$

As long as $u > 0$ we may separate the variables, obtaining

$$\log u = -\lambda^{\frac{1}{2}} x, \quad \text{for } m = 1, \tag{5.1.14}$$

$$\frac{2}{1-m}\left(u^{\frac{1-m}{2}} - 1\right) = -\left(\frac{2\lambda}{m+1}\right)^{\frac{1}{2}} x, \quad \text{for } m \neq 1. \tag{5.1.15}$$

Now a dead core appears if and only if u vanishes at some finite x_0. This happens only if $m < 1$ and we have

$$x_0 = \frac{1}{1-m}\left(2\frac{m+1}{\lambda}\right)^{\frac{1}{2}}. \tag{5.1.16}$$

Thus the necessary and sufficient conditions for the existence of a dead core is $m < 1$ and $x_0 < \frac{1}{2}$, i.e. (5.1.9) and (5.1.10). □

Exercise: Solve (5.1.6), (5.1.7) in the absence of a dead core.

Consider the family of Cauchy problems

$$u'' = \lambda u^m, \{x > 0\} \cap \{u > 0\} \cap \left\{u' < 0\right\}, \tag{5.1.17}$$

$$u(0) = 1, \tag{5.1.18}$$

$$u'(0) = \gamma < 0, \tag{5.1.19}$$

depending on the parameter γ.
Multiplying (5.1.17) by u' and integrating we obtain

$$u' = -\left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-u^{m+1}\right)\right\}^{\frac{1}{2}}, \text{ as long as } \left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-u^{m+1}\right)\right\} \geq 0 \qquad (5.1.20)$$

and a further integration yields

$$\int_{u(x)}^{1} \left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-\xi^{m+1}\right)\right\}^{-\frac{1}{2}} d\xi = x \qquad (5.1.21)$$

up to the possible minimum of u.

We want to show that both $u(x)$ and $u'(x)$ are increasing functions of γ. Differentiating (5.1.21) with respect to γ and setting $\dfrac{\partial u}{\partial \gamma} = u_\gamma$, we get

$$0 = -u_\gamma \left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-u^{m+1}\right)\right\}^{-\frac{1}{2}} - \int_u^1 \gamma \left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-\xi^{m+1}\right)\right\}^{-\frac{3}{2}} d\xi$$

i.e.

$$\frac{u_\gamma}{u'} = \gamma \int_u^1 \left\{\gamma^2 - \frac{2\lambda}{m+1}\left(1-\xi^{m+1}\right)\right\}^{-\frac{3}{2}} d\xi. \qquad (5.1.22)$$

Since $\gamma u' > 0$, (5.1.22) implies $u_\gamma > 0$.

Now, integrating (5.1.17)

$$u' = \gamma + \lambda \int_0^x u^m(\xi)\, d\xi$$

and differentiating w.r.t. γ we find an expression for $\dfrac{\partial u'}{\partial \gamma} = u'_\gamma$:

$$u'_\gamma = 1 + m\lambda \int_0^x u^{m-1} u_\gamma d\xi,$$

which implies that $u'_\gamma > 1$. Defining $\gamma^* = -\left(\dfrac{2\lambda}{1+m}\right)^{\frac{1}{2}}$, we see that for $\gamma \in (\gamma^*, 0)$ the function u reaches the positive minimum $u_m = \left[1 - \left(\dfrac{\gamma}{\gamma^*}\right)^2\right]^{\frac{1}{m+1}}$ at a point x_m deducible from (5.1.21). For $\gamma < \gamma^*$, u' is still negative when u vanishes.

For $\gamma = \gamma^*$ (as we already know) we have two cases:
($\bullet$) $m \geq 1 \Rightarrow u > 0$ and $u' < 0$, $\forall x > 0$, $\lim\limits_{x\to+\infty} u = 0$,
($\bullet\bullet$) $0 \leq m < 1 \Rightarrow$ there exits a dead core $\left(x > x_0 = \dfrac{2}{1-m}|\gamma *|^{-\frac{1}{2}}\right)$.

Thus the solution of (5.1.6), (5.1.7) with no dead core must in any case correspond to a value of γ in $(\gamma^*, 0)$.

From the pieces of information we have collected so far we can draw the pictures represented in fig. 5.1.2, concluding that $x_m(\gamma)$ is a monotone function of γ in $(\gamma^*, 0)$ ranging from 0 to $+\infty$ for $m \geq 1$ and from 0 to x_0 for $0 \leq m < 1$.

Problem (5.1.6), (5.1.7) has no dead core if $m \geq 1$ or if $0 \leq m < 1$ and $x_0 > \frac{1}{2}$. In both cases there exists one and only one $\gamma \in (\gamma^*, 0)$ such that $x_m = \dfrac{1}{2}$.

Thus we have found the unique solution.

An alternative approach is the following. Solve the Cauchy problem

$$u'' = \lambda u^m, 0 < x < \frac{1}{2},$$
$$u\left(\frac{1}{2}\right) = \alpha \in (0, 1)$$
$$u'\left(\frac{1}{2}\right) = 0$$

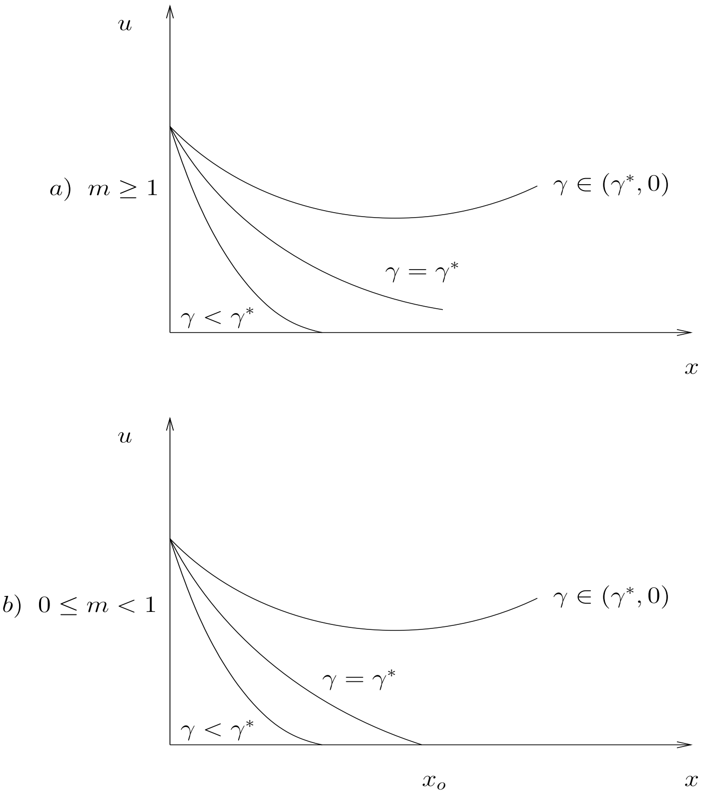


Figure 5.1.2. *Dependence of* u *on* γ.

and find α such that $u(0) = 1$.

From the first integral

$$\frac{1}{2} u'^2 = \frac{\lambda}{m+1}\left(u^{m+1} - \alpha^{m+1}\right)$$

we find

$$\int_{u(x)}^{\alpha} \frac{du}{\sqrt{u^{m+1} - \alpha^{m+1}}} = -\sqrt{\frac{2\lambda}{m+1}}\left(\frac{1}{2} - x\right),$$

thus determining the equation for α:

$$\int_{\alpha}^{1} \frac{du}{\sqrt{u^{m+1} - \alpha^{m+1}}} = \sqrt{\frac{\lambda}{2(m+1)}}.$$

For instance, for $m = 0$ we obtain $\alpha = 1 - \frac{\lambda}{8}$, which requires $\lambda < 8$, in agreement with (5.1.9), (5.1.10).

For $m = 1$ we find

$$\frac{\sqrt{1+\alpha}+\sqrt{1-\alpha}}{\sqrt{1+\alpha}-\sqrt{1-\alpha}} = e^{\frac{\sqrt{\lambda}}{2}} \Rightarrow$$

$$\frac{\left[\sqrt{1+\alpha}+\sqrt{1-\alpha}\right]^2}{2\alpha} = e^{\frac{\sqrt{\lambda}}{2}} \Rightarrow$$

$$\frac{1}{\alpha} = \frac{1}{2}\left(e^{\frac{\sqrt{\lambda}}{2}} + e^{-\frac{\sqrt{\lambda}}{2}}\right),$$

which does not imply any limitation on λ for α to be in $(0,1)$.

5.2. The oxygen diffusion-consumption problem

The dead core problem with $m = 0$ is known as the oxygen diffusion-consumption problem (constant absorption rate).

Rescaling lengths by some L (e.g. $\frac{1}{2}$ the thickness of the sample), time by $t_0 = \frac{L^2}{d}$, and concentration by $c_0 = A\exp\left(-\frac{E}{RT}\right)t_0$, the dead core problem in one space dimension is stated as follows: (we shall come back later on to the question of selecting the initial data)

$$\frac{\partial u}{\partial t} - \frac{\partial^2 u}{\partial x^2} = -1, \quad 0 < x < s(t), \quad 0 < t < T, \tag{5.2.1}$$

$$s(0) = 1, \tag{5.2.2}$$

$$u(x,0) = u_0(x), \quad 0 < x < 1, \quad u_0(1) = 0, \quad u_0'(1) = 0, \tag{5.2.3}$$

$$u_x(0,t) = 0, \quad 0 < t < T, \tag{5.2.4}$$

$$u(s(t),t) = 0, \quad 0 < t < T, \tag{5.2.5}$$

$$u_x(s(t),t) = 0, \quad 0 < t < T. \tag{5.2.6}$$

For u_0 we may select the stationary solution of (5.2.1), (5.2.5), (5.2.6)

$$u_0(x) = \frac{1}{2}(1-x)^2$$

with dead core at $x = 1$. Note that the steady state requires a constant supply at $x = 0$ with the rate $u_x = -1$. Thus problem (5.2.1) – (5.2.6) arises when (at $t = 0$) we switch off the oxygen supply.

We must remark that the statement of the above problem is not precise, unless we exclude a priori that a new dead core is formed in the interval $(0, s(t))$ for all $t \in (0,T)$: equation (5.2.1) applies only in the set $\{u > 0\}$.

Lemma 5.2.1. *As long as $s(t) > 0$ the function $u(x,t)$ does not vanish in $(0, s(t))$.*

Proof.

Let us consider the initial-boundary value problem satisfied by $v = u_x$:

$$v_t - v_{xx} = 0, \tag{5.2.7}$$

$$v(x,0) = u_0'(x) = -(1-x), \tag{5.2.8}$$

$$v(s(t), t) = 0, \tag{5.2.9}$$

$$v(0,t) = 0 \tag{5.2.10}$$

(discontinuous at the origin). The strong maximum principle implies $v < 0$ at all inner points. Thus $u(x,t)$ is decreasing in x for all t and consequently positive in $(0, s(t))$.

Remark 5.2.1. The proof above is valid for any $u_0(x)$ with $u_0' < 0$. Releasing this assumption may produce the onset of a negativity set of u. This is nonphysical in the framework of the diffusion consumption model and just says that one more dead core appears inside. □

As we shall see, Problem (5.2.1) – (5.2.6) can be studied in the general framework of 1-D problems with Cauchy data on the free boundary. However, still at the present level we can obtain some more a priori results. For instance, integrating (5.2.1) over $0 < x < s(\tau)$, $0 < \tau < t$ leads to the mass balance equation

$$\int_0^1 u_0(x)\,dx - \int_0^{s(t)} u(x,t)\,dx = \int_0^t s(\tau)\,d\tau$$

(showing that $\int_0^t s(\tau)\,d\tau$ represents the total mass loss up to time t), from which we see that either the solution is terminated in a finite time, or $s(t)$ must be summable over $(0, \infty)$.

We can go deeper into this question if we look at the problem satisfied by $\omega = u_t = u_{xx} - 1$ (supposing we have enough regularity):

$$\omega_t - \omega_{xx} = 0, \quad 0 < x < s(t), \quad 0 < t < T, \tag{5.2.11}$$

$$\omega(x,0) = \omega_0(x), \quad 0 < x < 1, \quad s(0) = 1, \tag{5.2.12}$$

$$\omega_x(0,t) = 0, \quad 0 < t < T, \tag{5.2.13}$$

$$\omega(s(t), t) = 0, \quad 0 < t < T, \tag{5.2.14}$$

$$\omega_x(s(t), t) = -\dot{s}(t), \quad 0 < t < T, \tag{5.2.15}$$

where the last condition is obtained by differentiating (5.2.6). Now the conditions on the free boundary are precisely the Stefan conditions. Let us discuss the initial condition (5.2.12). If

u_0 is twice differentiable, then $\omega_0(x) = u_0''(x) - 1$. This seems to imply $\omega_0(x) = 0$ when $u_0 = \frac{1}{2}(1-x)^2$ (the stationary solution). Indeed, if we had assumed $u_x(0,t) = -1$ instead of $u_x(0,t) = 0$, we would have obtained precisely (5.2.11) – (5.2.15) with $\omega_0 \equiv 0$ (i.e. the equilibrium solution). However, as we have noted, (5.2.4) implies a discontinuity for u_x and a singularity for u_{xx}. By reflection around $x = 0$ we see that the initial concentration for the reflected problem is

$$u_0(x) = \frac{1}{2}(1-|x|)^2$$

so that $u_0''(x) = 1 - 2\delta(x)$, δ being the Dirac distribution. Hence in (5.2.12) we have $\omega_0(x) = -2\delta(x)$, for the extended problem, which makes the solution nontrivial.

Now we realize that if $\omega_0(x) \le 0$ (as in the latter case), (5.2.11) – (5.2.15) is nothing but a supercooled Stefan problem with $\dot{s} < 0$.

We can also perform the usual global balance, obtaining

$$s(t) = 1 + \int_0^1 \omega_0(x)\,dx - \int_0^{s(t)} \omega(x,t)\,dx. \tag{5.2.16}$$

It is worth noting that in all cases related to the oxygen diffusion-consumption problem we have

$$1 + \int_0^1 \omega_0(x)\,dx = 0. \tag{5.2.17}$$

Indeed, either $u_0'(0) = 0$, in which case $\int_0^1 u_0''dx = 0$, or $u_0'(0) \neq 0$, and then $\omega_0(x) = u_0''(x) - 1 + 2u_0'(0)\,\delta(x)$, so that (5.2.17) is satisfied.

Thus (5.2.16) is in fact

$$s(t) = -\int_0^{s(t)} \omega(x,t)\,dx, \tag{5.2.18}$$

which allows us to deduce the following:

Theorem 5.2.1. *There exists some finite time $T > 0$ such that for Problem (5.2.1) – (5.2.6)*

$$\lim_{t \uparrow T} s(t) = 0. \tag{5.2.19}$$

Proof.

We know that $\Gamma(x,t) = \frac{1}{\sqrt{2\pi t}} e^{-\frac{x^2}{4t}}$ satisfies the heat equation and tends to zero as $t \downarrow 0$, $\forall x \neq 0$. In addition $\Gamma_x(0,t) = 0$, $-\Gamma(s(t),t) < 0$, and $\int_0^{s(t)} \Gamma(x,t)\,dx = \frac{1}{\sqrt{\pi}} \int_0^{\frac{s(t)}{2\sqrt{t}}} e^{-\eta^2} d\eta \to \frac{1}{2}$ as $t \downarrow 0$.

Therefore we may conclude that $\omega(x,t) > -2\Gamma(x,t)$, and from (5.2.18)

$$s(t) < 2\int_0^{s(t)} \Gamma(x,t)\,dx = \frac{2}{\sqrt{\pi}} \int_0^{\frac{s(t)}{2\sqrt{t}}} e^{-\eta^2} d\eta. \tag{5.2.20}$$

Clearly $s(t)$ cannot have a positive limit for $t \to \infty$ (the r.h.s. tends to 0).

In addition, from (5.2.20) we deduce $1 < \frac{1}{\sqrt{\pi t}}$ (just use the inequality $e^{-\eta^2} < 1$), which prevents t from going to ∞ and provides the estimate $T < \frac{1}{\pi}$ for the extinction time.

Bibliographical remarks.

The general question of existence or non-existence of free boundary problems for the heat equations with a shrinking phase (e.g. oxygen diffusion-consumption, supercooled Stefan problem) has been treated for the one-dimensional case in the papers quoted at the end of this chapter. In particular the conditions leading to blow-up have been identified and the possibility of continuing the solution beyond the blow-up point has been discussed.

The question of the occurrence of singularities in free boundary problem in more than one dimension has been treated extensively in several papers. We just quote[3] .

5.3. Bingham flows

It is well known that in Newtonian fluids the stress tensor is defined as

$$T_{ij} = -p\delta_{ij} + \sigma_{ij} \tag{5.3.1}$$

with p pressure, δ_{ij} Kronecker symbol, and, for *incompressible* fluids

$$\sigma_{ij} = \eta\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \tag{5.3.2}$$

where $\vec{v}$ is the velocity field and $\eta > 0$ is the fluid viscosity.

The corresponding momentum balance equation $\rho\left(\vec{f} - \vec{a}\right) + div\mathbf{T} = \mathbf{0}$ ($\vec{f} =$ body force density, $\vec{a} = \frac{d\vec{v}}{dt}$), is the *Navier-Stokes* equation

$$\frac{\partial \vec{v}}{\partial t} + curl\ \vec{v} \times \vec{v} = -\nabla B + \nu\Delta\vec{v}, \tag{5.3.3}$$

where B (after Bernoulli) plays the role of the *total energy* density

$$B = \frac{1}{2}v^2 + u + \frac{p}{\rho} \tag{5.3.4}$$

($\frac{1}{2}v^2$ kinetic energy, $\vec{f} = -\nabla u$, $\frac{p}{\rho}$ potential energy due to pressure), and $\nu = \frac{\eta}{\rho}$ is the kinematic viscosity. We have assumed $\eta = const.$, which is true in several applications, but not always (e.g. η depends on temperature).

For a one-dimensional flow $\vec{v} = v\vec{e}$, if we take x_1 in the direction of the unit vector $\vec{e}$, we have necessarily $v = v\left(x_2, x_3\right)$, because of incompressibility ($\nabla \cdot \vec{v} = \frac{\partial v}{\partial x_1} = 0$). Hence the deviatoric stress tensor has the expression $\eta\begin{pmatrix} 0 & \frac{\partial v}{\partial x_2} & \frac{\partial v}{\partial x_3} \\ \frac{\partial v}{\partial x_2} & 0 & 0 \\ \frac{\partial v}{\partial x_3} & 0 & 0 \end{pmatrix}$ and the stress on the planes with normal vector $\vec{n}$ orthogonal to the flow is $\vec{\sigma} \cdot \vec{n} = \eta\frac{\partial v}{\partial n}\vec{e}$. Usually one sets $\dot{\gamma} = \left|\frac{\partial v}{\partial n}\right|$ (strain rate) and calling τ the shear stress we have

$$\tau = \eta\dot{\gamma} \tag{5.3.5}$$

This explains why (5.3.5) is referred to as the constitutive relationship for Newtonian fluids in condition of laminar flow.

A *Bingham* (or *viscoplastic*) fluid in the same situation is described by the nonlinear law

$$(\tau - \tau_0)_+ = \eta \, \dot{\gamma}, \tag{5.3.6}$$

exhibiting the presence of a threshold τ_0 (called the yield stress), below which $\dot{\gamma} = 0$, i.e. there is no deformation.

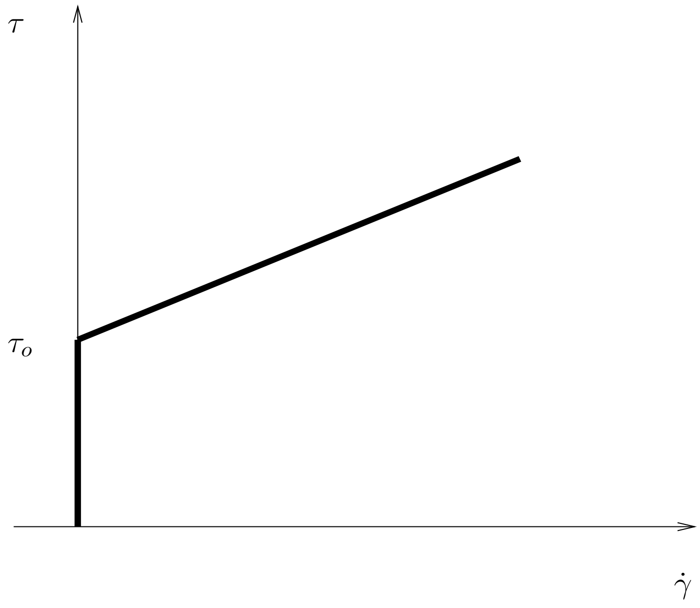


Figure 5.3.1. *Constitutive law for Bingham fluids.*

As a consequence the regions in which $\tau < \tau_0$ move like a rigid body.

For general flows the relationship defining σ_{ij} in terms of the velocity gradient is much more complicated, but here we are interested only in Bingham flows of simple type, like for instance the flow in a horizontal cylinder of circular cross section.

Such a flow is characterized by the presence of a core moving with uniform velocity and coinciding with the region $0 \le \tau < \tau_0$ (on the axis $\tau = 0$ by symmetry).

In this geometry we can easily see that $\vec{v}$, parallel to the axis, can depend only on time and on the radial coordinate r, because of incompressibility, and moreover $\vec{a} = \dfrac{\partial \vec{v}}{\partial t}$, so that for the pair of scalar unknowns p,v we get the system

$$\frac{\partial v}{\partial t} = -\frac{\partial}{\partial z}\left(u + \frac{p}{\rho}\right) + \nu \Delta_r v, \quad \Delta_r v = \frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r}, \quad \tau > \tau_0, \tag{5.3.7}$$

$$0 = -\nabla_{\vec{t}}\left(u + \frac{p}{\rho}\right), \tag{5.3.8}$$

where z is the coordinate along the flow and $\nabla_{\vec{t}}$ is the component of the gradient transversal to the flow. From (5.3.8) we deduce that $u + \dfrac{p}{\rho}$ may depend on z, t only, and separating the variables in (5.3.7) we see that $-\dfrac{\partial}{\partial z}\left(u + \dfrac{p}{\rho}\right) = G(t)$, representing the driving force, i.e. the longitudinal pressure gradient (that has to be prescribed), divided by ρ.

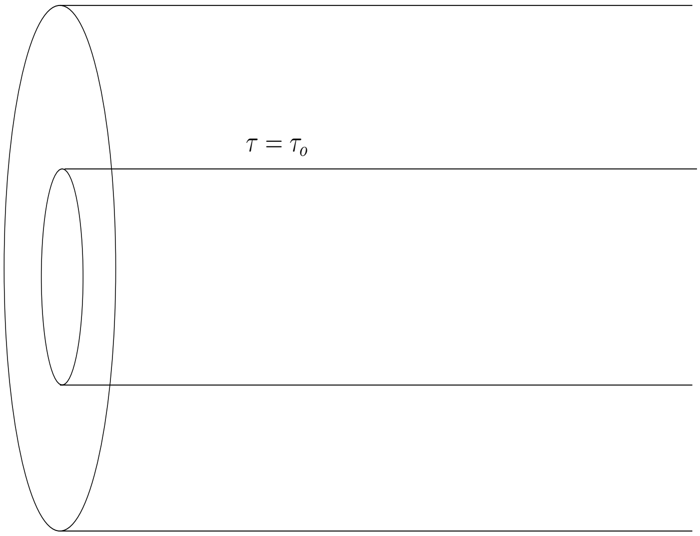


Figure 5.3.2. *Bingham flow in a cylinder exhibiting the undeformed core.*

Thus (5.3.7) becomes

$$\frac{\partial v}{\partial t} - \nu \left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} \right) = G\left(t\right), \tag{5.3.9}$$

to be solved in $s\left(t\right) < r < R$, $t > 0$, with initial conditions (actually just one condition: see Remark (5.3.1) below)

$$s\left(0\right) = s_0 \in \left(0, R\right), \tag{5.3.10}$$

$$v\left(r, 0\right) = v_0\left(r\right), \quad s_0 < r < R, \tag{5.3.11}$$

and the no-slip condition at the pipe wall:

$$v\left(R, t\right) = 0. \tag{5.3.12}$$

The boundary $r = s\left(t\right)$ of the rigid core is the free boundary of the problem and in order to complete the model we have to find out the free boundary conditions.

The first condition expresses the fact that $r = s\left(t\right)$ bounds the no-deformation zone:

$$\left. \frac{\partial v}{\partial r} \right|_{r=s(t)} = 0. \tag{5.3.13}$$

The second condition is obtained by writing down the equation of motion of the unit length of the core.

The acceleration of this body is due to the combined action of the pushing force $\pi s^2 G \rho$ and of the drag force $2\pi s \tau_0$. The mass of the body is $\rho \pi s^2$.

Note: in order to evaluate the rate of change of momentum it must be observed that (if $\dot{s} < 0$) the velocity gradient arising in the "skin" of the element in an infinitesimal time interval dt has no influence on the momentum balance (if $\dot{s} > 0$ there is a slight change of the stress, equally immaterial). Thus we have the second free boundary condition

$$\left. \frac{\partial v}{\partial t} \right|_{r=s(t)} = \frac{1}{\rho} \left(\rho G - \frac{2\tau_0}{s} \right). \tag{5.3.14}$$

Note that (5.3.13), (5.3.14) are neither of Stefan, nor of Cauchy type.

A natural choice for the initial conditions (5.3.10), (5.3.11) is the steady state solution corresponding to $G(0) = G_0$. The steady state solution has a core of radius

$$s_0 = \frac{2\tau_0}{\rho G_0}, \tag{5.3.15}$$

requiring the condition

$$\rho G_0 > \frac{2\tau_0}{R}, \tag{5.3.16}$$

while the velocity field is obtained by integrating

$$\frac{d}{dr}\left(r\frac{dv_0}{dr}\right) = -\frac{G_0}{\nu}r, \quad s_0 < r < R \tag{5.3.17}$$

and imposing $v_0(R) = 0$, $v_0'(s_0) = 0$. The result is

$$v_0(r) = \frac{G_0}{2\nu}\left[\frac{R^2 - r^2}{2} - \left(\frac{2\tau_0}{\rho G_0}\right)^2 \log\frac{R}{r}\right]. \tag{5.3.18}$$

Note that for $\tau_0 \to 0$ we obtain the velocity profile for the flow of a Newtonian fluid in a pipe (Hagen-Poiseuille).

Exercise: Compute the discharge Q corresponding to (5.3.18).

Hint: $Q = 2\pi \int_0^R r v_0(r)\, dr + \pi s_0^2 v_0(s_0)$.

Remark 5.3.1. In the evolution problem the initial value of s is deducible (if the data are prescribed correctly) imposing compatibility of (5.3.9), (5.3.11), (5.3.13), (5.3.14) for $t = 0$, $r = s_0$, obtaining $s_0 = -\dfrac{2\tau_0}{\eta v_0''(s_0)}$. Check that (5.3.15), (5.3.18) satisfy this condition. □

Rescaling Navier-Stokes equations: the Reynolds number.

A typical procedure for rescaling the Navier-Stokes equation is to select a characteristic length L and a characteristic velocity v_0 (e.g. the dischange over the cross section area) to rescale space coordinates and $\vec{v}$, respectively. Time is rescaled by $t_0 = \dfrac{L}{v_0}$. Setting

$$\vec{v}' = \frac{\vec{v}}{v_0}, \quad t' = \frac{t}{t_0}, \quad u' = \frac{u}{v_0^2}, \quad p' = \frac{p}{\rho v_0^2}$$

and defining the operators $curl'$, ∇', Δ' corresponding to the non-dimensional space coordinates, we can write

$$\frac{\partial \vec{v}'}{\partial t'} + curl'\vec{v}' \times \vec{v}' = -\nabla'\left(\frac{1}{2}v'^2 + u' + p'\right) + \frac{1}{Re}\Delta'\vec{v}', \tag{5.3.19}$$

where

$$Re = \frac{L v_0}{\nu} = \frac{L\rho v_0}{\eta} \tag{5.3.20}$$

is the *Reynolds number*.

If $Re \ll 1$ we can neglect the inertia terms. If we also neglect body forces we arrive at the simplified *quasi-steady* (Stokes) equation:

$$\frac{1}{Re}\Delta'\vec{v'} = \nabla' p'. \tag{5.3.21}$$

When the same approximation is applicable to the Bingham flow problem, equations (5.3.15), (5.3.18), with G (slowly) varying with t, provide the quasi-steady solution.

Reducing the Bingham flow problem to a problem with Cauchy data.

If we set $v_r = \xi$, assuming enough regularity we can reformulate the problem as follows

$$\xi_t - \nu\left(\xi_{rr} + \frac{1}{r}\xi_r\right) + \frac{\nu}{r^2}\xi = 0, \quad s(t) < r < R, \quad t > 0 \tag{5.3.22}$$

$$\xi(r,0) = v_0'(r), \tag{5.3.23}$$

$$\left(\xi_r + \frac{1}{R}\xi\right)_{r=R} = -\frac{G}{\nu}, \tag{5.3.24}$$

$$\xi(s(t), t) = 0, \tag{5.3.25}$$

$$\xi_r(s(t), t) = -\frac{2\tau_0}{\eta s(t)}. \tag{5.3.26}$$

Condition (5.3.24) comes from $v_t(R,t) = 0$ and (5.3.9).

We use again (5.3.9) to derive (5.3.26) from (5.3.14).

The system (5.3.22) – (5.3.26) is a free boundary problem with Cauchy data prescribed on the free boundary.

Reducing the Bingham flow problem to a Stefan problem.

We assume some more regularity and we take the acceleration as a new unknown:

$$\omega = v_t. \tag{5.3.27}$$

The system satisfied by ω is

$$\omega_t - \nu\left(\omega_{rr} + \frac{1}{r}\omega_r\right) = \dot{G}, \quad s(t) < r < R, \quad t > 0, \tag{5.3.28}$$

$$s(0) = s_0, \tag{5.3.29}$$

$$\omega(R,t) = 0, \tag{5.3.30}$$

$$\omega(r,0) = G(0) + \nu\left(v_0'' + \frac{1}{r}v_0'\right), \quad s_0 < r < R, \tag{5.3.31}$$

$$\omega(s(t), t) = G - \frac{2\tau_0}{\rho s}, \tag{5.3.32}$$

$$\omega_r\left(s\left(t\right),t\right)=\frac{2\tau_0}{\eta}\frac{\dot{s}}{s}. \tag{5.3.33}$$

The last pair of conditions is of Stefan type, although with space dependent "melting temperature" and "latent heat".

Note that (5.3.29) is now really necessary, while it was not for the original problem (see Remark (5.3.1)), nor for problem (5.3.22) – (5.3.26).

Bibliographical remarks.

The derivation of the model can be found in[119] .

The 1-D Bingham flow (classical statement) was studied for the first time in[32] .

5.4. More estimates for the Bingham flow problem

.

We derive some a priori properties for the problem

$v_t-\nu\left(v_{rr}+\frac{1}{r}v_r\right)=G\left(t\right)>0, \quad s\left(t\right)<x<L, \quad 0<t,$

$v\left(R,t\right)=0, \quad 0<t,$

$v\left(r,0\right)=v_0(r), \quad s_0<x<L,$

$v_r\left(s\left(t\right),t\right)=0,$

with $v_0\left(L\right)=0, \quad v_0'\left(r\right)\leq 0, \quad \left[v_0''+\frac{1}{r}v_0'\leq 0\right].$

Lemma 5.4.1. $v\geq 0, \quad v_r\leq 0.$

Proof.

Use the maximum principle for v and for ξ. □

Lemma 5.4.2. *For a pair of problems with data* $\left(s_i\left(0\right),v_i\left(r,0\right)\right)$ *such that* $s_1\left(0\right)>s_2\left(0\right)$, $0\geq v_{1r}\left(r,0\right)\geq v_{2r}\left(r,0\right)$ *we have* $s_1\left(t\right)>s_2\left(t\right)$.

Proof.

Define $w=\xi_1-\xi_2$, where ξ_1, ξ_2 are the corresponding solutions of (5.3.22)-(5.3.26). At least for some time $s_1>s_2$. Suppose $\overline{t}$ is the first time instant such that $s_1\left(\overline{t}\right)=s_2\left(\overline{t}\right)$.

The function w satisfies the following set of equations in $s_1\left(t\right)<r<L$, $0<t<\overline{t}$:

$w_t-\nu\left(w_{rr}+\frac{1}{r}w_r\right)+\frac{\nu}{r^2}w=0,$

$w\left(r,0\right)\geq 0,$

$\left(w_r+\frac{1}{R}w\right)_{r=R}=0,$

$w\left(s_1\left(t\right),t\right)=-\xi_2\left(s_1\left(t\right),t\right)>0,$

$w_r\left(s_1\left(\overline{t}\right),\overline{t}\right)=0.$

Owing to the maximum principle $w>0$ inside and it takes its absolute minimum for $x=s_1\left(\overline{t}\right)$, $t=\overline{t}$. Thus the boundary point principle is contradicted.

We conclude that $s_1(t) > s_2(t)$ in the common existence time interval. □

Lemma 5.4.3. *Suppose*
(*) $v_0(R) = 0, \quad v_0'(r) \le 0, \quad v_0'' + \frac{1}{r}v_0' \le 0.$
Then $\omega - G \le 0$.

Proof.
Use the maximum principle. □

Lemma 5.4.4. *Add the assumption* $G =$ *constant and*
(**) $\left(v_0'' + \frac{1}{r}v_0'\right)' \le 0, \quad \frac{d}{dr}\left(v_0'' + \frac{1}{r}v_0'\right)\Big|_{r=s_0} < 0.$
Then $\dot{s}(t) < 0$.

Proof.

The function $z = \omega_r = v_{rt}$ satisfies the problem

$$
\begin{aligned}
& z_t - \nu\left(z_{rr} + \frac{1}{r}z_r\right) + \frac{\nu}{r^2}z = 0, \\
& z(r,0) = \nu\left(v_0'' + \frac{1}{r}v_0'\right)' \le 0, \\
& z_r(R,t) = -\frac{1}{R}z(R,t), \\
& z(s(t),t) = \frac{2\tau_0}{\eta s}\dot{s}, \\
& \nu z_r(s(t),t) = -\frac{2\tau_0\dot{s}^2}{\eta s},
\end{aligned}
$$

Having supposed $z(s_0,0) < 0$, we have $\dot{s}(0) < 0$ and therefore $\dot{s}(t) < 0$ at least up to some time $\bar{t}$. For $0 < t \le \bar{t}$ we have $z(r,t) < 0$ for $s(t) < r \le R$, because of the maximum principle and Hopf's lemma (Theorem 2.1.3). Suppose there exists $\bar{t}$ such that $\dot{s}\left(\bar{t}\right) = 0$. Hence $z\left(s\left(\bar{t}\right),\bar{t}\right) = 0$ is the absolute maximum. However the last equation in the above system provides a contradiction to the boundary point principle. □

5.5. One-dimensional free boundary problems with Cauchy data

As we have seen in the previous sections, the oxygen diffusion-consumption problem and the Bingham flow problem (both in 1-D) can be reduced to a Stefan problem. The former is formulated directly as a free boundary problem with Cauchy data, the latter can be also recast into such a form.

Here we want to address the question of reducing 1-D free boundary problems with Cauchy data to Stefan-like problems in a more general framework.

Problem 5.1.
Let f, g be two given functions in the quarter plane $x > 0$, $t > 0$, which are at least continuous, find a pair (s,u), with $u(x,t)$ in the usual class and $s(t)$ continuous for $t \in [0,T]$, $T > 0$ being also unknown, such that

$$u_t - u_{xx} = q(x,t), \quad 0 < x < s(t), \quad t \in (0,T), \tag{5.5.1}$$

$$u(x,0) = h(x), \quad 0 < x < s(0), \quad \text{if } s(0) > 0, \tag{5.5.2}$$

$$u(0,t) = \varphi(t), \quad [u_x(0,t) = \psi(t)], \quad 0 < t < T, \tag{5.5.3}$$

$$u(s(t),t) = f(s(t),t), \quad 0 < t < T, \tag{5.5.4}$$

$$u_x(s(t),t) = g(s(t),t), \quad 0 < t < T. \tag{5.5.5}$$

Assumptions.

The data h, φ $[\psi]$ are also continuous and q is in a Hölder class. Matching conditions are required.

Remark 5.5.1. The value $s(0)$ is defined (possibly not uniquely) by the matching condition

$$h(s_0) = f(s_0, 0). \tag{5.5.6}$$

Existence of s_0 must be assumed. □

Remark 5.5.2. The need of having u_x continuous on the free boundary usually requires more regularity on f and also more regularity is expected for s, although this may not be necessarily true. □

Remark 5.5.3. What we are going to say is confined to the case in which the coefficients of the derivatives in the governing p.d.e. are constant (a slightly more general form of the equation - e.g. in radial symmetry - is instead allowed). □

The most convenient way of studying Problem 5.1 is to reduce it to a Stefan problem. In the following we want to investigate this possibility. We remark that:

(i) in (5.5.3) we choose the Dirichlet condition, leaving the other case as an exercise

(ii) we will tacitly suppose that the data and the solutions have all the regularity required.

Lemma 5.5.1. *Suppose*

$$f_x - g \neq 0. \tag{5.5.7}$$

Then Problem 5.1 is reducible to a Stefan problem.

Proof.

We take

$$v = u_x \tag{5.5.8}$$

as a new unknown. The problem satisfied by v is

$$v_t - v_{xx} = q_x, \tag{5.5.9}$$

$$v\left(x,0\right)=h'\left(x\right),\quad s\left(0\right)=s_0, \tag{5.5.10}$$

$$v_x\left(0,t\right)+q\left(0,t\right)=\dot{\varphi}\left(t\right), \tag{5.5.11}$$

$$v\left(s\left(t\right),t\right)=g\left(s\left(t\right),t\right), \tag{5.5.12}$$

$$\left(f_x-g\right)\dot{s}=v_x+q-f_t \quad \text{for } x=s\left(t\right). \tag{5.5.13}$$

Therefore, thanks to (5.5.7), all solutions of Problem 4.1 that are sufficiently regular, satisfy a Stefan problem. □

Lemma 5.5.2. *Let* (s,v) *be a solution of* (5.5.9) − (5.5.13). *Then*

$$u\left(x,t\right)=-\int_x^{s(t)}v\left(\xi,t\right)d\xi+f\left(s\left(t\right),t\right) \tag{5.5.14}$$

solves Problem 5.1.

Proof.
Just check. □

Thus, within the chosen class of regularity, Problem 5.1 and Problem (5.5.9) − (5.5.13) are equivalent.

For the problem of oxygen diffusion-consumption we have $f=g=0$, so that (5.5.7) *is not* satisfied.

For the Bingham flow problem in the Cauchy form (see (5.3.22)-(5.3.26)) we have $f=0$, $g=\dfrac{2\tau_0}{\mu x}$ and (5.5.7) is satisfied.

Let us now work with the opposite assumption.

Lemma 5.5.3. *Suppose*

$$f_x\equiv g \tag{5.5.15}$$

and that

$$f_t-f_{xx}\neq q. \tag{5.5.16}$$

Then Problem 5.1 is reducible to a Stefan problem.

Proof.
We take

$$w=u_{xx}=v_x \tag{5.5.17}$$

and we note that conditions (5.5.12), (5.5.13) are once more of Cauchy type

$$v\left(s\left(t\right),t\right)=f_x\left(s\left(t\right),t\right), \tag{5.5.18}$$

$$v_x\left(s\left(t\right),t\right)=\left(f_t-q\right)_{x=s(t)}. \tag{5.5.19}$$

Therefore the procedure followed in Lemma 5.5.1 works, provided that $f_{xx}\neq f_t-q$, i.e. if (5.5.16) is satisfied. The resulting problem of Stefan type is

$$w_t-w_{xx}=q_{xx} \tag{5.5.20}$$

$$w\left(x,0\right)=h''\left(x\right),\quad s\left(0\right)=s_0, \tag{5.5.21}$$

$$w\left(0,t\right)=\dot{\varphi}\left(t\right)-q\left(0,t\right), \tag{5.5.22}$$

$$w\left(s\left(t\right),t\right)=\left(f_t-q\right)_{x=s(t)}, \tag{5.5.23}$$

$$\left(f_{xx}-f_t+q\right)\dot{s}=w_x+q_x-f_{xt}\quad\text{for } x=s\left(t\right).\qquad\Box \tag{5.5.24}$$

Conversely we have

Lemma 5.5.4. *Let* (s,w) *solve* (*5.5.20*) $-$ (*5.5.24*). *Then*

$$u\left(x,t\right)=f\left(s\left(t\right),t\right)+f_x\left(s\left(t\right),t\right)\left(x-s\left(t\right)\right)+\int_x^{s(t)}\left(\eta-x\right)w(\eta,t)d\eta \tag{5.5.25}$$

is a solution of Problem 5.1.

Proof.
Elementary. □

At this point the natural question arises on how to proceed is f is a solution of the governing p.d.e. in the original problem, namely

$$f_t-f_{xx}=q. \tag{5.5.26}$$

If we try to iterate the procedure setting $z=w_x$, we start with the free boundary conditions (obtained from (5.5.23), (5.5.24))

$$w\left(s\left(t\right),t\right)=f_{xx}\left(s\left(t\right),t\right), \tag{5.5.27}$$

$$w_x\left(s\left(t\right),t\right)=f_{xxx}\left(s\left(t\right),t\right), \tag{5.5.28}$$

with f_{xx} satisfying the differential equation (5.5.20) and we see that we are back to the situation (5.5.15). It means that we cannot modify the Cauchy character of the boundary conditions.

Thus the cases contemplated in Lemmas 5.5.1, 5.5.3 are the only ones in which Problem 5.1 is equivalent to a Stefan problem (in some regularity classes).

It is little surprise that (5.5.26) + (5.5.15) is a critical case. Indeed, take $u = f$ in Problem 5.1. For any arbitrary $s(t)$ (irrespectively of the regularity), equations (5.5.1), (5.5.4), (5.5.5) are satisfied. Therefore either we have $h(x) = f(x, 0)$ and $\varphi(t) = f(0, t)$, implying that (s, f) is a solution with arbitrary s, or the problem has no solution.

Remark 5.5.4. Lemma 5.5.3 applies to the oxygen diffusion-consumption case. The equivalent problem for $v = u_x$ (see (5.2.7) − (5.2.10) with the addition of $v_x(s(t), t) = 1$) falls in the category of Lemma 5.5.1. □

Bibliographical remarks.

More on the problems discussed in this chapter can be found in the papers[59–61] .
See also[66,67] .

A note on reaction-diffusion problems.

Reaction-diffusion problems have been shortly analyzed here with reference to the one-dimensional dead core problem. However they make a class of impressive variety, with quite important applications, in many cases involving free boundaries. This is particularly true in biology. A remarkable example is the morphological process leading to the formation of coloured patterns on animals coat, based on the diffusion of a pigment reacting with a substrate: a basic reference is[95] . It is absolutely astonishing how some specialized cells in the body can exploit reaction-diffusion to set up feedback mechanisms so to regulate processes like bone growth[55] or blood coagulation[116] .

For lack of space we will not deal with this rich and fundamental class of problems. Fortunately there are good review papers (see[88]).

Reaction-diffusion processes take place also in the dynamics of populations able to detect the concentration gradient of substances acting as attractors or repellents, a phenomenon known as *chemotaxis*. For a review on chemotaxis see[89] . Chemotaxis is a phenomenon of great importance not only for the self-organization of microbial populations, but it operates constantly within our body, helping for instance white blood cells to chase intruding micro-organisms. It is also at the basis of many phenomena leading to the development of the blood vessels network (the *vascularization* of organs), as well as to the vascularization of tumours (*angiogenesis*), having dramatic consequences in their growth.

Chapter 6

Some processes in porous media with free boundaries

6.1. Flows through porous media

A porous medium is made of a solid matrix with a distribution of pores (i.e. voids). The case we are interested in is the one in which pores are connected, so that a fluid can flow through the system.

In the case of an incompressible liquid the pores can be totaly filled or only partially filled. We say that the medium is *saturated* or *unsaturated*, respectively. It is important to understand that the structure of a porous medium is characterized by two scales: the scale of the pores, in which the laws of fluid dynamics can be applied, and the macroscale, in which the flow exhibits some average behavior. Macroscopic quantities are defined as averages on a representative elementary volume, containing a large number of pores, but still being "small" with respect to the size of the system. A typical macroscopic quantity is the medium *porosity* n, i.e. the volume fraction occupied by the pores.

The process leading from the study of the fluid dynamics at the microscopic level to the macroscopic laws of the flow is a well developed branch of mathematics (also applied to different contexts), known as *homogenization*: see e.g.[91,105] .

For a general introduction to porous media, to homogenization and to some important applications (e.g. oil recovery from reservoirs) see[42] .

Basic books in porous media are[8–10] .

Historically homogenization came relatively recently to provide a rigorous justification of the laws commonly used for describing the flow through porous materials. As we said in the preface, the first experimental law for incompressible, saturated flows was given by H. Darcy (1855): let $\vec{q}$ be the volumetric velocity of the flow ($\vec{q}\cdot\vec{n}$ the volume of liquid crossing the unit area of normal $\vec{n}$ per unit time) and γ, μ be the specific weight and the viscosity of the liquid; then

$$\vec{q} = -\frac{K}{\mu}\left(\nabla p + \gamma\vec{e}\right) \tag{6.1.1}$$

where p is the pressure, $\vec{e}$ is the vertical upward directed unit vector, and K is a constant called the medium *permeability*. The sum $p+\gamma z$ has the role of a kinetic potential and is called *hydraulic* *head.*

The presence of the term $\gamma\vec{e}$ means that no motion takes place when the pressure field coincides with the hydrostatic one.

Assuming for instance that a dry medium is penetrated by a fluid supplied at its surface (supposed horizontal: $z = 0$), that the fluid moves under the effect of gravity, and that the wet region is always saturated (meaning that *capillarity* is neglected), a sharp front will move inside the medium separating the wet region and the dry region. In such conditions (6.1.1) holds throughout the wet region and mass balance reduces to $\nabla \cdot \vec{q} = 0$, i.e.

$$\Delta p = 0. \tag{6.1.2}$$

If everything depends only on the vertical coordinate z, (6.1.2) means that p is linear in z and we can set it equal to zero at the penetration front $z = s\,(t)$. The velocity of the front coincides with the molecular velocity. The latter is obtained dividing q by the porosity n, thus

$$\dot{s}\,(t) = -\frac{K}{n\mu}\left(\frac{\partial p}{\partial z} + \gamma\right), \quad s\,(0) = 0. \tag{6.1.3}$$

This simple problem is known as the Green-Ampt problem[83] and its solution depends on the condition prescribed at $z = 0$. For instance, if $p\,(0,t) = p_0 > 0$, then $\dfrac{\partial p}{\partial z} = -\dfrac{p_0}{s\,(t)}$ and equation (6.1.3) becomes

$$\dot{s} + \frac{K}{n\mu}\left(\frac{p_0}{-s} + \gamma\right) = 0 \tag{6.1.4}$$

yielding the solution

$$s + \frac{p_0}{\gamma}\log\left(1 - \frac{\gamma}{p_0}s\right) = -\frac{K}{n\mu}\gamma t. \tag{6.1.5}$$

This formula suggests the appropriate length scale $L = \dfrac{p_0}{\gamma}$ and time scale $t_0 = \dfrac{\mu L}{nK\gamma}$, according to which it reduces to

$$\sigma + \log(1-\sigma) = -\tau,$$

where $\sigma = s/L$, $\tau = t/t_0$. Thus the *short* and *long* time behaviour correspond to $\tau \ll 1 \Leftrightarrow |\sigma| \ll 1$, and to $\tau \gg 1 \Leftrightarrow |\sigma| \gg 1$, respectively. For $\tau \ll 1$ expanding the l.h.s. up to the second order in σ leads to $\sigma^2 \simeq 2\tau$, which means $s(t) \simeq -\Big(\dfrac{2nKp_0}{\mu}t\Big)^{1/2}$. Thus gravity has no role during the first stage of the process, which is dominated by the injection pressure p_0. For $\tau \gg 1$ we can use the approximation $\sigma \simeq -\tau$, i.e. $s(t) \simeq -\dfrac{nK\gamma}{\mu}t$, where the influence of p_0 has disappeared and gravity dominates.

For further discussions and generalizations see[43] .

As we said, the case just examined is an extreme situation in which *capillarity* is neglected. The presence of capillarity eliminates the sharp interface between the saturated and the dry region. It acts through the capillary pressure, which is a given decreasing function of the *saturation* S (the volume fraction of the pores occupied by the liquid). Capillary pressure is the difference between the pressure of air in the pores (which we can set equal to zero) and the pressure of the liquid. Thus we may write $p_c = -p$ in the unsaturated zone and consequently we may consider p as a given increasing function of S.

Dividing pressure by the specific weight γ we define the length

$$\psi = p/\gamma = f(S), \tag{6.1.6}$$

f being invertible. Now we write mass conservation in the form

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} = 0, \quad \theta = nS \tag{6.1.7}$$

and we replace (6.1.1) (in one space dimension) with

$$g'(\psi)\frac{\partial \psi}{\partial t} - \frac{\partial}{\partial z}\left[\kappa(\psi)\left(\frac{\partial \psi}{\partial z} + 1\right)\right] = 0, \tag{6.1.8}$$

(*Richards' equation*) where $g = f^{-1}$ and we let κ depend on ψ in some smooth way (various proposals can be found in the literature). The condition $g'(\psi) > 0$ implies that it is parabolic, although when $\psi \uparrow 0$ (i.e. in the saturation limit) g' may not be bounded and the equation is in that case degenerate. As we shall see, Richard's equation can be used only for sufficiently slowly varying flows.

This simple framework can be complicated in several ways. For instance the liquid may solidify or polymerize becoming extremely viscous (both phenomena are found in the *manufacturing of composite materials*[112]). Or the structure of the porous medium may change during the process (for instance if it contains granules which absorb water, increasing their volume and changing the medium porosity, like in *diapers*[50]). Another case is the displacement of free solid particles in the medium induced by the flow (this has been analyzed in connection with the modelling of the *espresso-coffee brewing*[74]). Another very important case is when we have two immiscible fluids moving in the medium (*displacement of oil by water* in reservoirs, see[42] and the references therein). A large class of problems is provided by those processes in which the medium chemically reacts with the flowing materials (i.e. *combustion*[21,22]). Many industrial applications have been described in the book[44] and in[43] .

More recently the model proposed in[57] for *frying processes* includes massive evaporation and vapour flow. *Penetration of solvents in polymers*[69] and *dry pasta cooking*[73] are other processes in which the penetration of a liquid into a porous material is accompanied by porosity changes.

These generalizations are invariably very difficult.

The inadequacy of Richards' equation to describe unsaturated flows with a fast dynamics has been pointed out by S.M. Hassanizadeh and coworkers,[86] who proposed a model including a relaxation phenomenon, leading to a balance equation of higher order. The corresponding mathematical theory has been developed in[106] . The physical reason for the failure of Richard's equation is to be found in the variation of the curvature of the microscopic gas-liquid interfaces, affecting capillarity.

We also mention that diffusion taking place in a porous medium is usually enhanced by a phenomenon called *dispersion*. This was studied long time ago by G.I. Taylor,[128] but only very recently[1] a rigorous mathematical justification has been provided.

Here we want to deal with two more problems, whose structure is not too far from what we have already illustrated.

6.2. Penetration of rain water into the ground

Obviously this problem is quite classical, but it contains some very delicate aspects concerning in particular the boundary conditions at the inflow surface that have been considered only recently. In the one-dimensional setting the problem has to be solved in a layer between $z = 0$ (the so-called *water table*, bounding the *aquifer*), where saturation is the natural condition

$$\psi(0,t) = 0, \tag{6.2.1}$$

and $z = Z$ (the ground surface), exposed to the action of rain. It is exactly the condition to be specified at $z = Z$ that we want to discuss. The basic reference is[19] .

We may suppose that at time $t = 0$ (when rain starts falling) moisture is distributed in $(0, Z)$ according to the equilibrium solution of (6.1.8)

$$\psi(z,0) = -z. \tag{6.2.2}$$

In this way the whole region is initially unsaturated. Thus it is natural to impose that the inflow boundary condition for $t > 0$ is

$$\kappa(\psi)\left(\frac{\partial\psi}{\partial z} + 1\right)\bigg|_{z=Z} = N(t), \tag{6.2.3}$$

when $N(t)$ is the rainfall rate (water volume per unit surface of the ground, per unit time, can be measured in mm/sec).

However, this situation may not go on indefinitely. Indeed the function $\psi(Z,t)$ solving Richards' equation with the given initial and boundary data can reach the saturation value $\psi(Z,t) = 0$ at some time $\bar{t}$.

For $t > \bar{t}$ the first thing to be observed is that once saturation is reached, a saturation front $z = s(t)$ (free boundary) will propagate in the ground, carrying the conditions

$$\psi(s(t),t) = 0 \tag{6.2.4}$$

$$\left[\frac{\partial\psi}{\partial z}\right] = 0, \tag{6.2.5}$$

the symbol $[\cdot]$ denoting the jump, as usual.

The mass balance in the saturated region $s(t) < z < Z$ yields simply

$$\kappa(0)\frac{\partial\psi}{\partial z} + 1 = N(t), \tag{6.2.6}$$

as long as the ground is able to absorb all the incoming water.

Thus we need a correct criterion to establish when $N(t)$ exceeds the maximum flow rate that the ground can allow. This criterion can be translated into an upper bound for the pressure at $z = Z$. Indeed rain drops hitting the ground in an anelastic way transfer to it their momentum. The momentum transfer rate per unit surface is a pressure, that has been introduced in[19] with the name of *rain pressure*[a]

$$p_{rain} = \rho v N(t) \tag{6.2.7}$$

---

[a] This quantity is usually rather small, being of the order of a few $mm\ H_2O$

(ρ = water density, v = velocity of the rain drops). Dividing p_{rain} by γ we obtain the desired upper bound ψ_{rain} for $\psi(Z,t)$

$$\psi(Z,t) \leq \psi_{rain} = \frac{p_{rain}}{\gamma}. \tag{6.2.8}$$

Therefore the boundary condition (6.2.6) applies as long as the constraint (6.2.8) is satisfied. If solving the problem with condition (6.2.6) the constraint (6.2.8) is violated, then it becomes necessary to change the boundary condition. The way to perform this change must be in agreement with the physical process really taking place at the ground surface. Two extreme situations can arise (intermediate cases are also possible):

(i) all excess water accumulates on the ground surface, creating a pond [b],

(ii) complete runoff of excess water.

The boundary condition for the complete runoff is obvious:

$$\psi(Z,t) = \psi_{rain}. \tag{6.2.9}$$

However we must keep in mind that this new problem is in turn subject to a constraint, since in no case the water flux can exceed the incoming rain water flux.

$$\left(\kappa(0)\frac{\partial\psi}{\partial z} + 1\right)\bigg|_{z=Z} \leq N(t). \tag{6.2.10}$$

Violating this constraint forces to return to the previous regime.

The corresponding doubly constrained free boundary problem has been studied in[19] .

Complete ponding is more complicated, since we can say that the pressure at $z = Z$ exceeds p_{rain} by an amount corresponding to the hydrostatic pressure of the pond which is created. The latter however is an additional unknown of the problem, since the growth rate of the pond is in turn determined by the difference between the rainfall rate and the actual absorption rate of the ground. Of course the existence of the pond is temporary and when it disappears the usual flux condition has to be imposed (possibly with $N = 0$ if rain has stopped).

We stress that in all the analysis we have performed evaporation has been neglected, as well as the migration of water vapour within the porous medium.

There are situations in which on the contrary these processes are the leading ones, as it happens very typically in *drying*[137] .

6.3. Degradation of marble by sulphur dioxide

It is unfortunately well known that many marble (and even more sandstone) monuments have been badly damaged (sometimes devastated) by air pollution. An interesting reference is[98] .

One of the main processes responsible for marble degradation is *sulphation*, a process in which SO_2 and water vapour transform $CaCO_3$ (the basic ingredient of marble) into $CaSO_4$ (*gypsum*) through a chain of chemical reactions, also involving air moisture. The atom of carbon goes into a CO_2 molecule. Gypsum has a higher porosity, a much lower mechanical resistance and can be removed by rain and wind. A mathematical model for this process has been proposed only very

---

[b] The first model with ponding was proposed in.[82]

recently[6] (as in[31] here we follow a slightly different approach). In its simplest form it has the structure of a Stefan problem.

Indeed, if we suppose that the reaction is "infinitely fast" (i.e. the reciprocal of the kinetic constant of the slowest of the reactions in the chain leading from $CaCO_3$ to $CaSO_4$ is much smaller than the typical "diffusion time" (see Sect. I, 3) of SO_2 in air), then we can say that there exists a *reaction front* penetrating the pure marble and leaving behind the gypsum, whose pores are filled with air and impurities SO_2, CO_2, etc.

We have implicitly admitted that diffusion is the transport mechanism for SO_2. Indeed SO_2 is an extremely diluted component of the gas mixture which consists almost totally of air and it is quite obvious that Fickian diffusion comes into play. If we select the frame of reference in which marble is at rest, we should also consider two other phenomena generated by the volume production rate accompanying the reaction: the displacement of gypsum and the flow of air within the gypsum.

In a one-dimensional geometry the velocity of gypsum is proportional and opposite to the velocity $\dot{s}(t)$ of the penetration front $x = s(t)$, the proportionality constant being the ratio between the molar density of gypsum and the one of marble.

Not so simple is the flow of air, originated by the pressure drop associated to the volume production at the reaction front. The air displacement can be described by Darcy's law (in terms of volumetric velocity)

$$n_g (v_a - v_g) = -\kappa_a \frac{\partial p}{\partial x} \tag{6.3.1}$$

(v_a =molecular velocity of air, v_g =velocity of gypsum, n_g =porosity of gypsum) and the mass balance equation is

$$\frac{\partial (n_g c_a)}{\partial t} + \frac{\partial (c_a v_a n_g)}{\partial x} = 0, \tag{6.3.2}$$

where c_a is the density of air in the pores, expressed in terms of pressure via the state equation

$$c_a = c_a(p) \tag{6.3.3}$$

(we are supposing that the process is isothermal). Combining the equations above we obtain a nonlinear parabolic equation for p

$$\frac{\partial}{\partial t}[n_g c_a(p)] + \frac{\partial}{\partial x}\left[-\kappa_a \frac{\partial p}{\partial x} c_a(p) + v_g n_g c_a(p)\right] = 0. \tag{6.3.4}$$

The external boundary $x = \sigma(t)$ moves backward due to the volume change in the reaction, hence

$$\sigma(t) = -\frac{m_g}{m_m} s(t), \tag{6.3.5}$$

where m_m is the number of $CaCO_3$ moles per unit volume in marble and m_g is the analogous quantity in gypsum.

On $x = \sigma(t)$ pressure equals the atmospheric pressure (if the action of wind is neglected). On the reaction front we must say that in the infinitesimal time interval dt the amount of air $c_0 n_m \dot{s} dt$ (where c_0 is the pore density of air in the marble) is replaced by $c_a n_g \dot{s} dt$ and the difference has to be supplied by the air flux. Thus the condition for p on the reaction front can be written as follows

$$-\kappa_a \frac{\partial p}{\partial x} c_a(p) + v_g n_g c_a(p) = (n_g c_a(p) - c_0 n_m)\,\dot{s}. \tag{6.3.6}$$

So the problem for p is well formulated, once the front reaction is known.

The core of the model is the problem for the pore concentration c_s of SO_2:

$$\frac{\partial (n_g c_s)}{\partial t} + \frac{\partial j_s}{\partial x} = 0, \quad \sigma(t) < x < s(t), \tag{6.3.7}$$

$$j_s = n_g \left[-d_s \frac{\partial c_s}{\partial x} + c_s v_a \right], \tag{6.3.8}$$

$$c_s(\sigma(t), t) = c_{s0}(t), \tag{6.3.9}$$

$$c_s(s(t), t) = 0, \tag{6.3.10}$$

$$-d_s \frac{\partial c_s}{\partial x} \frac{n_g}{M_s} = \frac{\rho_m}{M_m} \dot{s}. \tag{6.3.11}$$

The first equation is mass balance. The expression (6.3.8) of the SO_2 flux assumes that the SO_2 flow relative to air is of Fickian type with diffusivity d_s. The free boundary conditions are written supposing that the chemical reaction is "infinitely fast" (all SO_2 is consumed) and (6.3.11) represents the mass balance in the reaction (M_s, M_m are molar weights), keeping into account that, because of (6.3.10), the SO_2 flux on the front is purely diffusive. The simple structure of the diffusive transport of SO_2 in air we have assumed is justified if the pressure field is sufficiently flat.

Introducing non-dimensional variables it is possible to realize that this is indeed the case and that the approximation

$$v_a \simeq v_g$$

makes sense. If one performs the transformation to the Lagrangian coordinate $\xi = x - \sigma(t)$, it is immediately realized that problem (6.3.7) $-$ (6.3.11) reduces exactly to the Stefan problem studied in Sect. 2, Chapter III, so that if $c_{s0} = const.$ we have the explicit solution. In our case we can further simplify the problem exploiting the fact that the time scale of the front penetration is by several order of magnitude larger than the time scale of diffusion, so that diffusion of SO_2 within the gypsum may be considered quasi-stationary (i.e. the SO_2 concentration is linear).

The problem however is not as simple as it may look at this stage, because the role that water vapor plays in the process is intrinsically complicated. Indeed there is a threshold for moisture below which the sulphation process stops completely. This is an intriguing phenomenon, which we may try to explain.

The sulphation reaction requires the simultaneous presence of a molecule of SO_2 and of two molecules of H_2O at the same point of the reaction front. If H_2O is just at the gaseous state such an event has an extremely low probability. If all incoming SO_2 molecules have to react then necessarily H_2O must be present as a liquid film coating the reaction front. Indeed marble is hygroscopic and the moisture threshold corresponds to the formation or dissolution of the film. Of course there will be an intermediate regime in which the reaction is incomplete (humid spots replace the continuous water film). In that case the correct boundary conditions are no longer (6.3.10), (6.3.11), but they must be replaced by

$$\frac{1}{M_s} j_s = \frac{\rho_m}{M_m}\dot{s} + n_g \frac{c_s}{M_s}\dot{s}, \tag{6.3.12}$$

$$\frac{\rho_m}{M_m}\dot{s} = \alpha n_g c_s, \tag{6.3.13}$$

where $\alpha \in [0, +\infty]$ is a function of the H_2O concentration (and of temperature and pressure). The first equation is the total molar balance. The r.h.s. contains not only the consumption rate, but also the advection flux of the residual SO_2 on the moving front. The second equation specifies the efficiency of the reaction though the coefficient α. When the H_2O concentration approaches the value of maximum efficiency $\alpha \to +\infty$, forcing c_s to go to zero. In that case we are back to full speed boundary conditions (6.3.10), (6.3.11). On the contrary, if the relative humidity decreases to the no-reaction threshold then $\alpha \to 0$, the front stops and the SO_2 flux vanishes (meaning in this case $\frac{\partial c_s}{\partial x} = 0$).

During the intermediate regime it becomes important to study the transport of H_2O within the gypsum. If c_w denotes the pore concentration of water vapour and d_w is its diffusivity in air, the vapour flux is given by

$$j_w = n_g\Big(- d_w \frac{\partial w}{\partial x} + c_w v_a\Big) \tag{6.3.14}$$

with the boundary condition $w = w_0$ (concentration in air) at the outer surface.[c]

The balance equation for H_2O provides the governing differential equation

$$\frac{\partial (n_g c_w)}{\partial t} + \frac{\partial j_w}{\partial x} = 0. \tag{6.3.15}$$

On the reaction front j_w has to provide two moles for each mole of reacted $CaCO_3$ and the amount of H_2O which travels together the front, namely

$$\frac{j_w}{M_w} = 2\frac{\rho_m}{M_m}\dot{s} + n_g \frac{c_w}{M_w}\dot{s} \tag{6.3.16}$$

(neglecting water content in the pristine marble).

We remark that when the typical time scale for diffusion $\frac{\sigma^{*2}}{d_s}$ (where σ^* is a typical thickness of the gypsum layer) is much smaller than the typical time scale of the penetration of marble sulphation, then the SO_2 transport can be considered quasi-steady: $\frac{\partial j_s}{\partial x} = 0$. In the regime of complete reaction, this leads to conclude that

$$-n_g\Big(d_s \frac{\partial c_s}{\partial x} + \omega c_s \dot{s}\Big) = \frac{M_s}{M_m}\rho_m \dot{s}. \tag{6.3.17}$$

---

[c] We are supposing that the stone is in thermal equilibrium with air. In the opposite case, not considered here, temperature will in fact play an important role, since the continuity of H_2O concentration at the outer surface must be replaced with the continuity of vapour pressure.

Since $s(t)-\sigma(t)=(1+\omega)s(t)$, we immediately get

$$c_s=-\Sigma+(c_{s0}+\Sigma)e^{-c_0\dot{s}(x-\sigma)/d_s} \tag{6.3.18}$$

with $\Sigma=\dfrac{M_s\rho_m}{M_m n_g\omega}$. Imposing (6.3.10) we find an o.d.e. for $s(t)$, leading to the solution

$$s(t)\simeq\Big[\frac{2d_s}{\omega(1+\omega)}\frac{1}{\Sigma}\int_0^t c_{s0}(\tau)d\tau\Big]^{1/2}, \tag{6.3.19}$$

where we have used $\dfrac{c_{s0}}{\Sigma}\ll 1$.

In particular, if $c_{s0}=$ *constant* (6.3.19) exhibits the typical $\sqrt{t}$ behaviour of the self-similar solutions of the Stefan problem (see Chapt. 3, Sect. 3). Thus we get the interesting information that SO_2 is particularly aggressive during the first stage of the process, while later the gypsum layer has a protective action. Therefore it is not advisable to remove the gypsum layer too frequently.

Also, from (6.3.19) we can derive a useful indication about the way of rescaling the whole problem. Taking e.g. the seasonal average c_{s0}^* of the SO_2 concentration and for instance the time scale $t^*=3$ *months*, the correct length scale is provided by (6.3.19):

$$\sigma^*=\Big(\frac{2d_st^*}{\omega(1+\omega)}\frac{c_{s0}^*}{\Sigma}\Big)^{1/2}. \tag{6.3.20}$$

For instance, taking $d_s=0.1\cdot10^{-4}\mathrm{m}^2/\mathrm{sec}$, $n_g=0.3$, $\Sigma\simeq3\cdot10^3$, $\omega=2$, we obtain $\sigma^*=23.6\mu\mathrm{m}$, in agreement with experiments.

Chapter 7

Deposition of solid wax from crude oils

7.1. Waxy crude oils

It is well known that petroleum is a mixture of hydrocarbons. Oils with a high content of heavy hydrocarbons are called *Waxy Crude Oils* (WCO's). The rheological behaviour of WCO's is complicated by a series of factors.

(i) Below some temperature (*cloud point* or WAT = *Wax Appearance Temperature*) the complex of heavy hydrocarbons (collectively called *wax*) begins to crystallize. The crystals segregate forming a suspension.
(ii) When a lower temperature (*pour point*) is reached the crystals develop a strong tendency to become entangled generating a gel-like structure.
(iii) When the segregated phase is present, the rest of the system can be considered a saturated solution of wax in oil. If a temperature gradient is applied, since the concentration of wax at saturation is an increasing function of temperature, a gradient of concentration is generated, parallel to the gradient of temperature. Consequently the dissolved wax migrates from the warmer to the colder regions. This phenomenon is responsible for the formation of solid wax deposits on the wall of pipelines exposed to a sufficiently cold environment.

The rheological implications of (i), (ii) have been studied in a number of papers (see the survey paper[52]). The system can be considered a Bingham fluid (see Capt. 5, Sect. 3) whose yield stress depends on the concentration of the segregated phase and on its degree of entanglement, which evolves according to a kinetics driven by two contrasting phenomena: spontaneous aggregation and disaggregation induced by internal friction.

Here we want to discuss very briefly the phenomenon of deposition at the wall. Such a problem is critical for the operation of pipelines, because it is necessary to remove the deposit periodically, before it becomes too thick. The cleaning procedure is expensive and therefore predicting the growth rate of the deposit is crucial.

Modelling wax deposition encounters several difficulties related to the impossibility of performing direct measures of wax diffusivity in oil. As a matter of fact, diffusivity is measured indirectly, precisely through the effect of solid wax deposition under a controlled thermal gradient. The experimental apparatus devoted to it is known as the *cold finger* and there are several very delicate questions in interpreting the data obtained in terms of deposited mass vs. time. These aspects have been discussed at length in the papers[34] ,[35] , treating the two cases of the instrument with no agitation of the WCO sample and with agitation, respectively. Here we will not deal with the cold finger problem, because of its complexity.

The general framework of diffusion induced in saturated solutions by thermal gradients (not to be confounded with the so-called *Soret effect*[a]) has been investigated in[70–72] for a number of different scenarios.

More recently it has been emphasized that at sufficiently low temperatures the effect of gel formation becomes quite important. The paper[53] studies the complex problem of gel formation in static conditions, coupled with wax diffusion. Such a process may involve several stages and its mathematical formulation include many free boundaries problems of different character and is therefore very complicated.

Here we will not consider gel formation, but instead we illustrate some basic ideas about modelling wax deposition in pipelines.

7.2. The wax deposition problem

Let us refer for simplicity to a one-dimensional problem in which the sample has been prepared at time $t = 0$ as follows. For $t < 0$ the layer $0 < x < L$ is occupied by a WCO at a uniform temperature above WAT with a dissolved wax concentration c_{tot}. Let $c_s(T)$ be the saturation concentration of wax in oil as a function of the temperature T. Typically $c_s'(T) > 0$. The walls $x = 0$, $x = L$ are cooled to the respective temperatures $T_1 < T_2$, both below WAT. If we can assume that the thermal diffusivity of the system is considerably larger than wax diffusivity, the system can be brought to thermal equilibrium i.e. with the temperature

$$T_0(x) = T_1 + \frac{x}{L}(T_2 - T_1), \quad 0 < x < L, \tag{7.2.1}$$

in a time which is too short for any significant mass transfer to take place.

Thus we may assume that (7.2.1) is the thermal profile at time $t = 0$ and that the system is initially composed by a saturated solution with concentration

$$c_0(x) = c_s(T_0(x)) \equiv: C_s(x), \quad 0 < x < L, \tag{7.2.2}$$

and by a suspension of crystallized segregated phase with concentration

$$G_0(x) = c_{tot} - C_s(x). \tag{7.2.3}$$

Since $c_0'(x) = c_s'(T_0(x))\dfrac{T_2 - T_1}{L} > 0$, diffusion in the solution is activated with the result of transporting wax to the colder wall, where the incoming wax has to crystallize, forming the deposit. In the following we will assume that all the components have the same density, so that no volume change takes place in the system during the process.

As to the segregated phase we have various possibilities:

---

[a] The Soret effect consists in the creation of inhomogeneities in fluid mixtures subject to a thermal gradient.

(a) we may consider it immobile (which is the most likely scenario if gelification has occurred) or we can suppose it has some diffusivity,

(b) we may suppose that it is always in thermodynamical equilibrium with the solute or, on the contrary, that mass exchange between the two phases occurs via some kinetics characterized by a finite rate constant. Large deviations from equilibrium are normally observed in calorimetric experiments in samples exposed to sufficiently large cooling rates (see[101]).

Each of these choices (dictated in practice by the rate of variation of the thermal field) is going to influence the mathematical structure of the model, thus we are faced with a multiplicity of problems. In addition:

(c) the wax diffusivity in the solution (provided *Fick's law* is applicable) may or may not depend on temperature and/or on the concentration of the segregated phase and the same is true for the thermal conductivity of the mixture,

(d) the system oil+dissolved wax+crystallized wax should be treated as a mixture, unless wax concentration is small enough (and the deposit growth is slow enough) to disregard the oil displacement; a model including oil displacement has been presented in[71] ,

(e) if the thermal conductivity of the deposit is different from the one of the mixture, the temperature profile will change as the deposit grows.

The latter situation, discussed in[72] , is the source of a considerable complication because it continuously modifies the profile of the saturation concentration within the sample.

7.3. Statement of a specific problem

To be specific, let us select the following (largely simplified) situation:

- the dissolved wax has a constant diffusivity D,
- the segregated phase has a constant non-zero diffusivity $D_G < D$,
- the difference between the thermal conductivity of solid wax and the one of the mixture is negligible, hence the thermal field is described by (7.2.1) for all $t > 0$,
- the segregated crystallized phase is always in thermodynamical equilibrium with the solution (thus it exists only in the presence of saturation),
- the oil displacement can be neglected,
- the deposit has no oil inclusion,
- the saturation concentration c_s is a linear function of T:

$$c_s'(T) = b > 0, \text{ constant.} \tag{7.3.1}$$

We will denote by $G(x,t)$ the concentration of the segregated phase.
We consider the one-dimensional process described in the previous section.
Owing to the assumptions listed above, the system will go through the following three stages.

Stage 1. $G > 0$ everywhere, the solution remaining saturated. This stage terminates at some finite time t_1, at which G vanishes at some point. We will consider a situation in which G is decreasing in x for each t. Therefore G will first vanish at $x = L$.

Stage 2. For $t > t_1$ the wax supply from the segregated phase replacing the dissolved wax leaving the wall $x = L$ by diffusion is discontinued. As a consequence a *desaturation front* proceeds from $x = L$ inwards. This will be a second free boundary, evolving simultaneously with the deposition front. This stage too is bound to finite time extinction.

Stage 3. At the time t_2 at which the whole solution becomes unsaturated we return to a problem with only one free boundary (the deposition front). The system will tend asymptotically to equilibrium.

Let us write down the governing equations for the three stages under the largely simplifying assumptions listed above.

Stage 1 $(0 < t < t_1)$(onset of deposition, solution everywhere saturated).

$$\frac{\partial G}{\partial t} - D_G \frac{\partial^2 G}{\partial x^2} = 0, \quad \sigma(t) < x < L, 0 < t < t_1, \tag{7.3.2}$$

$$G(x,0) = G_0(x) = c_{tot} - c_s(x), \quad 0 < x < L, \tag{7.3.3}$$

$$D_G \frac{\partial G}{\partial x}|_{x=L} = -\omega, \quad 0 < t < t_1, \tag{7.3.4}$$

$$\frac{\partial G}{\partial x}|_{x=\sigma(t)} = 0, \quad 0 < t < t_1, \tag{7.3.5}$$

$$[\rho - C_s(\sigma(t)) - G(\sigma(t),t)]\dot{\sigma} = \omega, \quad 0 < t < t_1, \tag{7.3.6}$$

$$\sigma(0) = 0, \tag{7.3.7}$$

where $\omega = Db\dfrac{T_2 - T_1}{L}$.
The initial condition (7.3.3) is nothing but (7.2.3) with the assumption (7.3.1). Equation (7.3.4) is the mass balance at $x = L$. Equation (7.3.5) says that no diffusive flux of the segregated phase takes place at the deposition front. More generally one could suppose that only a fraction $\chi \in (0,1)$ of the incoming flux ω will give rise to the deposit. In that case (7.3.5) should be modified to $-D_G\dfrac{\partial G}{\partial x} = (1-\chi)\omega$. We will continue our analysis with $\chi = 1$. In writing (7.3.6) we made the assumption that the advancing front $x = \sigma(t)$ captures the wax crystals it finds on its way. Similarly, the presence of C_s in (7.3.6) is motivated by the fact that (if we neglect the oil displacement by the deposit) the mass $C_s d\sigma$ is replaced by the mass $\rho d\sigma$. It must be stressed however that ignoring oil displacement is consistent only with $C_s \ll \rho$. Therefore it would be admissible to write (7.3.6) without it. Of course $C_s + G$ is always less than the common density ρ of all the components (prove it as an exercise). Finally we note that equation (7.3.2) is homogeneous, consistently with assumption (7.3.1). When (7.3.1) is not true (i.e. $c_s''(T) \neq 0$) the supposed thermodynamical equilibrium between the two waxy phases would imply a mass

exchange: if $c_s'' > 0$ the solution tends to become super-saturated and part of dissolved wax has to crystallized, leading to

$$\frac{\partial G}{\partial t} - D_G \frac{\partial^2 G}{\partial x^2} = D \frac{d^2}{dx^2} c_s(x).$$

If $c_s'' < 0$ the solution tends to desaturate and the appropriate amount of G has to be dissolved to maintain saturation (the equation is still the same).
We leave the proof of the following simple lemma to the reader:

Lemma 7.3.1. *Let* (σ, G) *be a solution of (7.3.2)-(7.3.6). Then* $\frac{\partial G}{\partial x} < 0$ *for* $0 < x \leq L$, $0 \leq t \leq t_1$.

This result guarantees that G vanishes for the first time at $x = L$.

Stage 2 $(t_1 < t < t_2)$(evolution of the desaturating front).

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0, \quad s(t) < x < L, t_1 < t < t_2, \tag{7.3.8}$$

$$s(t_1) = L, \tag{7.3.9}$$

$$\frac{\partial G}{\partial t} - D_G \frac{\partial^2 G}{\partial x^2} = 0, \quad \sigma(t) < x < s(t), t_1 < t < t_2, \tag{7.3.10}$$

$$G(x, t_1+) = G(x, t_1-) =: G_1(x), \quad \sigma(t_1) < x < L, \tag{7.3.11}$$

$$\omega = D \frac{\partial c}{\partial x}|_{x=s(t)+} - D_G \frac{\partial G}{\partial x}|_{x=s(t)-}, \quad t_1 < t < t_2, \tag{7.3.12}$$

$$[\rho - C_s(\sigma) - G]\dot{\sigma} = \omega, \quad \sigma(t_1+) = \sigma(t_1-), \quad t_1 < t < t_2, \tag{7.3.13}$$

$$c(s(t), t) = C_s(s(t)), \tag{7.3.14}$$

$$G(s(t), t) = 0. \tag{7.3.15}$$

Equation (7.3.8) describes diffusion in the unsaturated region. Equation (7.3.12) means that at the desaturation front the segregated phase provides the mass flux compensating the unbalance between the incoming flux from the unsaturated region and the outgoing flux in the saturated region.

Stage 3 $(t_2 < t < +\infty)$(solution everywhere unsaturated, reaching equilibrium).
The following scheme requires no particular comment:

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0, \quad \sigma(t) < x < L, t_2 < t, \tag{7.3.16}$$

$$c(x,t_2+) = c(x,t_2-) =: c_2(x), \quad \sigma(t_2) < x < L, \tag{7.3.17}$$

$$\frac{\partial c}{\partial x}|_{x=L} = 0, \quad t_2 < t, \tag{7.3.18}$$

$$c(\sigma(t),t) = C_s(\sigma(t)), \quad t_2 < t, \tag{7.3.19}$$

$$(\rho - C_s(\sigma))\dot{\sigma} = D\frac{\partial c}{\partial x}|_{x=\sigma(t)}, \quad \sigma(t_2+) = \sigma(t_2-), t_2 < t. \tag{7.3.20}$$

7.4. Analysis of the three stages of the process

Stage 1.

Problem (7.3.2)-(7.3.7) is not in the class of Stefan-like problems, because $\frac{\partial G}{\partial x}$ (and not G) is prescribed on the free boundary and the velocity $\dot{\sigma}$ is related to G (and not to $\frac{\partial G}{\partial x}$), which makes the problem usually more complicated. A possible method for proving well-posedness stems from the global mass balance equation, which is obtained by integrating equation (7.3.2) over each domain $\sigma(\tau) < x < L$, $0 < \tau < t$:

$$\rho\sigma(t) = \int_0^{\sigma(t)} C_s(x)dx + \int_0^L G_0(x)dx - \int_{\sigma(t)}^L G(x,t)dx. \tag{7.4.1}$$

The latter has an obvious interpretation: although the deposit is created by the crystallization of the incoming solute flux, the ultimate source of the mass needed to reach the amount $\rho\sigma$ is the segregated phase.
Conversely, if (σ, G) solves (7.3.2)-(7.3.5) and (7.4.1), then it solves also the original problem, as it can be seen by differentiating (7.4.1). In other words, (7.3.6) can be replaced by (7.4.1). This fact suggests the following fixed point argument.

(i) Define the set

$$\Sigma = \{\sigma \in C([0,\vartheta]) | \sigma(0) = 0, 0 \le \dot{\sigma}(t) \le \frac{Db}{\rho - c_{tot}}, 0 \le \frac{|\dot{\sigma}(t') - \dot{\sigma}(t'')|}{|t' - t''|^\alpha} \le K, \forall t' \neq t''\},$$

with $\vartheta > 0$, $K > 0$ to be determined, and $\alpha \in (0, \frac{1}{2})$. For the moment we can take $0 < \vartheta \le L\frac{\rho - c_{tot}}{Db}$.

(ii) Take $\sigma \in \Sigma$ and solve (7.3.2)-(7.3.5) to find $G(x,t)$.

(iii) Define the mapping $M\sigma = \tilde{\sigma}$ via

$$\rho\tilde{\sigma}(t) = \int_0^{\sigma(t)} C_s(x)dx + \int_0^L G_0(x)dx - \int_{\sigma(t)}^L G(x,t)dx. \tag{7.4.2}$$

Solutions of the original problems are found in correspondence of fixed points of the mapping M, thanks to (7.4.1). It is easily seen that $\tilde{\sigma}$ has the same regularity as σ and that K, α can be chosen so that $M(\Sigma) \subset \Sigma$.

The underlying idea for the selection of the set Σ is that it is easy to prove that any $G(x,t)$ calculated by means of the above procedure will be decreasing in x and bounded above by $G_0(0)$, which in turn provides an a-priori uniform estimate for $\frac{d\tilde{\sigma}}{dt}$ and at the same time a lower bound for the extinction time t_1.

Thus applying Schauder's fixed point theorem is now equivalent to showing the continuous dependence (in the sup-norm) of the solution $G(x,t)$ of (7.3.2)-(7.3.5) on the C^1-norm of the boundary.

We sketch how to prove that the mapping is indeed contractive if ϑ is sufficiently small.

Lemma 7.4.1. *The mapping $M : \Sigma \to \Sigma$ is contractive in the C^1-norm for ϑ sufficiently small.*

Proof.

From (7.4.2) for any pair $\sigma_1, \sigma_2 \in \Sigma$, setting $\alpha(t) = \min(\sigma_1(t), \sigma_2(t))$, $\beta(t) = \max(\sigma_1(t), \sigma_2(t))$, we have

$$\tilde{\sigma}_1 - \tilde{\sigma}_2 = \frac{1}{\rho}\{\int_{\alpha(t)}^{\beta(t)} C_s(x)dx +$$

$$-\int_{\beta(t)}^{L} [G_1(x,t) - G_2(x,t)]dx + (-1)^{j+1}\int_{\alpha(t)}^{\beta(t)} G_j(x,t)dx\},$$

where j is the index of the minimum between σ_1, σ_2. Considering that $\frac{C_s}{\rho} < 1$, the nontrivial part of the proof is to find an estimate of $G_1 - G_2$.

To simplify notation we rescale x, t (without changing any symbol) so that $x = L$ becomes $x = 1$ and we can set $D_G = 1$ in (7.3.2).

Since G_0 is a linear function of x, the function

$$V(x,t) = G(x,t) - G_0(x) \tag{7.4.3}$$

satisfies

$$\frac{\partial V}{\partial t} - \frac{\partial^2 V}{\partial x^2} = 0, \quad \sigma < x < 1, 0 < t < \vartheta, \tag{7.4.4}$$

$$V(x,0) = 0, \quad 0 < x < 1, \tag{7.4.5}$$

$$\frac{\partial V}{\partial x}|_{x=\sigma(t)} = h_1 \quad 0 < t < \vartheta, \tag{7.4.6}$$

$$\frac{\partial V}{\partial x}|_{x=1} = h_2 \quad 0 < t < \vartheta, \tag{7.4.7}$$

where h_1, h_2 are known constants.

Now we use the representation formula (see Chapter 2)

$$V(x,t) = \int_0^t \mu_1(\tau)\Gamma(x,t;\sigma(\tau),\tau)d\tau + \int_0^t \mu_2(\tau)\Gamma(x,t;1,\tau)d\tau \tag{7.4.8}$$

by means of heat potentials, with μ_1, μ_2 satisfying the system

$$h_1 = -\frac{1}{2}\mu_1(t) + \int_0^t \mu_1(\tau)\Gamma_x(\sigma(t), t; \sigma(\tau), \tau)d\tau + \\ + \int_0^t \mu_2(\tau)\Gamma_x(\sigma(t), t; 1, \tau)d\tau, \tag{7.4.9}$$

$$h_2 = \frac{1}{2}\mu_2(t) + \int_0^t \mu_1(\tau)\Gamma_x(1, t; \sigma(\tau), \tau)d\tau, \tag{7.4.10}$$

obtained by imposing (7.4.6), (7.4.7), which we know to possess a unique continuous solution (μ_1, μ_2).
At this point, if we take $\sigma \in \Sigma$ and a perturbation $\delta\sigma$ such that $\sigma + \delta\sigma \in \Sigma$, we can evaluate the corresponding variations $\delta\mu_1$, $\delta\mu_2$ by taking the differences in (7.4.9), (7.4.10).
We invite the reader to write down the whole resulting system of Volterra integral equations and we just point out that, as in equations (7.4.9), (7.4.10), the kernels have a singularity of Abel type (i.e. of the order $(t-\tau)^{-1/2}$) and the free terms are in absolute value dominated by

$$M \int_0^t \frac{\|\delta\dot{\sigma}\|_\tau}{\sqrt{t-\tau}} d\tau$$

with M denoting a constant dependent on the data only and $\|f\|_\tau = \sup\limits_{\eta \in (0,\tau)} |f(\eta)|$. We conclude that $|\delta\mu_1|$, $|\delta\mu_2|$ possess a similar estimate and consequently the change δV of V can be estimated in the sup-norm up to time $t = \vartheta$

$$\|\delta V\|_C \leq N\sqrt{\vartheta}\|\delta\sigma\|_{C^1},$$

which proves the Lemma. □

Existence and uniqueness follow, as well as the possibility of extending the solution up to the extinction time of Stage 1.

Stage 2.
Stage 1 terminates at a time which is less than the time needed for consuming the wax amount $\int_0^L G_0(x)dx$ at the rate ω. We denote by t_1 the time at which $G(L,t)$ vanishes. Then $t_1 < \frac{1}{\omega}\int_0^L G_0(x)dx$.
By integrating (7.3.10), (7.3.8) in the respective domains and using the free boundary conditions, the new mass balance is obtained:

$$\rho(\sigma(t) - \sigma(t_1)) = \int_{\sigma(t_1)}^L G_1(x)dx - \int_{\sigma(t)}^{s(t)} G(x,t)dx + \\ + \int_{\sigma(t_1)}^{\sigma(t)} C_s(x)dx + \int_{s(t)}^L [C_s(x) - c(x,t)]dx. \tag{7.4.11}$$

This equation shows that, besides the contribution of the segregated phase similar to the one in (7.4.1), we have the additional wax amount coming from desaturation.

As it was shown in[71] ,[72] , adopting as a new variable the concentration of wax in excess or defect with respect to saturation, namely

$$u = G, \quad \text{if } G > 0, \quad u = c - c_s, \quad \text{if } G = 0, \tag{7.4.12}$$

for a given σ the problem including the desaturation front can be formulated in a weak form, in which existence and uniqueness are not difficult to be proved. Next, a fixed point argument can be set up to prove existence and uniqueness for the whole problem. We omit the details. Like in Stage 1, it is easy to see that $G_x(x,t) < 0$ in $\sigma(t) < x < s(t)$. The inequality $c < c_s$ in $s(t) < x < L$ is guaranteed by the maximum principle.

Stage 3. Problem (7.3.16)-(7.3.20) has the simple structure of a Stefan problem, therefore there is no need to discuss it. We just report the mass balance

$$\rho[\sigma(t) - \sigma(t_2)] = \int_{\sigma(t_2)}^{L} c_2(x)dx - \int_{\sigma(t)}^{L} c(x,t)dx \tag{7.4.13}$$

whose interpretation is obvious.
Since as $t \to \infty$ the residual concentration tends to $C_s(\sigma_\infty)$, from (7.4.13) we deduce

$$\rho[\sigma_\infty - \sigma(t_2)] = \int_{\sigma(t_2)}^{L} c_2(x)dx - (L - \sigma_\infty)C_s(\sigma_\infty). \tag{7.4.14}$$

Going back to (7.4.11)

$$\rho[\sigma(t_2) - \sigma(t_1)] = \int_{\sigma(t_1)}^{L} G_1(x)dx - \int_{\sigma(t_1)}^{L} C_s(x)dx - \int_{\sigma(t_2)}^{L} c_2(x)dx, \tag{7.4.15}$$

and to (7.4.1)

$$\rho\sigma(t_1) = \int_0^{\sigma(t_1)} C_s(x)dx + \int_0^L G_0(x)dx - \int_{\sigma_1}^{L} G_1(x)dx, \tag{7.4.16}$$

and summing up (7.4.14)-(7.4.16) we obtain the final equation

$$\rho\sigma_\infty = \int_0^L C_s(x)dx + \int_0^L G_0(x)dx - (L - \sigma_\infty)C_s(\sigma_\infty),$$

i.e.

$$\rho\sigma_\infty = c_{tot}L - (L - \sigma_\infty)C_s(\sigma_\infty) \tag{7.4.17}$$

which could have been written from the very beginning.
Since the function $\rho\sigma_\infty + (L - \sigma_\infty)C_s(\sigma_\infty)$ is increasing from $LC_s(0) < Lc_{tot}$ to $\rho L > Lc_{tot}$ for $\sigma_\infty \in [0, L]$, equation (7.4.17) provides a unique determination of σ_∞.

7.5. Application to the pipelining of waxy crude oils

In[33] a model is presented to predict the amount of wax deposited during the pipelining of a wax-saturated oil when the outside temperature is below WAT.
The specific case of turbulent regime (for which some field data are available) has been studied.

If R is the pipe radius and $\sigma_d(z,t)$ is the deposit thickness (z is the longitudinal coordinate along the pipe, t is time), the pipe lumen is $\nu = R - \sigma_d$. In the turbulent regime we have to consider a mechanical boundary layer of thickness σ_m (so that $R_m = \nu - \sigma_m$ is the radius of the turbulent core possessing a velocity V) and a thermal boundary layer of thickness σ_T (so that temperature can be considered homogeneous over cross sections of radius $R_T = \nu - \sigma_T$).
The thickness of the mechanical boundary layer in a quasi-steady flow can be grossly estimated by means of a simple momentum balance and it turns out to be $\sigma_m = \varepsilon_m \nu$ with

$$\varepsilon_m = \frac{2\eta Q}{G\pi\nu^4},$$

where G is the pressure gradient, η the oil viscosity, Q the pipe discharge. In the applications considered in[33] $\varepsilon_m \simeq 0.1$. Therefore, when convenient, the approximation $\nu \simeq R$ can be justified, e.g. to express $Q \simeq \pi\nu^2 V$. Using classical correlations expressing G by means of geometrical and dynamical flow quantities the final expression

$$\varepsilon_m = \frac{16}{Re} \ln^2 \left[\frac{0.27\chi}{R} + \left(\frac{7}{Re}\right)^{0.9} \right] \tag{7.5.1}$$

is found, where $Re = \dfrac{\rho V R}{\eta}$ is the Reynolds' number and χ is the so-called roughness of the wall (typical values are $R = 0.2m$, $Re = 6000$, $\chi = 4.5 \cdot 10^{-5} m$). The thermal boundary layer thickness $\sigma_T = \varepsilon_T \nu$ is given by classical correlations which lead to conclude $\varepsilon_T = 0.41\varepsilon_m$ for our purposes. For the details and references we refer to[33] .

The steady state profile in the thermal boundary layer can be found on the basis of a simple thermal balance (in which latent heat can be safely neglected) and it turns out to be

$$T(r,z) = (T_0 - T_e) \exp\Big\{ -\frac{2\pi\alpha}{\mu Q} z \Big\} \Big\{ 1 - \frac{1}{\mu} \ln\Big(\frac{r}{R}\Big) \Big\} + T_e, \tag{7.5.2}$$

where T_0 is the inlet temperature of the oil ($T_0 > T_{cloud}$), T_e is the outside temperature ($T_e < T_{cloud}$), α is the thermal diffusivity of the oil, and $\mu = \dfrac{k}{hR}$ (k =thermal conductivity, h =heat transfer coefficient through the pipe wall).

Thus we can express the temperature gradient

$$\frac{\partial T}{\partial r} = -(T_0 - T_e) \exp\Big\{ -\frac{2\pi\alpha}{\mu Q} z \Big\} \frac{1}{\mu r}, \tag{7.5.3}$$

which is the driving force for deposition.

Deposition may start when $T(r,z)$ drops below T_{cloud} and its rate results from two contrasting phenomena:

(i) molecular diffusion:

$$j_{dep} = -D C_s'(T) \frac{\partial T}{\partial r} \frac{1}{\psi}, \tag{7.5.4}$$

(ii) ablation:

$$j_{abl} = -\frac{A}{\psi} \frac{\eta Q}{\pi \varepsilon_m \nu^3}, \tag{7.5.5}$$

where ψ is the solid wax fraction in the deposit (typically $\psi \simeq 0.2$), A is the ablation coefficient (possibly depending on ψ) and the factor multiplying $\frac{A}{\psi}$ in (7.5.5) is the stress at the wall. The deposit is subject to progressive consolidation (aging) according to the kinetics

$$\frac{\partial \psi}{\partial t} = \frac{1}{t_a}(1-\psi), \qquad \psi_{initial} = \psi_0, \tag{7.5.6}$$

(t_a is a characteristic time, much larger than the typical time scale for deposition).
In order deposition to take place two conditions must be verified:

1. $T(R,z) < T_{cloud}$
2. $j_{abl} < j_{dep}$

The first condition requires $z > z_f$, with

$$z_f = \frac{\mu Q}{2\pi\alpha} \ln\Big[\frac{T_0 - T_e}{T_{cloud} - T_e}\Big]. \tag{7.5.7}$$

The second condition requires $z < z_e$, with

$$z_e = \frac{\mu Q}{2\pi\alpha} \ln\Big[\frac{(T_0 - T_e)\pi\varepsilon_m D b R^2}{\mu A \eta Q}\Big], \tag{7.5.8}$$

with $b = \frac{dC_s}{dT}$, considered constant.

Accordingly, if L is the pipe length, we have the following cases:

(a) $z_e > L$: deposition takes place for $z_f \le z \le L$,
(b) $z_f < z_e < L$: deposit is formed in the pipe segment $z_f \le z \le z_e$,
(c) $z_e < z_f$: deposition never starts.

The fact that $\frac{R}{L} \ll 1$ greatly simplifies the computation of the deposition rate.
Indeed the mass balance at the deposit interface (when deposition is active) can be written

$$\rho\frac{\partial \nu}{\partial t} + \Big(\frac{Db}{\psi}\frac{\partial T}{\partial z}\Big)\frac{\partial \nu}{\partial z} = \frac{D}{\psi}\frac{\partial T}{\partial r} + \frac{A\eta Q}{\psi\pi\varepsilon_m \nu^3}, \tag{7.5.9}$$

where ρ is the density of the wax.

After suitable rescaling it becomes apparent that the term with $\frac{\partial \nu}{\partial z}$ can be neglected (except for intervals in which $\frac{\partial \nu}{\partial z}$ is of the order of $\Big(\frac{L}{R}\Big)^2$). If aging is disregarded ($\psi \simeq \psi_0$), then the following expression is obtained for the deposit thickness for $z_f \le z \le \min(z_e, L)$

$$\sigma_d = R\frac{t}{t_0}\Bigg[\frac{T_0 - T_e}{\mu}\exp\Bigg\{-\frac{2\pi\alpha}{\mu Q}z\Bigg\} - \frac{A\eta Q}{\pi\varepsilon_m D b R^2}\Bigg]\frac{1}{T_{cloud}} \tag{7.5.10}$$

where t_0 is the typical time scale of the phenomenon, namely

$$t_0 = \frac{\psi_0 \rho R^2}{D b T_{cloud}}. \tag{7.5.11}$$

Using the values $\psi_0 = 0.2$, ρ =800 Kg·m^3, R =0.2m, $D = 1.5 \cdot 10^{-9}$m^{2}sec^{-1}, $b = 10^{-2}$Kg·m^{-3}°K^{-1}, $T_{cloud} = 300$°K, we have $t_0 \simeq 7.7 \cdot 10^6$sec (about 3 months).
Formula (7.5.10) is in good agreement with experimental data.
For more details and numerical examples see[33] .

Chapter 8

Diffusive processes in tumour cords

8.1. General description and main assumptions

A tumour cord consists of tumour cells proliferating around a blood vessel, from which they receive (by means of various transport mechanisms, including diffusion) all substances needed for proliferation. At some distance from the vessel the concentration of oxygen and other nutrients within a cord is too low to sustain life and a necrotic region is formed. Here we consider the ideal case in which we have a regular array of tumor cords which are parallel and identical, so that we may concentrate our attention on one of them, supposing that it is surrounded by a surface which, because of symmetry, prevents any exchange of matter with the neighboring cords.

For references about previous papers on tumour cords, and on mathematical models of tumours in general, we refer to[51] , which illustrates the recent trends in this fields. See also[4,30] and the book[113] .

As we shall see, the model we are going to present is far from being a precise picture, even for the idealized system described above. We will introduce a number of simplifications, which however respect the main qualitative features and allow to point out some aspects, which are common to other types of tumors, but have been rarely considered in the literature, despite their crucial influence. This is particularly true when, because of cell killing treatments, the tumor undergoes a volume reduction, followed by regrowth.

The simplifications we impose are of various kinds:

(i) The cord has rotational symmetry around its axial blood vessel.

(ii) Living cells can be in two states: proliferating (P) or quiescent (Q). Transition from P to Q takes place at a rate $\lambda(\sigma)$, σ denoting the oxygen concentration. The inverse transition is also possible with a rate $\gamma(\sigma)$. The two functions λ, γ are continuous and piecewise differentiable. More precisely $\gamma = \gamma_{\min} \geq 0$ for σ below a threshold σ_Q, $\gamma = \gamma_{\max} > \gamma_{\min}$ above a threshold $\sigma_P > \sigma_Q$ and $\gamma(\sigma)$ is increasing in (σ_Q, σ_P), while $\lambda(\sigma)$ is decreasing in the same interval from $\lambda_{\max}$ (its value below σ_Q) and $\lambda_{\min} \geq 0$ (its value above σ_P). Cells die when σ reaches the value $\sigma_N < \sigma_Q$.

(iii) The cell velocity $\mathbf{u}$ is radial.

(iv) All the relevant quantities depend on space only through the radial coordinate r. A first consequence is that the two main free boundaries in the problem, namely the boundary of the region containing viable cells (i.e. the internal boundary of the necrotic region) and the external boundary of the necrotic region are cylindrical.

(v) The oxygen concentration has locally the same value in the interstitial fluid and in the cells.

Even in this reduced framework there are several difficulties. First of all, there is a clear coupling between the evolution of the living cells and the oxygen diffusion-consumption process. Moreover the cells die, either spontaneously or because of the presence of cytotoxic substances (whose evolution has also to be modelled) and dead cells lose volume (possibly at different rates in the necrotic and non-necrotic regions). Then we must consider the flow of the interstitial liquid, whose velocity $\mathbf{v}$ cannot be just radial (it enters the cord from the blood vessel and leaves the system from the far ends, carrying to the cells the material needed for their replication and carrying away the waste products). Determining the motion of the various components should take into account their mutual mechanical interactions. This fact has been clearly pointed out in[14] . However, as we shall see, we can circumvent the study of the internal stresses and of the full dynamics of the interstitial fluid if we further simplify our approach computing just the average flux through each cylindrical surface in the cord, coaxial with the blood vessel. As we shall see, the evolution of the region occupied by living cells and the evolution of the surrounding necrotic region are characterized by the presence of a pair of unilateral constraints which produce the switch between two different evolution regimes. Here lies one of the most peculiar mathematical aspects of the problem. This model has been developed through several stages. We just quote the papers[13–16] . The proofs are too long and complicated to be reported here. We will confine ourselves to sketching some basic ideas.

8.2. The mathematical model: the oxygen consuming region

We start by modelling the region close to the blood vessel, containing living cells.
We denote by ν_P, ν_Q the volume fractions of the proliferating and quiescent cells. Dead cells occupy a fraction ν_A and the rest of the space is filled by extracellular liquid, whose volume fraction is ν_E:

$$\nu_P + \nu_Q + \nu_A = \nu^* = 1 - \nu_E. \tag{8.2.1}$$

All components are assumed to have the same density, so that conversions from one to another are not accompanied by volume change.
The equations describing the evolution of ν_P, ν_Q, ν_A are

$$\frac{\partial \nu_P}{\partial t} + \nabla \cdot (\nu_P \, \mathbf{u}) = \chi \nu_P + \gamma(\sigma)\nu_Q - \lambda(\sigma)\nu_P - \mu_P(r,t)\nu_P, \tag{8.2.2}$$

$$\frac{\partial \nu_Q}{\partial t} + \nabla \cdot (\nu_Q \, \mathbf{u}) = -\gamma(\sigma)\nu_Q + \lambda(\sigma)\nu_P - \mu_Q(r,t)\nu_Q, \tag{8.2.3}$$

$$\frac{\partial \nu_A}{\partial t} + \nabla \cdot (\nu_A \, \mathbf{u}) = \mu_P(r,t)\nu_P + \mu_Q(r,t)\nu_Q - \mu_A \nu_A. \tag{8.2.4}$$

In (8.2.2) χ is the proliferation rate, μ_P, μ_Q are the death rates of the corresponding species, μ_A is the conversion rate of dead (apoptotic) cells into liquid by degradation. We have already illustrated the role of the transition rates γ, λ. We remark that μ_P, μ_Q are here prescribed as functions of r, t in order to simplify the problem. Since they represent the effect of treatments, in real cases they must be expressed e.g. as functions of drugs concentration or radiation intensity. Another simplifying assumption is that ν_E is constant. Thus, denoting by $\mathbf{v}$ the fluid velocity, the fluid mass balance for the liquid is

$$\nu_E \nabla \cdot \mathbf{v} = \mu_A \nu_A - \chi \nu_P. \tag{8.2.5}$$

Now we assume that the quantity ν^* in (8.2.1) is constant and from (8.2.2)-(8.2.4) we deduce

$$\nu^\star \frac{1}{r}\frac{\partial}{\partial r}(ru) = \chi \nu_P - \mu_A(\nu^\star - \nu_P - \nu_Q), \tag{8.2.6}$$

where $u(r,t)$ is the radial component of the cell velocity, which has to satisfy the boundary condition

$$u(r_0, t) = 0 \tag{8.2.7}$$

at the boundary $r = r_0$ of the central blood vessel.

From the modelling point of view, we stress that we have supposed that all the cellular species (including dead cells) move with the same velocity. This confines the validity of the model to a situation in which dead cells are entrapped in a relatively coherent structure.

Now we write down the equation for oxygen consumption

$$\Delta \sigma = f_P(\sigma)\nu_P + f_Q(\sigma)\nu_Q \tag{8.2.8}$$

in a quasi-steady form, with f_P, f_Q consumption rates of the respective species. This is justified because the typical *diffusion time* for oxygen in the tumour is $t_d = \frac{L^2}{D}$ with $L \simeq 100\mu$, $D \simeq 10^{-5} cm^2/sec$, i.e. $t_d \simeq 10 sec$, to be compared with the basic time scale of tumour growth $\chi^{-1} \simeq 1\ day$. For the same reason no advection term appears in (8.2.8).

Functions f_P, f_Q are such that $f_P(\sigma) \geq f_Q(\sigma)$ (e.g. of Michaelis-Menten type). An important condition is $f_Q(\sigma_N) > 0$.

Equation (8.2.8) must be solved in the region occupied by living cells, whose size is not known a-priori. Thus we have a free boundary problem. The unknown interface $r = \rho_N(t)$ separates the oxygen consuming region from the necrotic region.

At the blood vessel wall we prescribe the oxygen concentration

$$\sigma(r_0, t) = \sigma_b. \tag{8.2.9}$$

At the interface $r = \rho_N(t)$ a typical situation (occurring e.g. when the tumour is in a steady state) is represented by the conditions

$$\sigma(\rho_N(t), t) = \sigma_N, \tag{8.2.10}$$

$$\frac{\partial \sigma}{\partial r}\Big|_{r=\rho_N(t)} = 0, \tag{8.2.11}$$

expressing the fact that the necrotic threshold σ_N has been reached and that no oxygen is exchanged with the necrotic region.
However, a crucial aspect of the phenomenon is that it may evolve in such a way that (8.2.10) has to be replaced. Roughly speaking, we can say that if a sufficiently intense killing action is exerted on the cells then, as long as (8.2.8)-(8.2.11) are satisfied, the corresponding sharp reduction of oxygen consumption tends to shift the interface $r = \rho_N(t)$ far from the blood vessel so fast that its velocity tends to exceed the cellular velocity u (which is of the order of 1μ/hour). On the other hand, the inequality $\dot{\rho}_N \leq u$ cannot be violated on physical grounds (dead cells cannot be recruited in the population of living cells). The way out is to allow $\sigma(\rho_N(t), t)$ to increase freely above σ_N, imposing that the interface becomes a material surface, moving with the velocity of the cells:

$$\dot{\rho}_N = u(\rho_N(t), t), \tag{8.2.12}$$

which replaces (8.2.10).
After the treatment the tumour tends to regrow and if we keep the conditions (8.2.11), (8.2.12) on the free boundary the oxygen concentration at the interface will eventually fall below σ_N. This too must be forbidden, imposing the constraint $\sigma \geq \sigma_N$ and reverting to the former interface conditions.

In summary, the problem itself selects the correct free boundary conditions during the tumour evolution, according to the unilateral constraints $\dot{\rho}_N \leq u_N$, $\sigma \geq \sigma_N$.

8.3. The extracellular fluid flow

We assume Darcy's law as the governing equation of the flow relative to the cells

$$(1 - \nu^*)(\mathbf{v} - \mathbf{u}) = -\kappa \nabla p \tag{8.3.1}$$

(p=pressure, κ=hydraulic conductivity). From (8.2.1)-(8.2.5) we get

$$\nabla \cdot (\mathbf{v} + \frac{\nu^*}{1 - \nu^*}\mathbf{u}) = 0. \tag{8.3.2}$$

The velocity $\mathbf{v}$ has a radial and a longitudinal component, respectively denoted by $v_r(r, z, t)$, $v_z(r, z, t)$. The analysis of the flow can be greatly simplified if we are mainly interested in knowing the total fluid discharge through cylindrical surfaces r =constant. To this end we introduce the average

$$v(r, t) = \frac{1}{2H} \int_{-H}^{H} v_r(r, z, t) dz$$

($2H$ is the cord length) and we take the same average in equation (8.3.2), obtaining

$$\frac{1}{r}\frac{\partial}{\partial r}(rv) + \frac{1}{2H}[v_z(r, H, t) - v_z(r, -H, t)] = -\frac{\nu^*}{1 - \nu^*}\frac{1}{r}\frac{\partial}{\partial r}(ru), \tag{8.3.3}$$

where $(1 - \nu^*)[v_z(r, H, t) - v_z(r, -H, t)]$ represents the local outflow rate of liquid from the cord ends. We assume that the latter is proportional to the difference $p(r, t) - p_\infty$ between the longitudinal average of pressure and a *far field* pressure p_∞, representing the pressure in the lymphatic vessels. Thus

$$\frac{1}{r}\frac{\partial}{\partial r}(rv) = -\frac{1}{1-\nu^*}\left[\chi\theta\nu_P - \mu_A(\nu^*-\nu_P-\nu_Q) + \frac{\zeta_{out}}{H}(p-p_\infty)\right], \tag{8.3.4}$$

with $\zeta_{out} > 0$, constant.
After averaging (8.3.1) we arrive at the equation

$$p(r,t) = p_0(t) - \frac{1-\nu^*}{\kappa}\int_{r_0}^{r}[v(r',t)-u(r',t)]\,dr', \tag{8.3.5}$$

where one more unknown appears, namely $p_0(t) = \lim\limits_{r\to r_0} p(r,t)$. The knowledge of $p_0(t)$ is necessary in order to specify the fluid inflow rate from the blood vessel

$$(1-\nu^*)v(r_0,t) = \zeta_{in}(p_b - p_0(t)), \tag{8.3.6}$$

with $\zeta_{in} > 0$, constant, and p_b equal to the longitudinally averaged blood vessel.

Concerning the question of prescribing both σ_b and p_b as given constants, a few remarks are in order. Both σ and p do vary along the blood vessel: the former because of progressive consumption, the latter in order to provide the pressure gradient forcing the blood along the vessel. Keeping the variation of σ low requires a sufficiently fast blood flow, hence a sufficiently large pressure gradient. Thus having a small variation of σ and a small variation of p along the vessel are contrasting requirements. However, the analysis performed in[13] proves that for the typical cord dimensions (2H$\simeq$1mm, $r_0 \simeq 20\mu$m) and the typical perfusion rates there is a reasonable compromise, allowing to consider σ_b, p_b constant along the vessel.

The role of equation (8.3.5) is to determine the average pressure profile within the cord once the difference $v-u$ and $p_0(t)$ are known. Finding p_0 is one of the most delicate aspects of the problem, even in the stationary case.

8.4. The necrotic region

The necrotic region occupies at each time the hollow cylinder $(\rho_N, B)\times(-H,H)$. The radius $B(t)$ is unknown and we recall that the outer boundary $r = B(t)$ is a no flux surface. Modelling the necrotic region is by no means a simple task, because we are dealing with a mixture of liquid and of a solid material degrading to a liquid. Excluding abnormal situations, both components enter the necrotic region from the interface $r = \rho_N(t)$ and the liquid leaves from the boundaries, $z = \pm H$. The picture adopted here is based on the arguments presented in[15] ,[13] .
We suppose that pressure has a uniform value $p_N(t)$, of course unknown, throughout the region and that the residual cellular component and the liquid occupy the respective volumes V_N^c, V_N^l, filling the whole space:

$$V_N = V_N^c + V_N^l = 2\pi H(B^2-\rho_N^2). \tag{8.4.1}$$

Two situations are possible:

(i) the solid component is floating within the liquid,

(ii) the solid component is fully packed (with the volume fraction ν^*).

The mechanical behaviour is very different in the two cases. The second case may occur when too much solid is supplied and/or too much liquid is removed. The first case is characterized by the inequality

$$\nu_N = \frac{V_N^c}{2\pi H(B^2 - \rho_N^2)} < \nu^*. \tag{8.4.2}$$

The unilateral constraint $\nu_N \leq \nu^*$ must be imposed and when it becomes active we shift to case (ii).

The volume balance reads as follows

$$\dot{V}_N^c = 4H\pi\rho_N\nu^\star[u(\rho_N, t) - \dot{\rho}_N] - \mu_N V_N^c, \tag{8.4.3}$$

$$\dot{V}_N^l = 4H\pi\rho_N(1 - \nu^\star)[v(\rho_N, t) - \dot{\rho}_N] + \mu_N V_N^c - q_{out}(t), \tag{8.4.4}$$

where μ_N is the volume loss rate of the solid and $q_{out}(t)$ expresses the liquid outflow rate from $z \pm H$:

$$q_{out} = 2\zeta_{out}^N(1 - \nu_N)\pi(B^2 - \rho_N^2)(p_N - p_\infty) \tag{8.4.5}$$

with $\zeta_{out}^N > 0$.
From (8.4.1)-(8.4.4) the total volume evolution can be found

$$\begin{aligned} \frac{dB^2}{dt} &= 2\rho_N[(1 - \nu^\star)v(\rho_N, t) + \nu^\star u(\rho_N, t)] + \\ &- \frac{\zeta_{out}^N}{H}(B^2 - \rho_N^2 - \frac{V_N^c}{2H\pi})(p_N - p_\infty). \end{aligned} \tag{8.4.6}$$

Now we have to distinguish between (i) and (ii).
In case (i) we may suppose that the larger is the total volume occupied by the system, the larger is the pressure. The underlying idea is that the pressure is created by the displacement of the surrounding tissue. Thus we assume that

$$p_N(t) = \Psi(B(t)), \tag{8.4.7}$$

where $\Psi(B)$ is a smooth increasing function (never less than p_∞).
Thus (8.4.6) together with (8.4.7) and (8.4.3) can be seen as the evolution law for B.
In case (ii) it is the solid part which takes on the stress (it will ultimately compress the blood vessel, even to the limit of collapse, but we disregard this phenomenon here). Now V_N^l is known in terms of V_N^c

$$V_N^l(t) = \frac{1 - \nu^*}{\nu^*} V_N^c \tag{8.4.8}$$

and

$$B(t) = \left(\rho_N^2 + \frac{V_N^c}{2H\pi\nu^*}\right)^{1/2}. \tag{8.4.9}$$

As a consequence, equation (8.4.4) has now the task of defining q_{out} and through (8.4.5) we can find the expression

$$p_N(t) = p_\infty + \frac{H}{\zeta_{out}^N}\left(\frac{2\rho_N[v(\rho_N,t) - u(\rho_N,t)]}{B^2 - \rho_N^2} + \frac{\mu_N}{1-\nu^*}\right), \tag{8.4.10}$$

replacing (8.4.7).

The regime (ii) may also come to an end. This happens precisely when p_N calculated through (8.4.10) tends to exceed $\Psi(B(t))$. In other words, besides the constraint $\nu_N \leq \nu^*$, we have to impose the constraint $p_N(t) \leq \Psi(B(t))$. When p_N reaches the constraint it means that the liquid takes over the supporting action and we go back to (i). Thus also the evolution of the necrotic region takes place via a doubly constrained mechanism.

The coupling between the two system of equations in the necrotic and in the non-necrotic region is provided by the pressure p_N, which has to match the pressure value for $r = \rho_N$ provided by (8.3.5).

8.5. Mathematical results and open questions

Global existence and uniqueness have been proved in the quoted papers. Two distinct approaches are needed for the stationary and for the evolution problem. Demonstrations are too long to be presented here.

The main open questions remain:

(a) The drugs kinetics. In[14] this problem was considered in the framework of rather severe restrictions (e.g. disregarding advection due to the fluid motion). However the problem of completing the model here illustrated with the equations describing the transport and the action of the drugs remains open.

(b) The case in which the tumoral mass breaks down and we can no longer adopt the simplified picture of a cell population moving with the radial velocity $\mathbf{u}$ of a fluid moving with the velocity $\mathbf{v}$.

(c) The study of more complicated geometries, which requires the description of the mechanical behaviour of the full system (in particular of the cell-cell interactions).

(d) The possibility of the collapse of the central blood vessel, that we have envisaged during the regime of the fully packed necrotic region. The question of vascular collapse has been considered e.g. in[5] and may have important consequences.

This chapter may give an idea of the complexity of the mathematical problem, but it is certainly far from describing the intricate set of phenomena which lead from the early stage to the invasive phase of a tumour. Moreover, referring to a *tumour* is hardly appropriate, because there is an enormous variety of tumours (even within a class affecting the same organ), each with its own phenomenology. Therefore, models referring to a generic tumour are necessarily idealized, although they may help to understand some basic features. Our feeling is that the mathematical modelling of tumour is still far from its target and for this reason it is a particularly fascinating and challenging research field.

Bibliographical remarks .

Since the first publications of these notes the development of the literature on cancer modelling has been impressive and various topics have been addressed. A recent survey is[11] .
A detailed analysis of the mechanical behaviour of tumours, based on the theory of evolution of natural configuration[117] , has been presented in[2] . Nevertheless, it has to be said that when we come to the choice of the constitutive equations we are faced with some arbitrariness and in any case with the hard question of retrieving the experimental data for the involved parameters.
Another subject that has received some attention is the influence of the acidic environment created by the glucose metabolism, when the latter takes place in anaerobic conditions. It is believed that tumour cells can stand a lower pH than normal cells, so that there is a ph range which is favourable to tumour expansion. See[17,123,130,136] for models including glucose metabolism, and[81] ,[54] for the analysis of travelling wave solutions related to acidic aggression (see also[18]).

Chapter 9

Modelling the Ziegler-Natta polymerization process

9.1. The general features of the process

The names of Ziegler and Natta (who got the Nobel prize in 1954) are linked to the creation of polypropylene. The most recent industrial process based on their ideas uses spherical aggregates of catalytical particles which are circulated in a reactor where they are kept in contact with propylene either in the gaseous or the liquid state, depending on pressure. The same process is used for producing polyethylene from the corresponding monomer ethylene. In both cases the action of the catalyst is to break a double bond between two carbon atoms in the monomer molecule, creating a bond between two monomer molecules. Such a reaction is repeated indefinitely, creating a polymer chain, which may contain thousands of the basic constituents. The reaction is usually highly exothermal. The final product is a spherical pellet with a diameter of few millimeters, which (differently from what happens with other polymerization processes) needs no further processing.

The agglomerate is a sphere of $70\mu m$ radius and contains a huge number (of the order of 10^{11}) of catalytic particles which are really very small (diameter of the order of $5nm$). The first exposure of the aggregate to the monomer requires some care, because if the temperature is not low enough the reaction is too violent and the aggregate can be damaged or deformed, largely reducing the process efficiency. During the very first stage of the process (which is very fast) around the catalytic particles reached by the monomer a polymer shell is created and a *fragmentation* front proceeds quickly towards the center, leaving behind a porous structure which is essential for the smooth development of the subsequent process. Fragmentation is followed by the so called *pre-polymerization*, in which the reaction temperature is still controlled so to reduce the reaction speed. Next, temperature is allowed to raise and full speed is achieved. The whole process has a duration of about 2 hours. From the point of view of modelling there is no difference between the last two stages, so we will discuss them under the common title *polymerization*.

The physics is very different if we deal with the low pressure (gaseous monomer) or with the

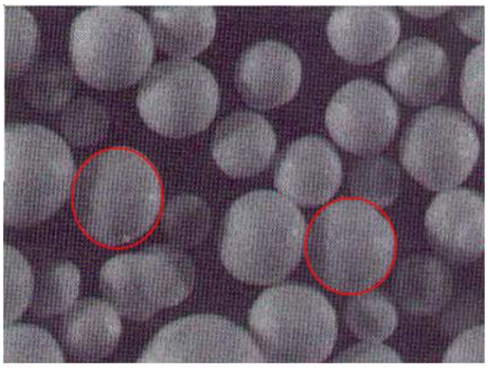


Figure 9.1.1. Pellets of polypropylene.

high pressure (liquid monomer) reactor. In the former case the monomer transport mechanism is diffusion (i.e. the driving force is concentration gradient), in the latter it can be described by Darcy's law (the driving force is pressure gradient).

Here we will deal only with low pressure reactors. The basic reference is[47] , where more information about the process and bibliography is contained. More recently a much more complex model has been proposed for high pressure reactors[56] , based on mixture theory[117] .

Polymer science is an immense source of fascinating mathematical problem. Other very important areas are *crystallization* (see the book[26] and the survey paper[48]) and the fluid dynamics of polymer melts (see e.g.[102] ,[39] ,[96]).

9.2. The two-scale approach

During the normal regime of the process we describe the agglomerate as a collection of growing microspheres. Growth is due to the monomer-polymer conversion which takes place at the surface of the catalytic particles, located inside the microspheres. In order to reach the reaction site the monomer diffuses through the pores of the agglomerate and then through the polymeric body of the microsphere, which behaves as another porous material, with lower porosity. The final product is very compact, thus we may assume that at each time the microspheres are ideally packed in a spherically symmetric arrangement. In this arrangement adjacent layers of microspheres have very similar history, so that they grow at the same rate and they have basically the same radius. Therefore, even if the microspheres in the outer layers in the agglomerate are larger than the ones in the inner layers, we may say that *locally* the agglomerate keeps the structure of an ideal porous medium made of spheres of equal radius with the minimum possible porosity (*rombohedric* configuration). In this condition porosity is independent of the radius of the *grains* (its value is easily computable and is about 0.26).

Thus we conclude that, despite the dishomogeneous distribution of radii, *the agglomerate porosity is uniform and constant in time.*

A very important property of the system is that during the entire process the size of the agglomerate is always much larger than the size of the largest microspheres (the ratio of diameters is of the order of 10^4). This circumstance suggests the *two-scale* approach (see fig. 9.2.1): the agglomerate is treated as a continuum with a *density* of catalytic sites. In this way we have a large (or macro) scale and a small (or micro) scale, on which we describe the evolution of the agglomerate and of the microspheres, respectively.

Typical variables on the large scale are:
porosity ε (constant),
radial coordinate r,

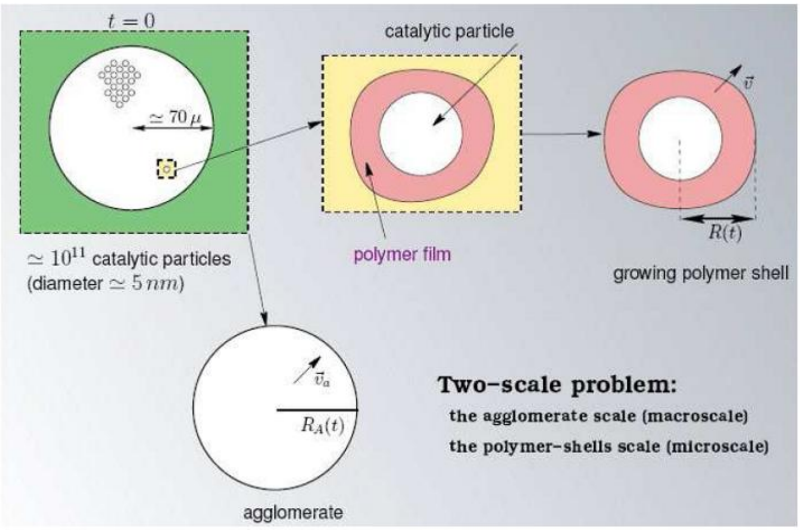


Figure 9.2.1. The two-scale approach.

microsphere density $\rho(r, t)$,
temperature $T(r, t)$,
monomer concentration in the pores $M(r, t)$,
expansion velocity field $v(r, t)$
outer radius $R(t)$.

On the small scale all quantities depend also on the macro-variable r (even if not explicitly stated):
porosity ε_p,
radial coordinate y,
temperature $T_p(y, t)$,
monomer pore concentration $M_p(y, t)$,
radius of microspheres $s(t)$,

expansion velocity field $v_p(y,t)$.

Phenomena occurring at the two scales are strictly coupled:

- the density ρ of the microspheres is determined by their local size:

$$\frac{4}{3}\pi s^3 \rho = 1 - \varepsilon, \tag{9.2.1}$$

- the expansion of the agglomerate is a consequence of the expansion of the microspheres,
- the heat generated at the microscale (proportional to polymerization rate) is perceived as a heat source on the macroscale,
- the monomer consumption at the catalytic sites is seen as a monomer sink on the macroscale.

9.3. The governing equations

A) Macroscale

Due to the constancy of porosity the overall expansion rate equals the growth rate of the solid component. The latter can be calculated as the ratio $\frac{d}{dt}(\frac{4}{3}\pi s^3)/\frac{4}{3}\pi s^3 = 3\frac{ds}{dt}/s$, where $\frac{d}{dt}$ denotes the Lagrangian derivative. Hence

$$\Big(\frac{\partial}{\partial r} + \frac{2}{r}\Big)v = 3\frac{1}{s}\frac{ds}{dt}. \tag{9.3.1}$$

It is easy to write down the heat and mass balance equations:

$$C\frac{\partial T}{\partial t} - \Big(\frac{\partial}{\partial r} + \frac{2}{r}\Big)\Big(k\frac{\partial T}{\partial r} - CTv\Big) = \rho S, \tag{9.3.2}$$

$$\frac{\partial M}{\partial t} - \Big(\frac{\partial}{\partial r} + \frac{2}{r}\Big)\Big(D\frac{\partial M}{\partial r} - Mv\Big) = -\frac{1}{\varepsilon}\rho Q, \tag{9.3.3}$$

where C is the macroscopic average of the product of specific heat by mass density, k is the macroscopic average of thermal conductivity (both quantities can be taken constant, consistently with ε=constant), D the monomer diffusivity in the pores, S is the heat release rate by the microparticles with macro-coordinates (r,t), Q is the mass absorption rate by the same particles.

Initial and boundary conditions are

$$v(0,t) = 0 \tag{9.3.4}$$

(corresponding to the choice of the frame of reference),

$$\dot{R}(t) = v(R(t),t), \qquad R(0) = R_0, \tag{9.3.5}$$

(the outer surface is a material surface),

$$M(r,0) = 0, \qquad 0 < r < R_0 \tag{9.3.6}$$

(this is a simplification: as a matter of fact $M(r,0)$ for pre-polymerization is the mass distribution at the end of the fragmentation stage),

$$\frac{\partial M}{\partial r}(0,t) = 0, \tag{9.3.7}$$

$$M(R(t),t) = M_R(t), \tag{9.3.8}$$

$M_R(t)$ being the monomer concentration in the reactor,

$$T(r,0) = T_0, \qquad 0 < r < R_0 \tag{9.3.9}$$

(T_0 is the temperature of the reactor, although -more precisely- the initial temperature should be identified with the temperature after fragmentation),

$$\frac{\partial T}{\partial r}(0,t) = 0, \tag{9.3.10}$$

$$-k\frac{\partial T}{\partial r}(R(t),t) = h[T(R(t),t) - T_0], \tag{9.3.11}$$

where h is the heat transfer coefficient.
The free terms S, Q in equations (9.3.2), (9.3.3) must be found by solving the set of equations at the microscale.

B) Microscale

The most difficult equation concerns the evolution of porosity ε_p. It must be present to our mind that microspheres *are not accessible to observation*, particularly during the process. This is one of the cases in which mathematics is the only tool we have to inspect the inner structure of the system. Setting up a model for the evolution of the growing polymer shells requires a full mechanical description, including the analysis of stresses and deformations. Even in spherical symmetry this is enormously complicated, particularly because new polymer is constantly created. This difficult task has been carried out very recently in[56] and it leads to an exceedingly complicated nonlinear hyperbolic system with free boundaries.
In principle one could tackle that level of complexity, but -as a general rule- when a model gets too complicated the question arises about whether or not this is a honest price to pay: does the additional difficulty produce more precision? The answer is often linked with the availability and reliability of the physical parameters involved. In our case such parameters are the ones entering the constitutive relationships defining the mechanical behaviour of the system. They can hardly be provided by experiments. Therefore we may conclude that the interest of the nonlinear hyperbolic model is mostly theoretical (in the sense that it can give a closer idea of the real behaviour of the polymer), but of not great practical importance.
This is a typical situation in which the *modeller* is allowed to take a shortcut. On the basis of this motivation we take ε_p =constant, being conscious that we are introducing a weak point in the model.

A first consequence of this assumption is that mass conservation implies

$$\Big(\frac{\partial}{\partial y}+\frac{2}{y}\Big)v_p=0,\qquad y_0<y<s(t),\quad t>0, \tag{9.3.12}$$

where y_0 is the radius of the catalytic core, and $y=s(t)$ is a free boundary.

We can also write down heat and mass conservation laws, but after suitable rescaling, taking into account the really small size of the microspheres, we conclude that both heat and mass transport are quasi-steady processes by far dominated by diffusion, i.e. the products $y^2\dfrac{\partial T_p}{\partial y}$ and $y^2\dfrac{\partial M_p}{\partial y}$, with T_p temperature and M_p monomer concentration in the pores of the polymer, are independent of y, meaning that heat flux and monomer flux are constant through the microspheres.

If we neglect the fragmentation stage we can set $s(0)=y_0$ and take the conditions

$$v_p(s(t),t)=\dot{s}(t), \tag{9.3.13}$$

$$v_p(y_0,t)=\lambda(T_p)M_p(y_0,t), \tag{9.3.14}$$

$$\frac{\partial M_p}{\partial y}(y_0,t)\simeq 0. \tag{9.3.15}$$

Condition (9.3.13) says that the free boundary is a material surface. However in this peculiar problem the necessary extra condition is prescribed not on the free, but on the fixed boundary $y=y_0$. Here we have (9.3.14) expressing polymerization rate: $4\pi y_0^2(1-\varepsilon_p)v_p$ is the polymer volume produced on the site per unit time, which is supposed to be proportional to $M_p(y_0,t)$ with a temperature dependent coefficient. The last condition should express the monomer mass balance, equating the incoming monomer flux $\varepsilon_p\Big(D\dfrac{\partial M_p}{\partial y}-v_pM_p\Big)$ to the monomer consumption rate per unit surface of the catalyst, again proportional to M_p. The fact that diffusion largely dominates the monomer transport justifies (9.3.15).

Now we may identify M_p throughout the microsphere with the value taken at its outer surface. The latter value is set equal to a given fraction of the concentration M in the agglomerate:

$$M_p=KM(r,t), \tag{9.3.16}$$

with the *partition factor* $K\in(0,1]$ (experimentalists suggest $K=0,3$).

9.4. The final scheme at the macroscopic scale

The analysis just performed allows to express the basic microscopic quantities as functionals of the macroscopic quantities.

Although the temperature gradient across the microspheres is not small, the total temperature drop across their radius is negligible. Hence in (9.3.14) we can take $T_p=T$. In addition the rate of volume increase of a microsphere is $4\pi s^2\dot{s}$ and it is also equal to $4\pi y_0^2v_p(y_0,t)$. Hence, according to (9.3.14), (9.3.16)

$$s^2\dot{s}=y_0^2\lambda KM(r,t), \tag{9.4.1}$$

which is nothing but the integral of (9.3.12), which says that the product $y^2 v_p$ is independent of y. Eliminating $\dot{s}$ between (9.4.1) and (9.3.1), we find that the latter takes the form

$$\frac{\partial}{\partial r}(r^2 v) = 3y_0^2 \lambda K r^2 M(r,t)\frac{1}{s^3}. \tag{9.4.2}$$

In order to express s as a functional of macroscopic quantities it is convenient to introduce the Lagrangian coordinate

$$x = \xi(r,t) \tag{9.4.3}$$

representing the radial position in the agglomerate at time $t = 0$ of the particle having the radial coordinate r at time t. Conversely we have

$$r = \eta(x,t) \tag{9.4.4}$$

where $\eta = \xi^{-1}$. Since $v = \frac{\partial \eta}{\partial t}$, $\frac{\partial}{\partial r} = \left(\frac{\partial \eta}{\partial x}\right)^{-1}\frac{\partial}{\partial x}$, we may rewrite (9.3.1) as

$$\frac{\partial^2 \eta}{\partial t \partial x}\left(\frac{\partial \eta}{\partial x}\right)^{-1} + \frac{2}{\eta}\frac{\partial \eta}{\partial t} = 3\frac{\dot{s}}{s}. \tag{9.4.5}$$

We can integrate this expression w.r.t. t, remembering that $\eta(x,0) = x$:

$$\eta^2 \frac{\partial \eta}{\partial x} = x^2 \left(\frac{s}{y_0}\right)^3 \tag{9.4.6}$$

(we have used also $\frac{\partial \eta}{\partial x}|_{t=0} = 1$), where s depends on t and on x. One more integration yields

$$\frac{1}{3}\eta^3 = \frac{1}{y_0^3}\int_0^x z^2 s^3(t;z)dz. \tag{9.4.7}$$

On the other hand, from (9.4.1) we get

$$s^3 - y_0^3 = 3Ky_0^2\lambda \int_0^t M(\eta(x,\tau),\tau)d\tau, \tag{9.4.8}$$

since we are integrating along the motion of the catalytic particle in the agglomerate. We have adopted the simplification λ =constant because it turns out that the temperature variation across the agglomerate is about 5°C and λ is not so sensitive to it.
Rewriting (9.4.2) in the form

$$\frac{\partial}{\partial x}(\eta^2 v) = 3y_0^2 \lambda K \eta^2 \frac{\partial \eta}{\partial x} M \frac{1}{s^3} \tag{9.4.9}$$

and using again (9.4.6), we see that v can be expressed as

$$v(\eta(x,t),t) = \frac{3\lambda K}{y_0}\int_0^x \xi^2 M(\eta(\xi,t),t)d\xi. \tag{9.4.10}$$

Now we can adopt the Lagrangian coordinate x in (9.3.2) and (9.3.3), defining $\vartheta(x,t) = T(\eta(x,t),t)$, $\mu(x,t) = M(\eta(x,t),t)$, with the additional advantage of working in the *fixed interval* $0 < x < R_0$, remembering again that $\frac{\partial}{\partial r} = \left(\frac{\partial \eta}{\partial x}\right)^{-1}\frac{\partial}{\partial x}$.
The velocity field, according to (9.4.10), is

$$\overline{v}(x,t) = \frac{3\lambda K}{y_0}\int_0^x \zeta^2 \mu(\zeta,t)d\zeta. \tag{9.4.11}$$

In the source term in (9.3.2)the function S is proportional to the polymerization rate, so that, in the new variable

$$\overline{S}(x,t) = \Lambda\mu(x,t), \tag{9.4.12}$$

and through (9.2.1)

$$\overline{\rho}(x,t) = \frac{3}{4\pi}(1-\varepsilon)\frac{1}{s^3(t;x)}, \tag{9.4.13}$$

where, from (9.4.8),

$$s^3 - y_0^3 = 3Ky_0^2\lambda \int_0^t \mu(x,\tau)d\tau. \tag{9.4.14}$$

In the sink term of (9.3.3) the function Q is the absorption rate by a single microsphere, hence

$$\overline{Q}(x,t) = \nu\lambda\mu(x,t), \tag{9.4.15}$$

where ν is a conversion factor which is typical of the reaction.
At this point the whole problem is reduced to a system of two parabolic p.d.e.'s for the functions ϑ, μ in which functionals of μ appear. The outer boundary can be recovered by integrating (9.3.5) with the help of (9.4.11) with $x = R_0$.
Existence and uniqueness have been proved by means of a fixed point argument.

9.5. Numerical simulations

Numerical simulations led to very interesting conclusions.
First of all they show that after some time the growth rate of the agglomerate is sharply reduced, marking the optimal duration of the process in terms of the input parameters. Next the intimate structure of the agglomerate can be described during the whole process. For instance it is possible to obtain a 3-D plot of the monomer concentration $M(r,t)$, showing, as expected, that peripheral regions are richer in monomer than inner regions (Fig. 9.5.1).

Also the distributions of the radii of the microspheres $s(t;r)$ can be calculated and it can be seen that accelerating the process (i.e. increasing M_R) it becomes more and more dishomogeneous (Fig. 9.5.2).

From this kind of information it is possible to look for a desired balance between the efficiency of the process and the quality of the product. A striking example of how mathematics can be a decisive tool to take important decisions.

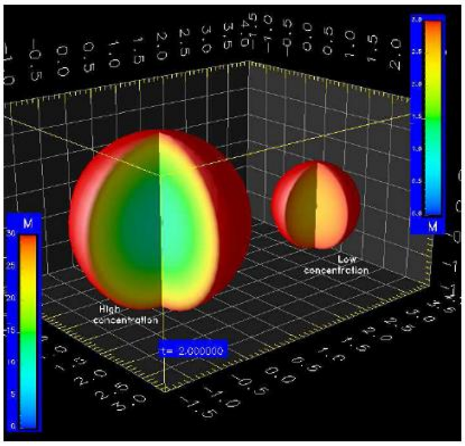


Figure 9.5.1. Monomer concentration within the agglomerate.

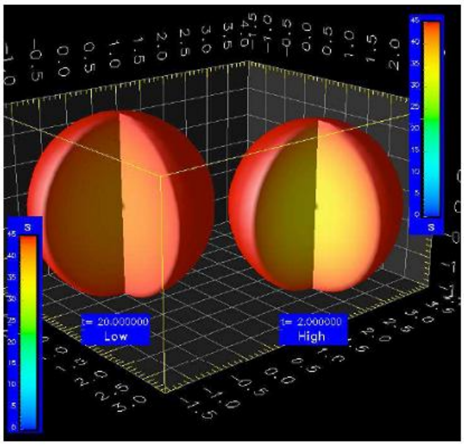


Figure 9.5.2. Distribution of radii of the microspheres.

Chapter 10

Appendix

10.1. Diffusion as the limit of a random walk

The striking feature of statistical mechanics is to identify the trend to some order in the seemingly chaotic behaviour of complex system. The tool to reach this goal is a smart way of taking averages[a] In this same spirit the heat equation can be seen as the deterministic law governing averages in a stochastic process known as random walk.

In order to illustrate this very classical results (see e.g.[29]) we sketch the simplest possible one-dimensional version of the process.

Consider a point which moves on a line according to the following rules:

i) it can occupy only the positions nl, with $n \in \mathbb{Z}$ and l a given length,
ii) from the position $n_0 l$ it can jump only to $(n_0 + 1)l$ or $(n_0 - 1)l$ with equal probability (i.e. $\frac{1}{2}$)
iii) its initial position is the origin.

Consider a set of N of such random steps: the final position can be any of the admissible points in $(-Nl, Nl)$. For a given integer m between $-N$ and N, what is the probability $P(m, N)$ that ml is the final position?

Let us denote by N_+ the number of steps in the positive direction and by N_- the number of steps in the negative direction. We must have $m = N_+ - N_-$. Since $N = N_+ + N_-$, we get $N_+ = \dfrac{N+m}{2}, N_- = \dfrac{N-m}{2}$. An important detail: N and m are necessarily both even or odd. Clearly, changing m to $-m$ produces an interchange between N_+ and N_-.

The number of ways we can perform N steps is $N!$. Thus the number of ways we can reach ml after N steps is $\dfrac{N!}{(N_+)!(N_-)!}$. Since each step has probability $\dfrac{1}{2}$ we obtain the final expression

$$P(m, N) = \frac{1}{2^N} \frac{N!}{(N_+)!(N_-)!} = \frac{1}{2^N} \binom{N}{N_+} \tag{10.1.1}$$

Note that, for a given N, m varies in the set $I(N) = \{-N, -N+2, ..., 0, ...N-2, N\}$, while

---

[a] For a didactical introduction to Statistical Mechanics see[58] .

N_+ takes all the values between 0 and N. Thus we can write

$$\sum_{m\in I(N)} P(m,N) = \frac{1}{2^N}\sum_{k=0}^{N}\begin{pmatrix} N \\ k \end{pmatrix} = 1$$

For our purposes we are interested in the case $N >> 1$, which allows us to use Stirling's formula

$$\log N! \simeq (N+\frac{1}{2})\log N - N + \log\sqrt{2\pi}. \qquad (10.1.2)$$

Let us compute

$$\log(N_+!) + \log(N_-!) \simeq \frac{N+1}{2}\log(N_+N_-) + \frac{m}{2}\log\frac{N_+}{N_-} - (N_+ + N_-) + 2\log\sqrt{2\pi} =$$

$$\frac{N+1}{2}\log\frac{N^2-m^2}{4} + \frac{m}{2}\log\frac{1+\frac{m}{N}}{1-\frac{m}{N}} - N + 2\log\sqrt{2\pi} \simeq$$

$$(N+1)\log\frac{N}{2} - \frac{N+1}{2}\frac{m^2}{N^2} + \frac{m^2}{N} - N + 2\log\sqrt{2\pi}$$

Taking the expansion up to the second order in $\frac{m}{N}$, we obtain

$$(N+1)\log\frac{N}{2} + \frac{m^2}{2N} - N + 2\log\sqrt{2\pi}.$$

Thus from (10.1.1) we get

$$\log P(m,N) = -\frac{1}{2}\log N - \log\sqrt{2\pi} - \frac{m^2}{2N} + \log 2,$$

hence

$$P(m,N) = \frac{2}{\sqrt{\pi N}} e^{-\frac{m^2}{2N}}. \qquad (10.1.3)$$

We may check that $\sum_{m\in I(N)} P(m,N) = 1$ in the limit $N\to\infty$ by taking the integral $\frac{1}{\sqrt{2\pi N}}\int_{-N}^{N} e^{-\frac{m^2}{2N}}dm$ and letting $N\to\infty$. Note that we have integrated $\frac{1}{2}P(m,N)$, remembering that m is allowed to take only odd or even values.

Remark 10.1.1. It can be objected that the formula above has been deduced for $\frac{m}{N} << 1$, while in the integral the variable m varies in $(-N,N)$. However we note that the main contribution to the integral comes from $|m|$ up to $O(\sqrt{N})$, compatible with $\frac{m}{N} << 1$, while for larger values the exponential becomes negligibly small. To pass to a continuum setting we can now define the space coordinate $x = ml$, and time, by introducing the *frequency* ν of steps, so that $N = t\nu$. □

The mean square displacement $< x^2 >$ can be computed by letting $N\to\infty$ in the integral $\int_{-N}^{N} m^2 l^2 P(m,N)dm$ and it turns out to be

$$< x^2 >= Nl^2 = \nu l^2 t.$$

Here we have in mind that, while $\nu \to \infty$, the product νl^2 stays finite. Thus the product νl^2 is somehow linked to the motility of our particle. Defining the *diffusivity*

$$D = \frac{1}{2}\nu l^2, \tag{10.1.4}$$

the main square displacement takes the form

$$< x^2 >= 2Dt \tag{10.1.5}$$

and with the substitutions $m = \dfrac{x}{l}, N = \nu t$ the probability $\dfrac{1}{2}P(m, N)$ reduces to

$$\frac{l}{2\sqrt{\pi D t}} e^{-\dfrac{x^2}{4Dt}},$$

expressing the probability of hitting a point x in an interval of length l. Therefore the *probability density* is

$$\Gamma(x,t) = \frac{1}{2\sqrt{\pi D t}} e^{-\dfrac{x^2}{4Dt}}, \tag{10.1.6}$$

having dimension $(\text{length})^{-1}$.

If $u_0(x)$ represents the distribution functions of a system of identical non-interacting particles at time $t = 0$, the distribution at time t will be

$$m(x,t) = \int_{-\infty}^{+\infty} \Gamma(x - \xi, t) u_0(\xi) d\xi, \tag{10.1.7}$$

i.e. the solution of $u_t - D u_{xx} = 0$.

REFERENCES

1. G. Allaire, A. Mikelic and A. Piatnitski, *Homogenization approach to the dipersion theory for reactive transport through porous media*, SIAM J. Math. Anal. **42** (2010), pp. 125–144.
2. D. Ambrosi, L. Preziosi, *Cell adhesion mechanisms and stress relaxation in the mechanics of tumours*, Biomech. Model. MechanoBiol. **8** (2009), pp. 397–413.
3. D. Andreucci, M.A. Herrero and J.J. Velazquez, *The classical one-phase Stefan problem: a catalogue of interface behaviours*, Surveys Math. Ind. **9** (2001), pp. 247–337.
4. R.P. Arajuo and D.L.S. McElwain, *A history of the study of solid tumour growth: the contribution of mathematical modelling*, Bull. Math. Biol. **66**, (2004), pp. 1039–11091.
5. R.P. Arajuo and D.L.S. McElwain, *New insights into vascular collapse and growth dynamics in solid tumours*, J. Theor. Biol. **228** (2004), pp. 335–346.
6. D. Aregba-Driollet, F. Diele and R. Natalini, *A mathematical model for the SO_2 aggression to calcium carbonate stones: numerical approximation and asymptotic analysis*, SIAM J. Appl. Math. **64** (2004) pp. 1636–1667.
7. R. Aris, *The mathematical theory of diffusion and reaction in permeable catalysts*, Clarendon Press (1975).
8. G.I. Barenblatt, V.M. Entov and V.M. Ryzhik, *Theory of Fluid Flows Through Natural Rocks*, Kluwer (1990).
9. J. Bear, *Dynamics of Fluids in Porous Media*, America Elsevier, N.Y. (1972).
10. J. Bear and A. Verruijt, *Modelling Ground Water Flow and Pollution*, Reidel, Dordrecht, N.Y. (1987).
11. N. Bellomo, N.K. Li and P.K. Maini, *On the foundations of cancer modelling: selected topics, speculations and perspectives*, Math. Mod. Meth. Appl. Sci., **18**, (2008) pp. 513–646.
12. H. Bénard, *Tourbillons cellulaires dans une nappe liquid*, Revue Gén. Sci. Pure Appl. **11** (1900), pp. 1261–1271.
13. A. Bertuzzi, A. Fasano and A. Gandolfi, *A mathematical model for tumour cords incorporating the flow of interstitial fluid*, Mathematical Models and Methods in Applied Sciences, **15** (2005), pp. 1735–1777.
14. A. Bertuzzi, A. Fasano and A. Gandolfi, *A free boundary problem with unilateral constraints describing the evolution of a tumour cord under the influence of cell killing agents*, SIAM Journal on Mathematical Analysis, **36** (2004), pp. 882–915.
15. A. Bertuzzi, A. Fasano, A. Gandolfi and C. Sinisgalli, *Interstitial pressure and extracellular fluid motion in tumour cords*, Mathematical Biosciences, **2** (2005), pp. 445–460.
16. A. Bertuzzi, A. Fasano, A. Gandolfi and C. Sinisgalli, *Cell resentisization after delivery of a cicle-specific anticancer drug and effect of dose splitting: learning from tumour cords*, J. Theor. Biol. **244** (2007), pp. 388–399.
17. A. Bertuzzi, A. Fasano, A. Gandolfi and C. Sinisgalli, *Necrotic core in EMT6/Ro tumour spheroids: is it caused by an ATP deficit?*, J. Theor. Biol. **262** (2010), pp. 142–150.
18. L. Bianchini and A. Fasano, *A model combining acid-mediated tumour invasion and nutrient dynamics*, Nonlinear Analysis Real World Applications **10** (2009), pp. 1955–1975.
19. I. Borsi, A. Farina and A. Fasano, *On the infiltration of rain water through the soil*

with runoff of the excess water, Nonlinear Analysis Real World Applications **5** (2004), pp. 763–800.

20. H.F. Bremer and E.L. Cussler. *Diffusion in the ternary system d-tartaric acid /c-tartaric acid/ water at 25 C.*, AIChE J. **16**(1980), pp. 832-838.
21. J.D. Buckmaster, (editor), *The Mathematics of Combustion*, SIAM, Frontiers in Applied Mathematics (1985).
22. J.D. Buckmaster and G.S.S. Ludford, *Lectures on Mathematical Combustion*, CBMS-NSF Conf. Series Appl. Math. **43**, SIAM (1983).
23. G. Caginalp, *The dynamics of a conserved phase field system: Stefan-lke, Hele-Shaw, and Cahn-Hilliard models as asymptotic limits.* I.M.A. J. Appl. Math. **44** (1990), pp. 216–226.
24. J.R. Cannon, *The one-dimensional heat equation*, Encyclopedia of Math. & its Appl. **23**, Addison-Wesley (1984).
25. J.R. Cannon, E. Di Benedetto and K.G. Knightly *The bidimensional Stefan problem with convection: the time dependent case*, Comm. in Part. Diff. Eqs. **8(14)** (1983),pp. 1549–1604.
26. V. Capasso, editor, *Mathematical Modelling for Polymer Processing*, Mathematics in Industry **2**, ECMI Series, Springer-Verlag (2003).
27. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press (Clarendon), London and N.Y. (1948).
28. C.R. Cattaneo, *Sur une forme de l'équation de la chaleur éliminant le paradox d'une propagation instantanée*, Comptes Rend. **247** (4) (1958), pp. 431–433.
29. S. Chandrasekar, *Stochastic problems in physics and astronomy*, Rev. Modern Physics **15** (1943), pp. 1-85.
30. M.A.J. Chaplain, *Special Issue on Mathematical Modelling and Simulations of Aspects of Cancer Growth*, J. Theor. Medicine **4** (2002).
31. F. Clarelli, A. Fasano, R. Natalini, *Mathematics and monuments conservation: a model for marble sulfation*, SIAM J. Appl. Math. **69** (2008), pp. 149–168.
32. E. Comparini, *A one-dimensional Bingham flow*, J. Math. Anal. Appl., **169** (1992), pp. 127–139.
33. S. Correra, A. Fasano, L. Fusi and D. Merino-Garcia, *Calculating deposit formation in the pipelining of waxy crude oils*, Meccanica **42** (2007), pp. 149–165.
34. S. Correra, A. Fasano, L. Fusi and M. Primicerio, *Modelling wax diffusion in crude oils: the cold finger device*, J. Appl. Math. Modelling **31** (2007), pp. 2286–2298..
35. S. Correra, A. Fasano, L. Fusi, M. Primicerio and F. Rosso, *Wax diffusivity under given thermal gradient: a mathematical model*, ZAMM **87** (2007) pp. 24-36.
36. R. Courant and D. Hilbert, *Methods of Mathematical Physics, Vol. I*, Interscience Publ. Inc., John Wiley & Sons, Inc., N.Y. (1953).
37. J. Crank, *Free and Moving Boundary Problems*, Clarendon Press, 1984.
38. J.I. Diaz, *Nonlinear Partial Differential Equations and Free Boundary Problems*, I, Elliptic Equations, Pitman (1985).
39. M. Doi and S.E. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford (1986).

40. G. Duvaut, *Résolution d'un problème de Stéfan (fusion d'un bloc de glace à zéro degré*, Compt. Rend. Acad. Sci. Paris, **A276** (1973), pp. 1461–1463.
41. C.M. Elliot, J.R. Ockendon, *Weak and variational methods for moving boundary problems*, Res. Notes Math. Pitman **59** (1981).
42. M.S. Espedal, K.M. Karlsen, *Numerical solutions of reservoir flow models based on large time step operator splitting algoritms*, in " Filtration in Porous Media and Industrial Applications" (CIME), M.S. Espedal, A. Fasano, A. Mikelic editors, Lect. Notes Math. **1734**, Springer (2000), pp. 9–77.
43. M.S. Espedal, A. Fasano and A. Mikelic, *Filtration in Porous Media and Industrial Applications*, (CIME) Lect. Notes Math. **1734**, Springer (2000).
44. A. Fasano, editor *Complex Flows in Industrial Processes*, MSSET, Birkhäuser (2000).
45. A. Fasano, editor *Mathematical Models in the Manufacturing of Glass*, Lecture Notes in Mathematics, **2010** Springer (2011).
46. A. Fasano, *La zonas pastosas en el problems de Stefan*, Cuadernos Inst. Mat. B. Levi Rosario, Argentina, **13** (1987).
47. A. Fasano, *Mathematical models for polymerization processes of Ziegler-Natta type*, in "Mathematical Modelling for Polymer Processing", V. Capasso, editor, Springer ECMI Series (2003), pp. 2–28.
48. A. Fasano, *Mathematical models in polymer processing*, Meccanica **35** (2000), pp. 163–198.
49. A. Fasano, *Phase transition with supercooling*, Boll. UMI **8** 1B (1998), pp. 46–69.
50. A. Fasano, *Porous media with hydrophile granules*, in "Complex Flows in Industrial Processes", A. Fasano editor, MSSET Birkhäuser (2000), pp. 307–332.
51. A. Fasano, A. Bertuzzi and A. Gandolfi, *Mathematical modelling of tumour growth and treatment*, in "Integration of Complex Systems in Biomedicine" (A. Quarteroni, L. Formaggia, A. Veneziani editors), Springer-Verlag Italia (2006), pp. 71–108.
52. A. Fasano, L. Fusi and S. Correra, *Mathematical models for waxy crude oils*, Meccanica **39** (2004), pp. 441–483.
53. A. Fasano, L. Fusi, M. Primicerio and J.R. Ockendon, *Gelification and mass transport in a static non-isothermal waxy solution*, Eur. J. Appl. Math. **20** (2009), pp. 93–122.
54. A. Fasano, M.A. Herrero and M. Rocha Rodrigo, *Slow and fast invasion waves in a model of acid-mediated tumour growth*, Math. Biosci. **220** (2009), pp. 45–56.
55. A. Fasano, M.A. Herrero, J.M. Lopez and E. Medina, *On the dynamics of the growth plate in primary ossification*, To appear on J. Theor. Biol.
56. A. Fasano, K. Kannan, A. Mancini and K.R. Rajagopal, *Modelling Ziegler-Natta polymerization in high pressure reactors*, in "Mathematical Substructures in Complex Bodies: from Atomic Level to Continuum, (G. Capriz, P. M. Mariano editors). Elzevier (2007) pp. 206–237.
57. A. Fasano and A. Mancini, *Modelling frying of a non-deformable specimen by immersion in edible oil*, Computers Mathematics with Applications Archive **55**, (2008), pp. 149–161.
58. A. Fasano and S. Marmi, *Analytical Mechanics*, Oxford Univerity Press (2006).
59. A. Fasano and M. Primicerio, *New results on some classical parabolic free boundary prob-*

lems, Quart. Appl. Math. **38** (1981), pp. 439–460.

60. A. Fasano and M. Primicerio, *Convexity of the free boundary in some classical parabolic free boundary problems*, Riv. Mat. Univ. Parma (4) **5** (1979), pp. 635–645.
61. A. Fasano and M. Primicerio, *A critical case for the solvability of Stefan-like problems*, Math. Meth. Appl. Sci. **5** (1983), pp. 84–96.
62. A. Fasano and M. Primicerio, *General free boundary problems for the heat equation, I*, J. Math. Anal. Appl. **57** (1977), pp. 694–723.
63. A. Fasano and M. Primicerio, *General free boundary problems for the heat equation, II*, J. Math. Anal. Appl. **58** (1977), pp. 202–231.
64. A. Fasano and M. Primicerio, *General free boundary problems for the heat equation, III*, J. Math. Anal. Appl. **59** (1977), pp. 1–14.
65. A. Fasano and M. Primicerio, *Free boundary problems for nonlinear parabolic equations with nonlinear free boundary conditions*, J. Math. Anal. Appl. **72** (1979), pp. 247–273.
66. A. Fasano, M. Primicerio, S.D. Howison and J.R. Ockendon, *Some remarks on the regularization of supercooled one-phase Stefan problems in one dimension*, Quart. Appl. Math. **48** (1990), pp. 153–168.
67. A. Fasano, M. Primicerio, S.D. Howison and J.R. Ockendon, *On the singularities of one-dimensional Stefan problems with supercooling*, in ”Mathematical Models for Phase Change Problems”, J.F. Rodrigues, editor. Int. Ser. Numerical Mathematics **88** (1989), Birkhäuser, pp. 215–225.
68. A. Fasano, M. Primicerio and S. Kamin, *Regularity of weak solutions of one-dimensional two-phase Stefan problems*, Ann. Mat. Pure Appl. **115** (1977), pp. 341–348.
69. A. Fasano, M. Primicerio and G.H. Meyer, *On a problem in the polymer industry: theoretical and numerical investigation of swelling*, SIAM. J. Math. Anal. **17** (1986), pp. 945–960.
70. A. Fasano and M. Primicerio, *Heat and mass transport in non-isothermal partially saturated oil-wax solutions*, In "New Trends in Mathematical Physics", P. Fergola, F. Capone, M. Gentile, G. Guerriero editors. World Sci. (2009).
71. A. Fasano and M. Primicerio, *Temperature driven mass transport in concentrated saturated solutions*, Progress in Nonlinear Differential Equations and Their Application **61** (2005), pp. 91–108.
72. A. Fasano and M. Primicerio, *Wax deposition in crude oils: a new approach*, Rend. Mat. Accad. Lincei IX, **16** (2005), pp. 251–263.
73. A. Fasano, M. Primicerio and A. Tesi, *A mathematical model for spaghetti cooking with free boundaries*, To appear on Appl.Math.J.: Networks and Heterogeneous Media (2011).
74. A. Fasano and F. Talamucci, *A comprehensive mathematical model for a multi-species flow through ground coffee*, SIAM J. Math. Analysis **31** (1999), pp. 251–273.
75. P. Fife, G.S. Gill, *A phase field description of mushy zones*, Physica D **35** (1989), pp. 267–275.
76. M. Frémond, *Variational formulation of the Stefan problem*, Int. Conf. Computational Methods in Nonlinear Mechanics, Austin (TX), J.T. Oden editor (1974), pp. 341–349.
77. A. Friedman, *Remarks on the maximum principle for parabolic equations and its applica-*

tions, Pacific J. Math. **8** (1958), pp. 201–211.

78. A. Friedman, *Partial Differential Equations of parabolic type*, Prentice Hall (1964).
79. A. Friedman, *The Stefan problem in several space variables*, Trans. Amer. Math. Soc. **133** (1968) pp. 51–87.
80. A. Friedman, *Variational Principles in Free Boundary Problems*, John Wiley & Sons, NY (1982).
81. R.A. Gatenby and E.T. Gavlinski, *A reaction-diffusion model for cancer invasion*, Cancer Res. **56** (1996), pp. 5745–5753.
82. R. Gianni, *A filtration problem with pounding*, Boll. U.M.I. **5B** (1991), pp. 875–891.
83. W.H. Green and G.A. Ampt, *Studies on soil physics. The flow of air and water through soils*, J. Agric. Sci. **4** (1911), pp. 1–24.
84. S.C. Gupta, *The classical Stefan problem. Basic concepts, modelling and analysis*, North-Holland Series in Appl. Math. and Mechanics **45** Elsevier (2003).
85. E.I. Hanzawa, *Classical solution of the Stefan problem*, Tohoku Math. **33** (1981), pp. 297–335.
86. S. M. Hassanizadeh and W.G. Gray,*Towards an improved description of two-phase flow*, Adv. Water Resour. **16** (1993), pp. 53–67.
87. J. Hernandez, *Qualitative methods for nonlinear diffusion equations*, in "Nonlinear Diffusion Problems" (CIME), A. Fasano, M. Primicerio Editors, Lecture Notes in Mathematics **1224**, Springer-Verlag (1986), pp. 47–118.
88. M.A. Herrero, *Reaction-diffusion systems: a mathematical biology approach*, in "Cancer modelling and simulation", L. Preziosi editor , Chapman and Hall (2003), pp. 367–420.
89. M.A. Herrero, *The Mathematics of Chemotaxis*, Handbook of Diff. Eqs., Evolutionary eqs. **3** (2007), pp. 137–193.
90. E. Hopf, *A remark on linear elliptic differential equation of second order*, Proc. Amer. Math. Soc. **3** (1952), pp. 791–793.
91. U. Hornung, *Homogenization and Porous Media*, Interdisciplinary Applied Math. **6**, Springer (1997).
92. S. Howison, *Practical Applied Mathematics: Modelling, Analysis, Approximation*, CUP (2005).
93. S.L. Kamenomostskaja, *On the Stefan problem*, Mat. Sb. **53** (1961), pp. 489–514.
94. D. Kinderlehrer and G. Stampacchia, *An introduction to variational inequalities and their applications*, Academic Press N.Y. (1980).
95. A. J. Koch and H. Meinhardt, *Biological pattern formation: from basic mechanisms to complex structures*, Rev. Mod. Phys. **66** (1994), pp. 1481–1507
96. M. Kröger, *Models for polymeric and anisotropic liquids*, Lecture Notes in Physics, Springer-Verlag, Berlin (2005).
97. O.A. Ladyzenskaja, V.A. Solonnikov and N.N. Ural'ceva, *Linear and quasilinear equations of parabolic type*, AMS Translations of Math. Monographs **27** (1968).
98. K. Lal Gauri and J.K. Bandyopadhyay, *Carbonate Stone, Chemical Behavior, Durability and Conservation*, John Wiley & Sons, Inc. (1999).

99. G. Lamé and B.P. Clapeyron, *Memoire sur la solidification par refroidissement d'un globe liquide*, Ann. Chimie Phys. **47** (1831), pp. 250–256.
100. E. Magenes, *Stefan problems with a concentrated capacity*, Boll. UMI **(8)** 1B (1998), pp. 71–81.
101. M. Margarone, R. Bagatin, C. Busto, P. D'Olimpio, L. Fusi, L. Faienza, A. Fasano, and M. Primicerio, *A wax crystallization model from DSC experiments*, submitted.
102. G. Marrucci and G. Ianniruberto, *Molecular theories of polymer viscosity*, in "Complex Flows in Industrial Processes, A. Fasano, editor, MSSET, Birkhäuser (2000), pp. 3–24.
103. A.M. Meirmanov, *On the classical solubility of the Stefan problem*, Soviet Math. Dokl. **20** (1979), pp. 1426–1429.
104. A.M. Meirmanov, *The Stefan Problem*, De Gruyter (1992).
105. A. Mikelic, *Homogenization theory and applications to filtration through porous media*, in "Filtration in Porous Media and Industrial Applications", (M.S. Espedal, A. Fasano, A. Mikelic) (CIME) Lect. Notes Math. **1734**, Springer (2000), pp. 127–214.
106. A. Mikelic, *A global existence result for the equations describing unsaturated flow in porous media with dynamic capillary pressure*, J. Differential Equations **248** (2010), pp. 1561-1577.
107. L.A. Niremberg, *A strong maximum principle for parabolic equations*, Comm. Pure Appl. Math. **6** (1953), pp. 167–177.
108. R.H. Nochetto, *Finite element methods for parabolic free boundary problems*, In Adv. Num. Analysis **1** (W. Light, editor) ,Oxford Academic Press, (1991), pp. 34–95.
109. R.H. Nochetto, C. Verdi, *An efficient linear scheme to approximate parabolic free boundary problems: Error estimates and implementation.* Math. Comp. **51** (1988), pp. 27–53.
110. O.A. Oleinik, *On a method for solving the general Stefan problem*, Dokl. Akad. Nauk SSSR **135** (1960), pp. 1054–1057.
111. S. Osher, J.A. Sethian, *Fronts propagating with curvature depending speed: Algorithms based on Hamilton-Jacobi formulations.* J. Comput. Phys. **79** (1988), pp. 12–49.
112. C. Preziosi, *The theory of deformable porous media and its applications to composite materials manufacturing*, Surveys Math. Ind. **6** (1996), pp. 167–214.
113. L. Preziosi, editor *Cancer Modelling and Simulations*, Chapman Hall/CRC Press (2003).
114. M. Primicerio, *Mushy regions in phase change problems*, In "Applied Nonlinear Functional Analysis", R. Gorenflo and K.H. Hoffmann editors, Lang, Frankfurt a.M. (1982), pp. 251–269.
115. M.H. Protter and H.F. Weinberger, *Maximum Principles in Differential Equations*, Prentice-Hall Inc., Englewood Cliffs, N.J. (1967).
116. D. Provan and J.G. Gribben, editors *Molecular Hematology*, 3^{rd} edition, Wiley-Blackwell (2010).
117. K.R. Rajagopal and L. Tao, *Mechanics of Mixtures*, World Scientific (1995).
118. Lord Rayleigh, *On convection currents in a horizontal layer of fluid, when the higher temperature is on the under side*, Phil. Mag. **32** (1916), pp. 529–546.
119. L.I. Rubinstein, *The Stefan Problem*, AMS Transl. Math. Monograph **27** (1971).
120. H. Schlichting and K. Gersten, *Boundary Layer Theory*, 8th Edition, Springer (2000).

121. J.A. Sethian, *Level Set Methods: Evolving interfaces in geometry, fluid mechanics, computer vision, and material science*, CUP (1996).
122. J.E. Shelby, *Introduction to Glass Science and Technology* 2nd edition, RSCP Publishing, London (2005).
123. K. Smallbone, R.A. Gatenby, R.J. Gillies, P.K. Maini and D.J. Gavaghan, *Metabolic changes during carcinogenesis: potential impact on invasiveness*, J. Theor. Biol. **244** (2007), pp. 703–713.
124. I. Stakgold, *Reaction-diffusion problems in chemical engineering*, in "Nonlinear Diffusion Problems" (CIME), A. Fasano, M. Primicerio Editors, Lecture Notes in Mathematics **1224**, Springer-Verlag (1986), pp. 119–152.
125. J. Stefan, *Über einige Probleme der Theorie der Wärmeleitung*, S.B. Kais. Akad. Wiss. Wien, **28** (1889), pp. 473–484.
126. J. Stefan, *Über die Theorie des Eisbildung*, insbesondere "Über die Eisbildung in Polarmeere", S.B. Kais. Akad. Wiss. Wien, **98** (1889), pp. 965–983.
127. J. Stefan, *Über die Theorie des Eisbildung*, Monatshefte math. Phys. **1** (1890), pp. 1–6.
128. G.I. Taylor, *Dispersion of soluble matter in solvent flowing slowly through a tube*, Proc. Roy. Soc. **219** (1953), pp. 186–203.
129. R. Taylor and R. Krishna, *Multicomponent Mass Transfer*, John Wiley & Sons (1993).
130. R. Venkatasubramanian, M.A. Henson and N.S. Forbes, *Incorporating energy metabolism into a growth model of multicellular tumor spheroids*, J. Theor. Biol. **242** (2006), pp. 440–453.
131. C. Verdi, *Numerical methods for phase transition problems*, Boll. UMI **(8) 1B** (1998), pp. 83–108.
132. P. Vernotte, *Les paradoxes de la theorie continue de l'équation de la chaleur*, Comptes Rend. **246** (22) (1958), pp. 3154–3155.
133. A. Visintin, *Introduction to the models of phase transitions*, Boll. UMI***(8)1B***(1998) pp. 1–47.
134. A. Visintin, *Models of Phase Transitions*, Birkhäuser, (1996) (with 598 titles of bibliographical references).
135. R. Vyborny, *On properties of solutions of some boundary value problems for equations of parabolic type*, Dokl. Acad. Nauk SSSR (N.S.) **117** (1957), pp. 563–565.
136. S.D. Webb, J.A. Sherrat, R.G. Fish, *Mathematical model of tumour acidity:regulation of intracellular pH*, J. Theor. Biol. **196** (1999), pp. 237–250.
137. S. Whitaker, *Simultaneous heat, mass, and momentum transfer in porous media:a theory of drying*, Adv. Heat Tranfer **13** (1977), pp. 119–203.