2 Free boundary problems

2.1 Introduction

A free boundary problem occurs when the region in which the problem is to be solved is unknown in advance and must be found as part of the solution. We will describe a canonical free boundary problem known as the *Stefan problem*, which describes the flow of heat through a material where a phase change occurs. For example, when a block of ice melts to form water (or when water freezes to form ice), we have to solve for the free boundary between the two phases as well as for the temperature field in each phase. As we will see, these problems can become ill posed, predicting pathologically unstable behaviour. We will show how a well-posed and physically realistic model may be formulated by introducing a "mushy region".

The Stefan problem is a canonical "codimension-one" free boundary problem: the free boundary has dimension one below that of the space in which the problem is solved. (For example, the free boundary between ice and water in three dimensions is a two-dimensional surface.) A slightly rarer situation is a "codimension-two" free boundary problem, where the free boundary has two fewer dimensions than the space in which the problem is solved. For example, this would describe a two-dimensional problem in which the free boundary consists of a set of points. We will analyse in detail a relatively simple codimension-two free boundary problem that describes electropainting of a metal surface. As we will see, such problems often lead to singular integral equations, and we will show how a simple example can be solved analytically.

2.2 Stefan problems

Industrial problem: electric welding

One convenient way to weld steel plates is to place them together, attach electrodes to the edges and then pass a large electric current through. This heats the metal, causing a neighbourhood of the interface between the plates to melt. When the current is switched off, the liquid metal solidifies and the two plates are welded together.

Since the interfacial region cannot be observed directly, we must know in advance how long the current should be applied to ensure that the metal melts without melting the entire plates. We must also calculate how long the plates should be left once the current has been switched off to ensure that they have solidified completely.

One-dimensional Stefan problem

Consider a slab of initially solid material occupying the region $0 < x < a$. The temperature $T(x,t)$ in the slab satisfies the *heat equation*

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right), \tag{2.1}$$

where ρ, c and k are the density, heat capacity and thermal conductivity. In (2.1) we have neglected any heat sources (for example electric heating) and assumed that the heat flux q satisfies *Fourier's law*

$$q = -k\frac{\partial T}{\partial x}. \tag{2.2}$$

We focus for the moment on a concrete problem in which the slab is initially at a uniform temperature T_0 and the face $x = a$ is insulated, while the temperature of the face at $x = 0$ is suddenly increased to a temperature $T_1 > T_0$. We then have to solve (2.1) subject to the initial and boundary conditions

$$T(x,0) = T_0, \quad 0 < x < a; \qquad T(0,t) = T_1, \quad t > 0; \qquad \frac{\partial T}{\partial x}(a,t) = 0, \quad t > 0. \tag{2.3}$$

If T_1 is high enough, then we expect the solid to melt and become liquid in some neighbourhood of $x = 0$. If so, we must seek a solution in which the slab is liquid in $0 < x < s(t)$ and solid in $s(t) < x < a$, where $x = s(t)$ is the *free boundary* separating the liquid and solid phases. The position of the free boundary is unknown in advance and must be found as part of the solution.

In general we have to solve the heat equation (2.1) in both solid and liquid phases, i.e., in $0 < x < s(t)$ and in $s(t) < x < a$, with different values of the parameters ρ, c and k on either side. We also need to impose conditions at the free boundary $x = s(t)$. First we assume that the phase change happens at a known melting temperature:

$$T(s(t),t) = T_{\mathrm{m}}. \tag{2.4}$$

The temperature is continuous so this applies on both sides of the free boundary.

The second condition comes from an energy balance. At a fixed boundary, the heat flux coming in from one side must equal the heat flux exiting from the other side, i.e., $q = -k\partial T/\partial x$ must be continuous. However, at a moving interface, we must also consider the energy associated with the phase change, known as the *latent heat* L. For example, the latent heat of water is $L = 334\,\mathrm{kJ/kg}$, meaning that it requires $334\,\mathrm{kJ}$ of energy to turn $1\,\mathrm{kg}$ of ice at $0°\mathrm{C}$ to $1\,\mathrm{kg}$ of water at $0°\mathrm{C}$. The latent heat acts as an energy source or sink at a moving solid–liquid interface, and the resulting boundary condition

$$k\frac{\partial T}{\partial x}\bigg|_{x=s(t)+} - k\frac{\partial T}{\partial x}\bigg|_{x=s(t)-} = \rho L\frac{\mathrm{d}s}{\mathrm{d}t} \tag{2.5}$$

is known as the *Stefan condition.*

In summary, the *Stefan problem* consists of the heat equation (2.1) on either side of the free boundary $x = s(t)$, where the two conditions (2.4) and (2.5) are applied. The problem is closed by suitable boundary and initial conditions, for example (2.3).

Before proceeding, we briefly review some of the assumptions that have been made so far. In using Fourier's law (2.2), we have assumed that the heat flux is purely due to thermal conductivity. If the liquid flows at all, then there will also be a contribution due to convection. Generally there is a change in density as the material melts, so that ρ is discontinuous across $x = s(t)$. This would inevitably mean there must be a nonzero velocity and therefore a nonzero convective heat flux. It is a good exercise to work out how the model should be modified to include convection. For the moment, we can avoid such complications by assuming that the density change at the solid–liquid interface is small enough to be neglected.

One-phase Stefan problem

To make progress we will make some more simplifying assumptions. We will assume that ρ, c and k are all constant on either side of the solid–liquid interface – in general they may all be functions of temperature. We will also for the moment suppose that the initial temperature T_0 is equal to the melting temperature T_{m}. This means that the solid region $s(t) < x < a$ is always at temperature T_{m} and we only need to solve the heat equation in the liquid phase $0 < x < s(t)$: this is a *one-phase* Stefan problem.

We non-dimensionalize as follows:

$$x = ax', \qquad t = \left(\frac{\rho L a^2}{k(T_1 - T_{\mathrm{m}})}\right) t', \qquad T = T_{\mathrm{m}} + (T_1 - T_{\mathrm{m}})u. \tag{2.6}$$

Then with primes dropped, we get a normalized one-phase Stefan problem in the form

$$\begin{aligned}
\mathrm{St}\frac{\partial u}{\partial t} &= \frac{\partial^2 u}{\partial x^2} && 0 < x < s(t), \quad t > 0, && (2.7\text{a})\\
u &= 1 && x = 0, \quad t > 0, && (2.7\text{b})\\
u = 0, \quad -\frac{\partial u}{\partial x} &= \frac{\mathrm{d}s}{\mathrm{d}t} && x = s(t), \quad t > 0, && (2.7\text{c})\\
s(0) &= 0. && && (2.7\text{d})
\end{aligned}$$

Clearly generalized versions of (2.7) would be obtained if we relaxed some of the simplifying assumptions made above.

The dimensionless parameter[1]

$$\mathrm{St} = \frac{c(T_1 - T_{\mathrm{m}})}{L}, \tag{2.8}$$

called the *Stefan number*, measures the relative importance of the *sensible* heat and the latent heat; in other words, the energy needed to raise the temperature of the material and the energy needed to melt it.

We can seek a *similarity solution* of (2.7) in which

$$s(t) = \beta\sqrt{t} \qquad \text{and} \quad u(x,t) = f(\eta), \qquad \text{where} \quad \eta = \frac{x}{\sqrt{t}}, \tag{2.9}$$

for some constant β, and

$$\begin{aligned}
\frac{\mathrm{d}^2 f}{\mathrm{d}\eta^2} + \frac{\mathrm{St}}{2}\eta\frac{\mathrm{d}f}{\mathrm{d}\eta} &= 0 && 0 < \eta < \beta, && (2.10\text{a})\\
f &= 1 && \eta = 0, && (2.10\text{b})\\
f = 0, \quad \frac{\mathrm{d}f}{\mathrm{d}\eta} &= -\frac{\beta}{2} && \eta = \beta. && (2.10\text{c})
\end{aligned}$$

This is again a free boundary problem: the three boundary conditions imposed on a second-order ODE in principle determine β as part of the solution.

The solution is given by

$$f(\eta) = 1 - \frac{\operatorname{erf}\left(\eta\sqrt{\mathrm{St}}/2\right)}{\operatorname{erf}\left(\beta\sqrt{\mathrm{St}}/2\right)}, \tag{2.11}$$

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[1] beware: some authors define the Stefan number to be the reciprocal of our definition

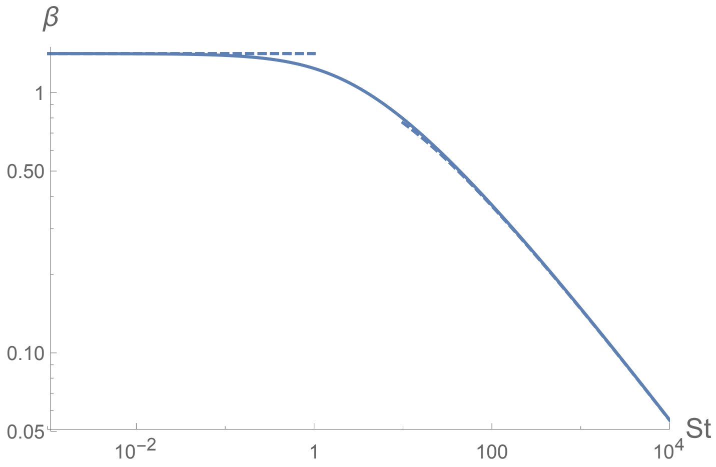

Figure 2.1: The relation between the parameter β and the Stefan number St determined by equation (2.12). The dashed curves show the asymptotic limits (2.13).

where β satisfies the transcendental equation

$$\frac{\sqrt{\pi}\beta \mathrm{e}^{\mathrm{St}\beta^2/4}\,\mathrm{erf}\left(\beta\sqrt{\mathrm{St}}/2\right)}{2\sqrt{\mathrm{St}}} = 1. \tag{2.12}$$

The relation between β and the Stefan number St is plotted in figure 2.1, along with the asymptotic limits

$$\beta \sim \begin{cases} \sqrt{2} & \text{as St} \to 0, \\ \dfrac{2}{\sqrt{\mathrm{St}}}\sqrt{\log\left(\dfrac{\mathrm{St}}{\sqrt{\pi}}\right)} & \text{as St} \to \infty. \end{cases} \tag{2.13}$$

Given the value of St, we can thus determine β and hence the evolution of the free boundary $s(t) = \beta\sqrt{t}$. This square-root behaviour of the free boundary as a function of time is characteristic of Stefan problems. The entire slab has melted when $s(t) = 1$, and the dimensionless time taken is thus given by $1/\beta^2$. By reversing the non-dimensionalization (2.6) and using (2.13), we find two alternative approximations for the dimensional melting time t_{m}, namely

$$t_{\mathrm{m}} \sim \begin{cases} \dfrac{\rho L a^2}{2k(T_1 - T_{\mathrm{m}})} & \mathrm{St} \ll 1, \\ \dfrac{\rho c a^2}{4k\log\left(\mathrm{St}/\sqrt{\pi}\right)} & \mathrm{St} \gg 1. \end{cases} \tag{2.14}$$

When the Stefan number is small, the melting of the slab is mainly limited by the latent heat required. At the other extreme, the main barrier is the energy needed to heat up the slab, and the melting time depends only weakly on the latent heat L.

The limit $\mathrm{St} \ll 1$ is very helpful and often valid: figure 2.1 suggests that the small-St approximation works well even for values of St up to around 1. For example, suppose we try to melt a block of ice by heating one face to 5°C. The relevant parameters are $L = 334\,\mathrm{kJ/kg}$ and $c = 4.2\,\mathrm{kJ/kg\,K}$ so that $\mathrm{St} \approx 0.06$. In this case, the value of β obtained by solving the transcendental equation (2.12) differs from the limiting value $\sqrt{2}$ by around 1%.

Two-phase Stefan problem

The two-phase version of the dimensionless Stefan problem considered above reads

$$\mathrm{St}\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \qquad 0 < x < s(t), \quad t > 0, \tag{2.15a}$$

$$\frac{\mathrm{St}}{\kappa}\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} \qquad s(t) < x < 1, \quad t > 0, \tag{2.15b}$$

$$u = 1 \qquad x = 0, \quad t > 0, \tag{2.15c}$$

$$\frac{\partial u}{\partial x} = 0 \qquad x = 1, \quad t > 0, \tag{2.15d}$$

$$u = 0, \quad K\left[\frac{\partial u}{\partial x}\right]^{+} - \left[\frac{\partial u}{\partial x}\right]^{-} = \frac{\mathrm{d}s}{\mathrm{d}t} \qquad x = s(t), \quad t > 0 \tag{2.15e}$$

$$u = -\theta, \quad s = 0 \qquad t = 0, \tag{2.15f}$$

where the new dimensionless parameters are

$$\kappa = \frac{c_1 k_2}{c_2 k_1}, \qquad K = \frac{k_2}{k_1}, \qquad \theta = \frac{T_{\mathrm{m}} - T_0}{T_1 - T_{\mathrm{m}}}. \tag{2.16}$$

Here we have denoted the values of the specific heat and thermal conductivity in the liquid and solid phases by c_1, k_1 in $0 < x < s$ and c_2, k_2 in $s < x < 1$.

In general, this problem must be solved numerically. However, analytical progress can be made in some special cases. As noted above, it is often valid and helpful to consider the limit $\mathrm{St} \to 0$, in which case the PDEs (2.15a) and (2.15b) are quasi-steady and may be integrated directly. We then quickly get

$$u(x,t) = \begin{cases} 1 - \dfrac{x}{s(t)} & 0 < x < s(t) < 1, \\ 0 & 0 < s(t) < x < 1, \end{cases} \tag{2.17}$$

and the Stefan condition (2.15e) then leads to

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{s}, \tag{2.18}$$

and hence

$$s(t) = \sqrt{2t}, \tag{2.19}$$

which is equivalent to (2.9) in the small-St limit where $\beta = \sqrt{2}$.

However, the approximate solution (2.17) does not satisfy the initial condition (2.15f), except in the special case where $\theta = 0$ (i.e., $T_0 = T_{\mathrm{m}}$). This may easily be resolved by considering a small-t boundary layer in which u adjusts from the initial value $-\theta$ to the "outer" solution (2.17).

Two-dimensional Stefan problem

A two-dimensional version of the problem (2.15) is depicted schematically in figure 2.2. To avoid confusion we now use the subscripts 1 and 2 to denote the normalized temperatures u_1 and u_2 in the liquid and solid phases respectively. Each of these now satisfies the two-dimensional heat equation. The free boundary between the two phases is now a curve in the

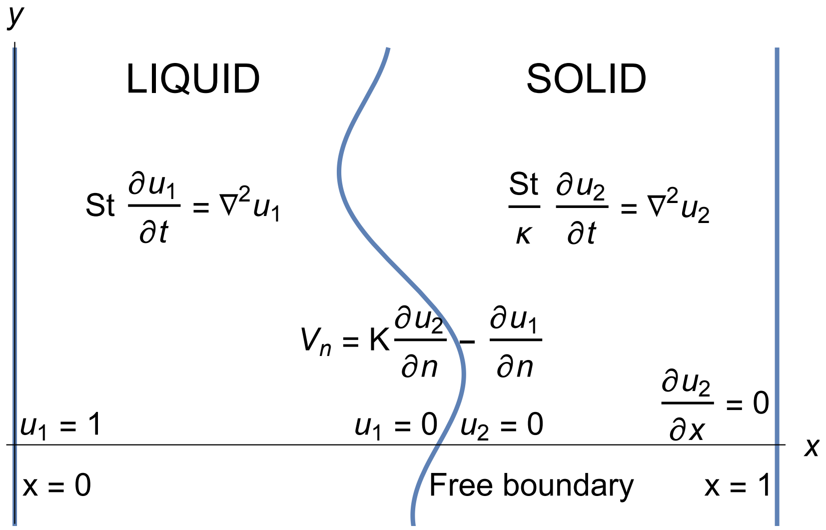

Figure 2.2: Schematic of a two-dimensional Stefan problem.

(x, y)-plane, on which both u_1 and u_2 are equal to the normalized melting temperature 0. Finally, the Stefan condition now relates the normal velocity V_n of the free boundary to the jump in the normal derivative of the temperature on either side. To close the problem, it only remains to specify suitable initial conditions, namely the value of the temperature everywhere in the domain and the position of the free boundary at $t = 0$.

As in the one-dimensional situation, the problem may be simplified somewhat if the Stefan number is small. In the limit $\mathrm{St} \to 0$, the temperature u just satisfies Laplace's equation on either side of the free boundary, and the resulting quasi-steady problem resembles the *Hele-Shaw* problem.

Linear stability

Now we can examine the stability of the one-dimensional solutions found above to two-dimensional perturbations. We first make some simplifying assumptions to make the calculations relatively straightforward. We take the limit $\mathrm{St} \to 0$ and focus on a one-phase Stefan problem in which $u_2 \equiv 0$ (in the notation of figure 2.2) — the problem is then equivalent to the one-phase Hele-Shaw problem. We also assume that the free boundary is moving at constant speed V under a constant temperature gradient $-\lambda$ before being perturbed. We therefore write the normalized temperature and the position of the free boundary in the forms

$$u(x, y, t) = -\lambda(x - Vt) + \tilde{u}(x, y, t), \qquad x = Vt + \xi(y, t), \tag{2.20}$$

before linearising the problem with respect to the small perturbations $\tilde{u}$ and ξ. Assuming as above that the material is solid in $x > Vt$ and liquid in $x < Vt$, we expect λ to be positive, so that the temperature is above the melting temperature in the liquid region.

At leading order, the Stefan condition relates the propagation speed V to the temperature gradient:

$$V = \lambda. \tag{2.21}$$

Then the linearised problem for the perturbations reads

$$\nabla^2 \tilde{u} = 0 \qquad x < Vt, \tag{2.22a}$$

$$\tilde{u} - \lambda \xi = 0 \qquad x = Vt, \tag{2.22b}$$

$$-\frac{\partial \tilde{u}}{\partial x} = \frac{\partial \xi}{\partial t} \qquad x = Vt. \tag{2.22c}$$

Now we seek a wave-like separable solution with

$$\tilde{u}(x, y, t) = A\mathrm{e}^{\sigma t + \mathrm{i}ky + k(x - Vt)}, \qquad \xi(y, t) = B\mathrm{e}^{\sigma t + \mathrm{i}ky}, \tag{2.23}$$

where $k > 0$ is the wavenumber in the y-direction and σ is the linear growth rate. This ansatz is chosen to satisfy Laplace's equation identically and to ensure that the perturbations decay as $x \to -\infty$. The free boundary conditions lead to two linear equations for the constants A and B, namely

$$\begin{pmatrix} 1 & -\lambda \\ k & \sigma \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \mathbf{0}. \tag{2.24}$$

This system admits nontrivial solutions if and only if the determinant of the matrix on the left-hand side is zero, and this condition leads to

$$\sigma = -\lambda k = -Vk, \tag{2.25}$$

after using (2.21).

Assuming that V is positive, so that the solid phase is melting into a liquid, we infer that $\sigma < 0$ for all wavenumbers k, and hence the propagating free boundary is stable. However, in the opposite case where the liquid is freezing into a solid, so that $V < 0$, we see that $\sigma > 0$ for all k and hence the free boundary is unstable. This is perhaps not surprising since V can be negative only if λ is negative, which means that the liquid temperature is *below* the melting temperature in the liquid phase ahead of the free boundary. This situation is referred to as the liquid being *supercooled*.

If V is negative, equation (2.25) implies that the growth rate is unbounded as $k \to \infty$. Hence infinitesimal perturbations to the free boundary can grow arbitrarily quickly. Moreover, the most dangerous modes occur for large wavenumbers, i.e., small wavelengths. This behaviour is characteristic of the problem being *ill posed*, in the sense that the solution does not depend continuously on the data: an arbitrarily small perturbation of the initial conditions may cause an arbitrarily large change in the solution. Such behaviour is physically unacceptable, and such ill posed problems are also effectively impossible to solve numerically.

If some of the assumptions we have made are relaxed, i.e., if we include temperature variations in the solid phase or retain the terms proportional to St, then more complicated stability criteria are found. However, it is still generally the case that, depending on the temperature gradients imposed, the free boundary problem may be unstable and indeed ill posed. Moreover, it is a familiar experience that, while a solid typically melts smoothly (e.g. an ice cube in a fizzy drink), a freezing liquid often exhibits a highly irregular "dendritic" free boundary (e.g. the ice crystals that fill up your freezer), as shown in figure 2.3.

These observations suggest that it is reasonable for a freezing boundary to be unstable at least under some conditions, but it is still not acceptable for the problem to be ill posed. Some additional physics must become important to "regularize" the problem by suppressing arbitrarily high wavenumbers. For example, surface energy effects may be incorporated to

Figure 2.3: "Ice crystals on the box" by Brocken Inaglory. Licensed under CC BY-SA 3.0 via Wikimedia Commons —
`http://commons.wikimedia.org/wiki/File:Ice_crystals_on_the_box.jpg`

penalise high curvature variations in the free boundary. Another possibility is "kinetic undercooling", based on the idea that temperature need not be continuous if the free boundary evolves rapidly enough to be out of thermodynamic equilibrium. More sophisticated models that include these and other physical effects are able to predict instability to small but finite wavelength perturbations which develop into dendrite-like structures.

Rather than trying to resolve this complicated microstructure, an alternative approach is to use a homogenised model for the "mushy region" where liquid and solid phases coexist, as described below.

One-dimensional welding problem

Consider the one-dimensional welding problem shown schematically in figure 2.4. The electric current J (per unit area) through the plate causes a volumetric heating J^2/σ, where σ is the conductivity of the metal, so the heat equation is modified to

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) + \frac{J^2}{\sigma}. \tag{2.26}$$

For simplicity, we assume that the parameters ρ, c, k and σ are constant *and the same in both phases* (i.e., $K = \kappa = 1$ in the notation of (2.15) — this is easily generalized). We assume symmetry about the centre $x = 0$ of the metal plate, as indicated in figure 2.4. We also need a thermal boundary condition at the electrode $x = a$: for simplicity we suppose that this is held at constant ambient temperature $T_0 < T_{\mathrm{m}}$.

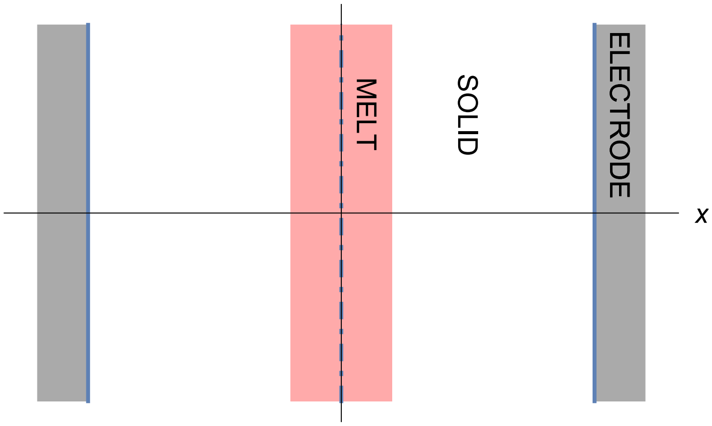

Figure 2.4: Schematic of a one-dimensional electric welding problem.

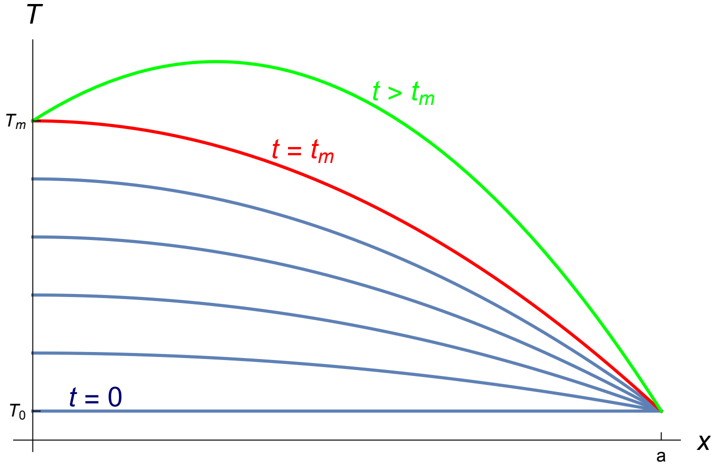

Figure 2.5: Schematic showing the anticipated evolution of the temperature profile in the one-dimensional welding problem.

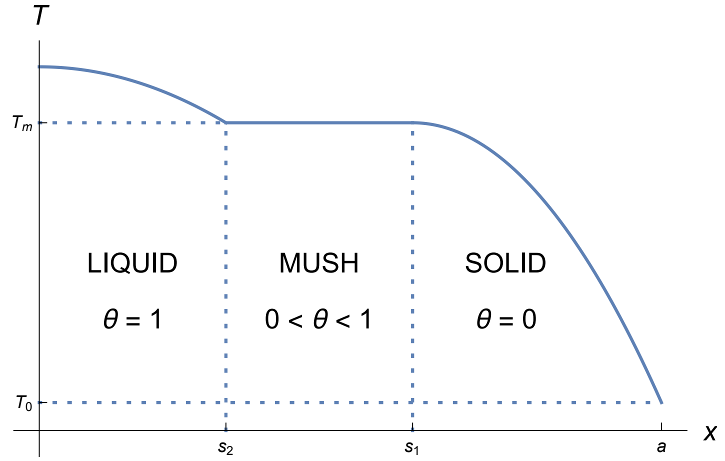

Figure 2.6: Schematic showing the anticipated temperature profile in the one-dimensional welding problem with a mushy region.

If the heating power J^2/σ is sufficiently large, then we expect the metal to melt in some neighbourhood of the centre $x = 0$ of the sample, as indicated in figure 2.4. We then expect to introduce a free boundary $x = s(t)$ and apply the Stefan conditions

$$T = T_{\mathrm{m}}, \qquad \left[k\frac{\partial T}{\partial x}\right]_-^+ = \rho L\frac{\mathrm{d}s}{\mathrm{d}t} \qquad \text{at } x = s(t). \tag{2.27}$$

However, by thinking about how the temperature profile must evolve, we can quickly see that something is wrong with this model.

As shown schematically in figure 2.5, the temperature must increase from its initially uniform profile, with a maximum at $x = 0$ where $\partial T/\partial x = 0$. Assuming the heat supplied is sufficiently high, the temperature at $x = 0$ eventually reaches the melting temperature T_{m} at some time $t = t_{\mathrm{m}}$, indicated as a red curve. Now, the temperature cannot immediately increase above T_{m} until enough additional energy has been supplied to overcome the latent heat required to melt the metal. Furthermore, the Stefan condition (2.27) implies that the free boundary cannot propagate away from the origin until $\partial T/\partial x > 0$ at $x = 0$. Hence for t slightly larger than t_{m}, the temperature profile must resemble the green curve in figure 2.5, which means that the metal in $x > 0$ is *superheated*: its temperature exceeds T_{m} even though it is still supposed to be solid. We might expect such a set-up to be catastrophically unstable, and indeed a linear stability calculation would confirm that the model is ill posed.

So, what must happen instead? In practice, it is observed that there is not a simple free boundary between pure liquid and pure solid phases. Instead, there is a "mushy region" in which both solid and liquid phases coexist, with the solid existing in a very fine dendritic crystalline structure as shown in figure 2.3. Rather than try to resolve this highly complicated structure, we construct a homogenised model that describes the net macroscopic behaviour of the mixture as a whole. The basic structure is shown schematically in figure 2.6: there are now two free boundaries $x = s_1(t)$ and $x = s_2(t)$, with solid material in $s_1 < x < a$, mush in $s_2 < x < s_1$ and liquid in $0 < x < s_2$. It just remains to construct a model for the mush.

The first observation is that, for both phases to coexist, the temperature must everywhere be close to the melting temperature, and to a first approximation we may set $T = T_{\mathrm{m}}$

everywhere in the mush. The energy source therefore does not serve to heat up the mixture but instead supplies the latent heat needed to melt the solid. The energy equation in the mush reads

$$\rho L \frac{\partial \theta}{\partial t} = \frac{J^2}{\sigma}, \tag{2.28}$$

where θ is the liquid fraction in the mixture: $\theta = 0$ in a pure solid and $\theta = 1$ in pure liquid. The condition for conservation of energy at each free boundary reads

$$\left[\rho L \theta \frac{\mathrm{d}s_j}{\mathrm{d}t} - k \frac{\partial T}{\partial x} \right]_-^+ = 0 \quad \text{at } s = s_j(t) \qquad (j = 1, 2). \tag{2.29}$$

Finally, we require one initial condition for the PDE (2.28), namely that θ is continuous across the advancing melting boundary $x = s_1(t)$ (so that the liquid fraction is zero as the mush first forms), i.e.

$$\theta = 0 \quad \text{at } x = s_1(t). \tag{2.30}$$

Note, though, that θ is not in general continuous at the mush-liquid boundary $x = s_2(t)$.

After suitable non-dimensionalization, the full equations and boundary conditions are

$$\begin{aligned}
\mathrm{St} \frac{\partial u}{\partial t} &= \frac{\partial^2 u}{\partial x^2} + q & 0 < x < 1, \quad t > 0, && \text{(2.31a)} \\
\frac{\partial u}{\partial x} &= 0 & x = 0, \quad t > 0, && \text{(2.31b)} \\
u &= -1 & x = 1, \quad t > 0, && \text{(2.31c)} \\
u &= -1 & 0 < x < 1, \quad t = 0, && \text{(2.31d)}
\end{aligned}$$

where q is the dimensionless heating power. If q is sufficiently large, then we have to introduce a mushy region $s_2(t) < x < s_1(t)$, as described above, with

$$\begin{aligned}
u = 0, \quad \frac{\partial \theta}{\partial t} &= q & s_2(t) < x < s_1(t), \quad t > 0, && \text{(2.31e)} \\
u = 0, \quad \left[\theta \frac{\mathrm{d}s_j}{\mathrm{d}t} + \frac{\partial u}{\partial x} \right] &= 0 & x = s_j(t), \quad t > 0. && \text{(2.31f)}
\end{aligned}$$

It may be shown that this modified free boundary problem is well posed. In general, numerical solution is required, and a very useful approach is to use the *enthalpy*, which measures the total internal energy in the material, including thermal energy and latent heat. However, the initial stages at least may be analysed analytically, and in the quasi-steady limit $\mathrm{St} \to 0$ the problem may be solved completely.

2.3 Codimension-two free boundary problems

Industrial problem: electrochemical painting

Metal objects (e.g. parts for cars or domestic appliances) are often coated using electrochemical painting. The object (“workpiece”) is immersed in an electrolyte solution, across which a potential difference V is imposed. This drives a current $\boldsymbol{j}$ of ions which attach themselves as a layer of paint on the workpiece. A simple example is depicted schematically in figure 2.7: here for simplicity the workpiece is assumed flat and parallel to the x-axis, and the painted region is the interval $x \in (-c, c)$. A model is needed to determine when (and if) the entire surface of the workpiece is covered in paint, and the thickness of the paint layer achieved.

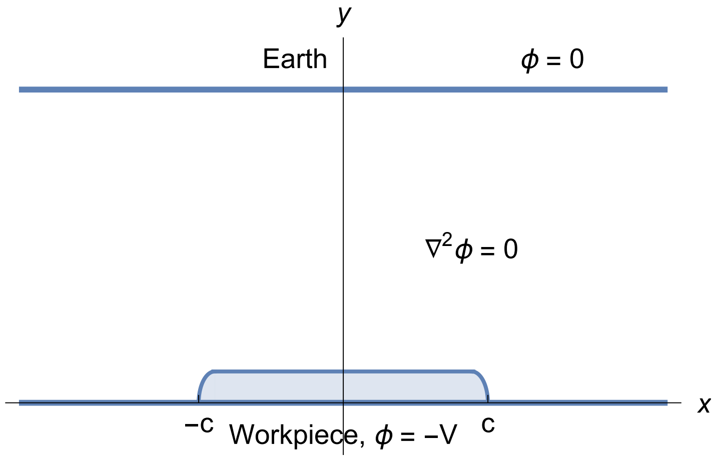

Figure 2.7: Schematic of a metal surface undergoing electrochemical painting.

Simple electrostatic problem

To derive a tractable model we make some simplifying assumptions. We assume that the concentration of ions in solution is sufficiently large that their depletion during the process is negligible, and we may therefore treat the concentration as a constant. The flux of ions in the solution due to the imposed electric field is then given by

$$\boldsymbol{j} = -\sigma \boldsymbol{\nabla}\phi, \tag{2.32}$$

where ϕ is the electric potential and σ is the conductivity (assumed constant). Conservation of charge then implies that $\boldsymbol{\nabla} \cdot \boldsymbol{j} = 0$ and hence that ϕ satisfies Laplace's equation. The imposed potential difference V prescribes $\phi = -V$ on the workpiece and $\phi = 0$ at the earthed outer surface.

Now, let the thickness of the paint layer (where it exists) be denoted by $h(x,t)$. The paint acts as a resistive layer with conductivity $\bar{\sigma}$ much lower than that of the solution. If the layer is thin, then it will act as a classical resistor with surface conductivity $\bar{\sigma}/h$. Hence we can relate the potential difference across the layer to the current across it by

$$\sigma\frac{\partial\phi}{\partial y} = \frac{\bar{\sigma}}{h}(V+\phi) \quad \text{at } y = h(x,t). \tag{2.33}$$

It is observed experimentally that, when the current is switched off, the paint dissolves back into solution at some rate d. The net rate at which the layer thickness increases (where it exists) is therefore given by

$$\frac{\partial h}{\partial t} = -d + \alpha\sigma\frac{\partial\phi}{\partial y} \quad \text{at } y = h(x,t), \tag{2.34}$$

where α is a constant of proportionality ($\alpha = V_{\mathrm{M}}/F$, where V_{M} is the molar volume of solid paint and F is Faraday's constant).

We normalize the problem as follows:

$$(x,y) = L\left(\tilde{x},\tilde{y}\right), \qquad \phi = -V + V\tilde{\phi} \qquad h = \epsilon L\,\tilde{h}, \qquad t = \frac{\epsilon L^2}{\alpha\sigma V}\,\tilde{t}, \tag{2.35}$$

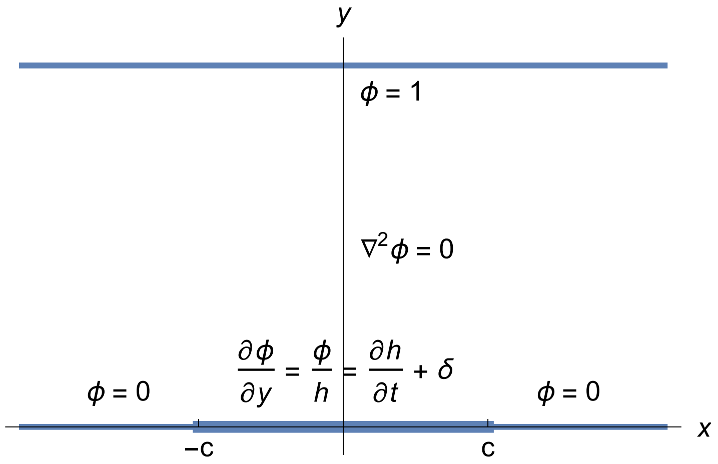

Figure 2.8: Schematic of a codimension-two free boundary problem for the electropainting process.

where L is a typical length scale for the workpiece and

$$\epsilon = \frac{\bar{\sigma}}{\sigma} \ll 1. \tag{2.36}$$

Then, with the tildes dropped, the boundary conditions (2.33) and (2.34) become

$$\frac{\partial\phi}{\partial y} = \frac{\phi}{h}, \quad \frac{\partial h}{\partial t} = \frac{\partial\phi}{\partial y} - \delta \quad \text{at } y = \epsilon h(x,t), \tag{2.37}$$

where

$$\delta = \frac{Ld}{\alpha\sigma V}. \tag{2.38}$$

Now, the smallness of ϵ implies that the thickness of the paint layer is small compared with the net size of the workpiece, as expected. By letting $\epsilon \to 0$, we can apply the boundary conditions (2.37) on the known surface of the workpiece rather than the unknown free boundary $y = \epsilon h(x,t)$. To justify this approximation, Taylor expand about $y = 0$ to get

$$\phi\big(x, \epsilon h, t\big) = \phi(x,0,t) + \epsilon h \frac{\partial\phi}{\partial y}(x,0,t) + O\left(\epsilon^2\right). \tag{2.39}$$

Hence as $\epsilon \to 0$, we can replace (2.37) by

$$\frac{\partial\phi}{\partial y} = \frac{\phi}{h}, \quad \frac{\partial h}{\partial t} = \frac{\partial\phi}{\partial y} - \delta \quad \text{at } y = 0. \tag{2.40}$$

This applies wherever the paint layer is present so that $h > 0$.

If there is a bare patch where $h = 0$, then since the resistive paint layer is no longer present, we instead impose

$$\phi = 0 \quad \text{at } y = 0. \tag{2.41}$$

This applies wherever $h = 0$ and $\partial\phi/\partial y \le \delta$, so that according to (2.40) it is not possible for the paint layer to grow.

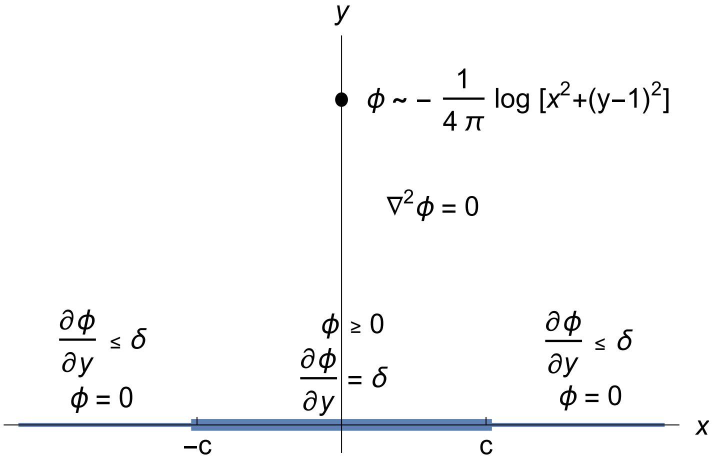

Figure 2.9: Schematic of a model codimension-two free boundary problem for the steady electropainting problem.

The resulting problem is as depicted in figure 2.8. This set-up is easily generalized to more complicated situations, for example where the workpiece and/or the earthed electrodes are not flat. This is not a classical free boundary problem since the geometry in which Laplace's equation is to be solved *is* specified in advance. However, the points where the painted layer begins and ends ($x = \pm c$ in our simple set-up), and the boundary conditions switch from Dirchlet to Robin boundary conditions, are *not* known in advance and must be found as part of the solution. In general we expect these points to vary with time as the painted region grows or shrinks. These points are the free boundaries in this problem. This is called a *codimension-two* free boundary problem, two being the codimension between the space in which the problem is posed (two dimensions) and the free boundaries (points, i.e., zero dimensions).

Steady model problem

Now we focus on a relatively simple concrete problem that is analytically tractable but not trivial. If the system has reached steady state, then the boundary condition on the painted region is just the Neumann condition

$$\frac{\partial\phi}{\partial y} = \delta \quad \text{at } y = 0. \tag{2.42}$$

The paint film thickness may then be recovered *a posteriori* by using

$$h(x) = \frac{\phi(x,0)}{\delta} \tag{2.43}$$

Since the thickness cannot be negative, it follows that $\phi \ge 0$ on the painted region.

Let us suppose that the earthed electrode is a single point $(x,y) = (0,1)$ in dimensionless coordinates. As illustrated in figure 2.9, this corresponds to a logarithmic singularity, with

$$\phi \sim -\frac{1}{2\pi}\log\big|(x,y)-(0,1)\big| = -\frac{1}{4\pi}\log\left(x^2+(y-1)^2\right) \quad \text{as } (x,y) \to (0,1), \tag{2.44}$$

where the strength of the source has been normalized to unity.

As a first step, it is helpful to subtract off the singular part of ϕ, along with an image singularity at $(x, y) = (0, -1)$, so that the boundary condition $\phi = 0$ on the unpainted workpiece $y = 0$, $|x| > c$ is preserved. We also note that $\phi = \delta y$ satisfies the boundary conditions on $y = 0$ exactly. We therefore set

$$\phi(x, y) = \delta y - \frac{1}{4\pi}\log\left(x^2 + (y-1)^2\right) + \frac{1}{4\pi}\log\left(x^2 + (y+1)^2\right) + \Phi(x, y). \tag{2.45}$$

Thus the new dependent variable Φ satisfies the problem

$$\begin{aligned}
&\nabla^2\Phi = 0 && y > 0, && (2.46a)\\
&\frac{\partial\Phi}{\partial y} \to -\delta && x^2 + y^2 \to \infty, && (2.46b)\\
\Phi = 0, \quad &\frac{\partial\Phi}{\partial y} \le -f(x) && y = 0,\ |x| > c, && (2.46c)\\
\Phi \ge 0, \quad &\frac{\partial\Phi}{\partial y} = -f(x) && y = 0,\ |x| < c, && (2.46d)
\end{aligned}$$

where

$$f(x) = \frac{1}{\pi\left(1 + x^2\right)}. \tag{2.47}$$

This is a *mixed boundary value problem*, and in general one expects the solution to have singularities at the points $(\pm c, 0)$ where the boundary conditions switch from Dirichlet to Neumann. In principle, the value of c can be determined as part of the solution by specifying how singular Φ is allowed to be: we require $\boldsymbol{\nabla}\Phi$ to be bounded at both free boundaries.

This problem can be solved in principle, for example by taking a Fourier transform in x, in terms of the function Φ at the surface of the workpiece, i.e.

$$\Phi_0(x) = \Phi(x, 0). \tag{2.48}$$

We have $\Phi_0(x) = 0$ for $|x| > c$ but otherwise Φ_0 is unknown as yet. We therefore find that

$$\frac{\partial\Phi}{\partial y} = \frac{1}{\pi}\int_{-c}^{c}\frac{(x-s)\Phi_0'(s)}{(x-s)^2 + y^2}\,\mathrm{d}s \tag{2.49}$$

for $y > 0$. Carefully letting $y \to 0$ and applying the boundary condition (2.46d), we therefore find that Φ_0 satisfies the singular integral equation

$$-f(x) = \frac{1}{\pi}⨍_{-c}^{c}\frac{\Phi_0'(s)}{x-s}\,\mathrm{d}s. \tag{2.50}$$

Here $⨍$ signifies that the principal value of this singular integral is taken, i.e.

$$⨍_{-c}^{c}\frac{\Phi_0(s)}{x-s}\,\mathrm{d}s = \lim_{\epsilon\to 0}\left(\int_{-c}^{x-\epsilon} + \int_{x+\epsilon}^{c}\right)\frac{\Phi_0(s)}{x-s}\,\mathrm{d}s. \tag{2.51}$$

We have to solve equation (2.50) for $\Phi_0(x)$, and find the value of c such that Φ is differentiable at $(\pm c, 0)$. The thickness of the painted layer is then recovered from

$$h(x) = \frac{\Phi_0(x)}{\delta}. \tag{2.52}$$

Solution of model problem

There are various techniques for tackling singular integral equations like (2.50), or equivalently mixed boundary value problems like (2.46). The most elegant approaches exploit complex variable theory. The first step is to recognise that, since Φ satisfies Laplace's equation, it may be written as the real part of a holomorphic function of $z = x + \mathrm{i}y$, i.e.

$$\Phi(x, y) + \mathrm{i}\Psi(x, y) = w(z), \tag{2.53}$$

where $w(z)$ is holomorphic in $\mathrm{Im}(z) > 0$. (The imaginary part Ψ is the *harmonic conjugate* to Φ; they are related through the Cauchy–Riemann equations.) Differentiation with respect to z gives

$$\frac{\partial \Phi}{\partial x} - \mathrm{i}\frac{\partial \Phi}{\partial y} = w'(z), \tag{2.54}$$

so our task is to find a function $w'(z)$ that is holomorphic in the upper half-plane and satisfies the conditions

$$\begin{aligned} w'(z) &\to \delta\mathrm{i} && z \to \infty, && (2.55\mathrm{a})\\ \mathrm{Re}\left[w'(z)\right] &= 0, && y = 0,\ |x| > c, && (2.55\mathrm{b})\\ \mathrm{Im}\left[w'(z)\right] &= f(x) && y = 0,\ |x| < c. && (2.55\mathrm{c}) \end{aligned}$$

The mixed character of the probem is reflected in the fact that we specify the imaginary part of w' on a segment of the boundary and the real part elsewhere. We can use a trick to transform this into a classical problem in which the real part is specified everywhere. Let

$$w'(z) = \sqrt{z^2 - c^2}\, W(z), \tag{2.56}$$

where $W(z)$ is holomorphic in the upper half plane. The square root function is defined as

$$\sqrt{z^2 - c^2} = \sqrt{z - c}\,\sqrt{z + c} = \sqrt{r_1 r_2}\, \mathrm{e}^{\mathrm{i}(\theta_1 + \theta_2)/2}, \tag{2.57}$$

where

$$r_1 = |z - c|, \qquad r_2 = |z + c|, \qquad \theta_1 = \arg(z - c), \qquad \theta_2 = \arg(z + c), \tag{2.58}$$

and the angles $\theta_{1,2}$ lie in the range $(-\pi, \pi)$ for z in the upper half plane. From this definition we see that $\sqrt{z^2 - c^2} \sim z$ as $z \to \infty$. Moreover, $\sqrt{z^2 - c^2}$ is real as $y \to 0$ with $|x| > c$ and imaginary as $y \to 0$ with $|x| < c$. Therefore the new function $W(z)$ satisfies a classical Dirichlet problem, with its real part specified everywhere on the boundary, namely

$$W(z) \sim \frac{\mathrm{i}\delta}{z} \qquad z \to \infty, \tag{2.59a}$$

$$\mathrm{Re}\left[W(z)\right] = \begin{cases} 0 & |x| > c, \\ \dfrac{f(x)}{\sqrt{c^2 - x^2}} & |x| < c \end{cases} \qquad y = 0. \tag{2.59b}$$

In principle this new problem (2.59) is now amenable to solution via classical techniques.

Before considering the solution, we make a few notes about the procedure carried out above. The first point is that mixed boundary value problems of the form (2.55) generally

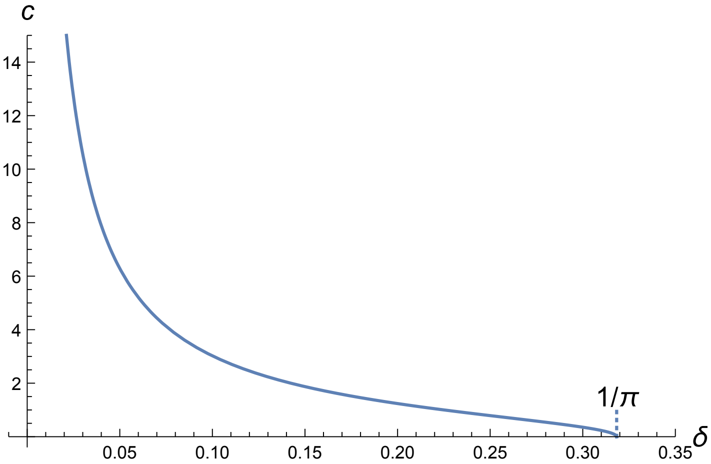

Figure 2.10: The relation between the half-length c of the painted region and the normalized dissolution current δ, given by equation (2.63).

can be tackled using the so-called *Plemelj formulae*: the decomposition employed in equation (2.56) is a shortcut that works in this particular case. Second, we should ask whether the decomposition (2.56) is unique, i.e., whether a different function could have been used instead of $\sqrt{z^2 - c^2}$ with the same property of being real on $y = 0$, $|x| > c$ and imaginary on $y = 0$, $|x| < c$? The answer is yes: any function of the form $(z - c)^{n+1/2}(z + c)^{m+1/2}$ would have worked, where m and n are any integers. The particular choice $n = m = 0$ was made here (with the benefit of hindsight) to ensure that $w'(z)$ is bounded as $z \to \pm c$ but does not grow too rapidly as $z \to \infty$.

Now, we can find the holomorphic function that satisfies the Dirichlet condition (2.59b) and decays as $z \to \infty$, by using Poisson's formula:

$$W(z) = \frac{1}{\pi \mathrm{i}} \int_{-c}^{c} \frac{f(t)\,\mathrm{d}t}{(t - z)\sqrt{c^2 - t^2}}. \tag{2.60}$$

Again this is really an application of the Plemelj formulae, but it could also be obtained by using a Green's function, for example; or one can easily just verify that (2.60) satisfies (2.59b) by taking the limit $y \to 0$. Taking the limit $z \to \infty$ in (2.60), we have

$$W(z) \sim \frac{\mathrm{i}K}{z} \quad \text{as } z \to \infty, \tag{2.61}$$

where

$$K = \frac{1}{\pi} \int_{-c}^{c} \frac{f(t)}{\sqrt{c^2 - t^2}}\,\mathrm{d}t = \frac{1}{\pi^2} \int_{-c}^{c} \frac{\mathrm{d}t}{(1 + t^2)\sqrt{c^2 - t^2}} = \frac{1}{\pi\sqrt{1 + c^2}}. \tag{2.62}$$

By comparing (2.61) with (2.59a), we obtain a relation between δ and c, namely

$$\delta = \frac{1}{\pi\sqrt{1 + c^2}} \qquad \text{and hence} \qquad c = \sqrt{\frac{1}{\delta^2\pi^2} - 1}. \tag{2.63}$$

The relation between c and δ is plotted in figure 2.10. This shows how the size of the painted region depends on δ. Recall from (2.38) that δ measures the dissolution current relative to the applied voltage. Small δ corresponds to a relatively high voltage and leads to a large portion of the surface being covered. As δ increases, c decreases and reaches zero at a finite critical value $\delta_{\mathrm{c}} = 1/\pi$. If $\delta > 1/\pi$, then the applied voltage is too weak to overcome the dissolution current, and none of the surface gets painted. In this case, the Dirichlet condition $\phi = 0$ is satisfied everywhere on $y = 0$, and the solution is

$$\phi(x, y) = \frac{1}{4\pi} \log\left(\frac{x^2 + (y+1)^2}{x^2 + (y-1)^2}\right), \tag{2.64}$$

with $\partial\phi/\partial y < \delta$ everywhere on $y = 0$.

To calculate the potential when $\delta < 1/\pi$, we need to perform the integral in equation (2.60). This can be done using contour integration, resulting in

$$W(z) = \frac{1}{\pi \mathrm{i}} \int_{-c}^{c} \frac{f(t)\,\mathrm{d}t}{(t - z)\sqrt{c^2 - t^2}} = \frac{\mathrm{i}}{\pi\left(1 + z^2\right)\sqrt{z^2 - c^2}} + \frac{\mathrm{i}z}{\pi\left(1 + z^2\right)\sqrt{1 + c^2}}. \tag{2.65}$$

We can easily see that this is consistent with the previous results (2.61) and (2.62) in the limit $z \to \infty$. By substitution into (2.56), we therefore have

$$w'(z) = \frac{\mathrm{i}}{\pi\left(1 + z^2\right)} + \frac{\mathrm{i}z\sqrt{z^2 - c^2}}{\pi\left(1 + z^2\right)\sqrt{1 + c^2}}. \tag{2.66}$$

To calculate the thickness of the painted layer using equation (2.52), we need to evaluate $\Phi(0, x)$ for $|x| < c$. Letting $y \searrow 0$ in (2.66) with $x \in (-c, c)$, we get

$$\frac{\partial\Phi}{\partial x} - \mathrm{i}\frac{\partial\Phi}{\partial y} = \frac{\mathrm{i}}{\pi\left(1 + x^2\right)} - \frac{x\sqrt{c^2 - x^2}}{\pi\left(1 + x^2\right)\sqrt{1 + c^2}} \quad \text{on } y = 0, \quad -c < x < c. \tag{2.67}$$

Thus the potential at the painted surface $\Phi_0(x) = \Phi(x, 0)$ satisfies

$$\frac{\mathrm{d}\Phi_0}{\mathrm{d}x} = \frac{-1}{\pi\sqrt{1 + c^2}} \, \frac{x\sqrt{c^2 - x^2}}{1 + x^2}, \tag{2.68}$$

and one further integration gives

$$\Phi_0(x) = \frac{1}{\pi}\left[\tanh^{-1}\left(\sqrt{\frac{c^2 - x^2}{1 + c^2}}\right) - \sqrt{\frac{c^2 - x^2}{1 + c^2}}\right]. \tag{2.69}$$

The resulting painted film thickness profile $h(x) = \Phi_0(x)/\delta$ is plotted in figure 2.11 for various values of δ between 0 and $1/\pi$. As expected, small values of δ produce a wide, thick film. As δ increases, the film gets thinner and shorter, and it disappears as δ approaches the critical value $1/\pi \approx 0.318$. It is apparent that $h(x)$ has zero slope as $x \to c$; local expansion of (2.69) gives

$$\Phi_0(x) \sim \frac{1}{3\pi}\left(\frac{c^2 - x^2}{1 + c^2}\right)^{3/2} \quad \text{as } x \to \pm c. \tag{2.70}$$

This is a consequence of our insisting that $\boldsymbol{\nabla}\Phi$ be finite at the two end points $(\pm c, 0)$, and thereby selecting the appropriate value of c.

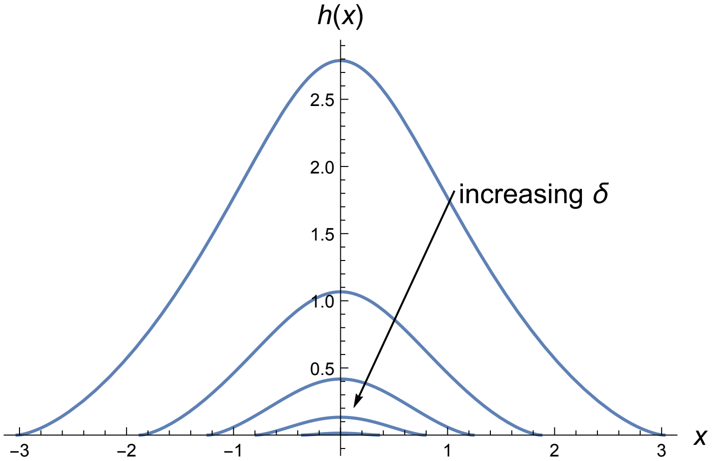

Figure 2.11: The painted film thickness profile $h(x)$ given by equation (2.69) for values of the normalized dissolution current $\delta = 0.1,\ 0.15,\ 0.2,\ 0.25,\ 0.3$.