So far, we have looked at some of the fundamentals associated with solidification of pure melts. When we try to solidify a solution of two or more components, salt and water, for example, the character of the solidification changes considerably. In particular, the presence of salt can depress the temperature at which ice and salt water can coexist in thermal equilibrium. This has an important consequence for the growth of sea ice: unless there is some other mechanism for the transport of the salt field, such as convection, the growth of the ice is limited by the rate at which excess salt can diffuse away from the interface. Finally, we will discuss the morphological instability in two-component melts. We shall see that the solute field is destabilizing and can give rise to morphological instability even when the liquid phase is not initially supercooled.

1 Two-component melts

1.1 A simple demonstration

We shall begin with a simple demonstration. Crushed ice at 0°C is placed in a cup with a thermometer. We add a handful of salt at room temperature and stir briskly. The ice begins to melt, but what happens to the temperature?

We notice that there is some melt water in the cup, which helps bring the ice and salt into contact, and see a fairly rapid decrease in the temperature measured by the thermometer: after a few minutes, it reads almost −10°C. What’s happening here is not melting. Rather, we are observing dissolution of the pure ice into the mixture of salt and water. In this lecture, we will attempt to make more explicit the distinction between melting and dissolution.

1.2 Equilibrium phase diagrams

In Figure 1, we show the equilibrium phase diagram for a simple 2-component mixture, or binary melt – in this case, salt and water. The equilibrium state of a given mixture of salt and water at temperature $T$ and composition $C$ (i.e., concentration of salt) and at constant pressure can be represented on this diagram by the point $(T, C)$. The phase diagram is divided into regions of different phase; this diagram is “simple” in the sense that there are only two possible solid phases: pure ice, or solid salt. In Figure 1 these lie along the vertical axes at 0% and 100% concentration respectively. Apart from these two solid phases, we can
also form a liquid solution of the two end members (i.e., salt or water), or some liquid/solid mixture of the two substances. Other materials have more complicated solid phases and necessarily more complicated phase diagrams, which we will examine briefly later.

The curved line in Figure 1 is the liquidus, representing the temperature at which a binary melt of a given composition $C$ can exist in equilibrium in both the liquid and solid phase. For 0% salt concentration, the liquidus temperature is simply the melting point of ice { 0°C { while for 100% salt it is 801°C.

When we contaminate pure water at 0°C with a small amount of salt, the equilibrium freezing temperature is lowered. Thus, when we added a small amount of salt to the ice in our experiment, we saw that we still had liquid even at temperatures as low as $10°C$.

Equivalently, one could start with pure molten salt at 801°C and contaminate it with a small amount of water to lower the melting point. The two liquidus curves meet at a point $(T_E, C_E)$, called the eutectic: this is the minimum temperature at which solid and liquid saltwater can coexist in thermodynamic equilibrium$^1$.

If we slowly change the temperature or composition, the mixture will trace a trajectory on the phase diagram, as shown in Figure 1 for the case of seawater. We start by cooling seawater to $2°C$ where it reaches the liquidus curve $T_L(C)$ and starts to freeze. Below this temperature, we start to form pure solid ice in equilibrium with seawater of higher concentration. As more and more solid ice is formed, less water is available and so the salt concentration increases steadily. We can invert the liquidus curve $T = T_L(C)$ to find the

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$^1$According to one popular story, German physicist Gabriel Fahrenheit (1686-1736) chose the triple eutectic temperature of water, salt and ammonium chloride, being the lowest temperature he could achieve in his laboratory, as the zero of his eponymous scale. Anders Celsius (1701-1744) chose 100°C to correspond with the boiling point of water at sea level; Fahrenheit likewise chose a reliable, easily reproducible, steady temperature for 100°F - the anal temperature of his horse. It should be noted, however, that wikipedia.org lists no less than six competing versions of the same story, so at the risk of punning, one should be advised to take such apocryphal tales with a pinch of salt.
composition of the remaining liquid: $C = C_L(T)$.

It is worthwhile to extend the simple phase diagram for salt and water to one more typical of other binary melts, as shown in Figure 2. In addition to the liquidus, there is a solidus further subdividing the phase diagram. There are now four distinct phases, which we describe below.

Region I is a liquid solution of the two end members.

In region II, the mixture is in a solid solution, where the end members are mixed on the lattice scale. An example of this is the silicate compound olivine, $(\text{Fe},\text{Mg})_2\text{SiO}_4$, although the phase diagram is quite different from the one shown in Figure 2. Iron and magnesium sit fairly equally in the lattice sites and will occur in different proportions depending upon the temperature. In contrast, salt and water do not form a solid solution, and will exist in the solid phase only as pure substances, at least as far as we are concerned in this course.

In region III, the solid solution and the liquid phase coexist in equilibrium.

Finally, in region IV, we have a mixture of crystals of the two end members: i.e., pure ice coexisting with pure salt crystals. In addition, there are regions of the equilibrium phase diagram mirroring region III, where pure crystals of one end members coexist with a solid solution of both end members. The exact location in the equilibrium phase diagram of the transition to this region, indicated in Figure 2 by a dashed line, is difficult to measure experimentally, because the compositional relaxation times below the eutectic are on the order of geological timescales. We ignore such detailed structure in our analysis.

Thus, the equilibrium phase diagram can tell us a great deal about what proportion of a mixture is in what phase, and what can coexist in equilibrium. However, it cannot tell us anything about the geometry of the solid phase formed; whether the ice forms in layers, or a slurry of ice crystals and salt water, or in the form of a mushy layer of dendritic ice crystals separated by interstitial seawater, as we shall examine in the next lecture. The microscopic details of the distribution of the phases depends strongly on how you lower the
temperature; however, the ratio of the phases will not depend on the history of the mixture.

1.3 A few approximations

Before we conclude this section, let us introduce some terminology and a few approximations. Firstly, we shall assume (when necessary) that the liquidus can be approximated by a straight line

\[ T_L \approx T_m - mC \]  \hspace{1cm} (1)

and that the solidus concentration is

\[ C_S (T) \approx k_D C_L (T) \]  \hspace{1cm} (2)

The parameter \( k_D \) is called the distribution coefficient, and is approximately zero for a salt and water solution. Thus we will assume that the solution will form only pure crystals of salt or ice.

2 Solidification of sea ice

2.1 The Stefan problem for a salt water solution

Let us now revisit the Stefan problem\(^2\); this time, however, we consider the case of salt water in contact with a boundary at a temperature below the liquidus temperature of the solution, as depicted in Figure 3.

We denote by \( T_i \) and \( C_i \) respectively the interfacial temperature and composition of the salt water, to be determined. We further demand that the ice and the salt water at the interface are in thermodynamic equilibrium so that \( T_i \) is the liquidus temperature and

\[ T_i = T_L (C_i). \]  \hspace{1cm} (3)

This is in contrast to the Stefan problem where the interfacial temperature was simply the melting temperature of pure ice \( T_m \). Here, however, the temperature at which the salt water freezes is set by the interfacial concentration of salt, and we shall see that the rate at which the interface advances is limited by the rate at which we can remove excess salt from the region near the interface.

The composition of salt inside the ice will be zero, as discussed above; however, we shall denote it by \( C_S \) to be a little more general. The far field temperature and composition of the sea water are \( T_\infty \) and \( C_0 \) respectively. The boundary temperature \( T_B \) will be below the liquidus temperature of the undisturbed solute field: \( T_B < T_L (C_0) \).

The equations to be solved are the diffusion equation in the ice and the sea water

\[ \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \] \hspace{1cm} in \( x < a \) and \( x > a \) \hspace{1cm} (4)

\(^2\)Note that in this treatment, we will neglect the effects of both kinetics and surface energy. The latter case would not arise anyway, as we are dealing only with a planar interface.
Figure 3: Freezing of salt water.

where, for simplicity, the thermal diffusivity $\kappa$ is assumed to be the same in both solid and liquid. In addition, we must solve for the salt field in the liquid region

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{in } x > a. \tag{5}$$

As the composition in the solid region is constant there will be no diffusion of salt there. The ratio of the solute diffusivity to the thermal diffusivity for seawater is of the order $10^{-2}$ and will play the role of a small parameter in our analysis.

In addition to the boundary and interfacial conditions, we have, as before, the Stefan condition for the interfacial heat flux:

$$\rho L \dot{a} = k \left( \frac{\partial T}{\partial x} \right)_{a-} - k \left( \frac{\partial T}{\partial x} \right)_{a+} \tag{6}$$

The final equation in this problem comes from the conservation of solute. The total quantity of salt must be conserved, so that the area under the composition curve must be constant:

$$C_s a + \int_{a(t)}^{\infty} C(x, t) dx = \text{const.} \tag{7}$$

The time derivative of this equation is

$$C_s \dot{a} - C_i \dot{a} + \int_{a}^{\infty} \frac{\partial C}{\partial t} dx = 0 \tag{8}$$

which, from the solute diffusion equation (5) becomes
\[(C_s - C_i) \dot{a} + \int_a^\infty \mathcal{D} \frac{\partial^2 C}{\partial x^2} \, dx = 0 \]  \hspace{1cm} (9)

and finally,

\[(C_i - C_s) \dot{a} = -\mathcal{D} \frac{\partial C}{\partial x} \bigg|_{x=a_i} \]  \hspace{1cm} (10)

Equation (10) has formally the same structure as the Stefan condition: instead of interfacial heat flux balancing the difference in heat content (enthalpy), however, equation (10) represents the balance of the difference in salt concentration with the flux of salt across the interface.

The solutions to the thermal diffusion equation (4) in the solid and liquid regions are, respectively,

\[T = T_B + (T_i - T_B) \frac{\text{erf}(\eta)}{\text{erf}\left(\frac{a}{2\sqrt{\kappa t}}\right)} \quad \text{in } x < a \]  \hspace{1cm} (11)

\[T = T_\infty + (T_i - T_\infty) \frac{\text{erfc}(\eta)}{\text{erfc}\left(\frac{a}{2\sqrt{\kappa t}}\right)} \quad \text{in } x > a \]  \hspace{1cm} (12)

Equations (11) and (12) are similarity solutions in the dimensionless variable

\[\eta = \frac{x}{2\sqrt{\kappa t}} \]  \hspace{1cm} (13)

A dimensionless interfacial position is \(\mu\), which is defined by

\[a = 2\mu\sqrt{\mathcal{D}t} \]  \hspace{1cm} (14)

where, in contrast to our previous analysis, \(a(t)\) scales with the solute diffusivity \(\mathcal{D}\) rather than the thermal diffusivity \(\kappa\). The dimensionless parameter \(\mu\) remains to be determined. We shall show, \textit{a posteriori}, that \(\mu\) is \(O(1)\). Had we chosen \(a(t)\) to scale with \(\kappa\) instead, we would find \(\mu\) to be \(O(\epsilon^{-1})\), where,

\[\epsilon = \sqrt{\frac{\mathcal{D}}{\kappa}} \]  \hspace{1cm} (15)

justifying our choice of the \(\mathcal{D}\) in equation (14) rather than \(\kappa\).

The solute diffusion equation (5) and boundary conditions yield the solution

\[C = C_0 + (C_i - C_0) \frac{\text{erfc}(\epsilon\eta)}{\text{erfc}(\epsilon\alpha)} \quad \text{in } x > a \]  \hspace{1cm} (16)

where \(\epsilon\) appears in the arguments because, in the case of the solute, it is \(\mathcal{D}\) rather than \(\kappa\) that should appear in the definitions of the dimensionless variable \(\mu\) in (14).

In addition to the parameter \(\mu\), the interfacial temperature \(T_i\) and interfacial concentration \(C_i\) will be determined using the Stefan condition (6), the solute conservation equation.
(10) and the liquidus relation (3). Substituting (11), (12) and (14) into the Stefan condition yields

$$\frac{L}{c_p} = \frac{T_i - T_B}{G(\epsilon \mu)} - \frac{T_\infty - T_i}{F(\epsilon \mu)}$$  \hspace{1cm} (17)

where,

$$G(z) = \sqrt{\pi} e^{z^2} \text{erf} z$$  \hspace{1cm} (18)

and

$$F(z) = \sqrt{\pi} e^{z^2} \text{erfc} z$$  \hspace{1cm} (19)

Similarly, the solute conservation equation (10) becomes

$$C_i - C_s = \frac{C_i - C_0}{F(\mu)}$$  \hspace{1cm} (20)

For salt water, $\epsilon$ is reasonably small, so let us examine the case of $\epsilon \to 0$. The functions $G(z)$ and $F(z)$ have the asymptotic behaviour

$$G(z) \approx 2z^2 \quad \text{as} \quad z \to 0$$  \hspace{1cm} (21)

$$F(z) \approx \sqrt{\pi} z \quad \text{as} \quad z \to 0.$$  \hspace{1cm} (22)

Thus, for small $\epsilon$, the three terms in the Stefan condition (17) are of order $1 : \epsilon^{-2} : \epsilon^{-1}$ and so, to lowest order, $T_i = T_B + O(\epsilon)$. Inverting the liquidus relation (3) now gives us the interfacial concentration to lowest order: $C_i = C_B + O(\epsilon)$, where $C_B = C_L(T_B)$ is the liquidus concentration associated with the temperature of the boundary. The solute conservation equation (20) then gives

$$F(\mu) \approx \frac{C_B - C_0}{C_B - C_S} \equiv C^{-1}$$  \hspace{1cm} (23)

As shown in Figure 4, the parameter $C$ is always strictly greater than or equal to one, with equality only for a pure melt. Thus, unlike the problem of a crystal growing into a supercooled melt, where we saw that for Stefan numbers of less than one there was no similarity solution, equation (23) always has a solution.

Furthermore, equation (23) implies that $\mu = O(1)$, justifying our choice of the solute diffusivity $D$ in (14) rather than the thermal diffusivity $\kappa$. Thus, the rate of advance of the planar interface is limited by the rate at which we can remove excess solute. Adjacent to the interface is a boundary layer of thickness $O\left(\sqrt{D\tau}\right)$, as shown in Figure 5. In fact, seawater does not behave like this because convection will also act to remove excess solute, which we have neglected here.
Figure 4: Proof that \( C \) is greater than or equal to unity. \( C \) is defined as the ratio of \( C_B - C_S \) to \( C_B - C_0 \). \( C_0 \) is the far-field composition and lies above the solid composition \( C_S \). \( C_B \) is the composition at the boundary and, by assumption, lies on the liquidus curve. As ice solidifies it leaves behind a residual of higher composition, so that \( C_B \) must be greater than that of the solution far from the boundary, \( C_0 \). Thus, the ordering of \( C_s \), \( C_0 \) and \( C_B \) is as shown in the figure, and \( C \) is necessarily greater than or equal to unity.

Figure 5: Comparison of the actual temperature field and the liquidus temperature associated with the compositional field. In the region where the \( T_L(C) > T \), the liquid is constitutionally supercooled.


2.2 Constitutional supercooling

Because the salt field and the temperature field have different scales of relaxation, there exists the possibility that, beside the interface, the actual temperature is below the local liquidus temperature. Thus the liquid is supercooled relative to its freezing temperature. The critical condition for such constitutional supercooling is that the liquidus temperature increase more rapidly than the actual temperature as we move away from the interface:

\[
\left( \frac{\partial T}{\partial x} \right)_{a_+} + \left( \frac{\partial T_L}{\partial x} \right)_{a_+} < 0.
\]

(24)

Approximating the liquidus by a straight line \( T_L(C) \approx T_m - mC \) and using our solutions for the temperature field and salt field in the liquid (12,16) we find that

\[
\frac{\left( \frac{\partial T}{\partial x} \right)_{a_+}}{\left( \frac{\partial T_L}{\partial x} \right)_{a_+}} = \frac{T_\infty - T_i}{(C_i - C_0) m} \epsilon^2 \frac{F(\mu)}{F(\epsilon \mu)}.
\]

(25)

From the asymptotic behaviour of \( F(z) \) for small \( z \) (19), we can see that the right-hand side of (25) is typically \( O(\epsilon) \). Thus, generically, the critical condition (24) is satisfied, and the liquid in the boundary layer is constitutionally supercooled.

Equation (25) can be solved to find the critical curve for constitutional supercooling on the equilibrium phase diagram, as depicted in Figure 6. Notice that the region of constitutional supercooling sits very close to the liquidus (for small \( \epsilon \)), so that we do not have to lower the temperature much below the liquidus temperature for constitutional supercooling to be prevalent. Note also that it is possible to avoid constitutional supercooling in a region close to 0% composition. This is of relevance to the semiconductor industry, where
constitutional supercooling is undesirable as it can give rise to morphological instability of a semiconductor crystal.

Finally, we show in Figure 7 how the temperature and composition change as we move from the boundary at \( x = 0 \), through the interface at \( x = a(t) \), to the far-field position at \( x \to \infty \). Within the ice \((0 < x < a_-)\), the temperature changes smoothly while the composition is identically zero. As we move across the boundary, the composition and temperature change discontinuously to the liquidus curve at \((C_i, T_i)\). From the interface, the two fields change differently until they reach their far-field values. Because the thermal and compositional diffusivities are different, the solute field changes more rapidly than the thermal field, and so the \((C, T)\)-curve dips below the liquidus, indicating constitutional supercooling.

2.3 Morphological instability of sea-ice growth

As we have already seen in this lecture series, ice growing into a supercooled melt is unconditionally unstable to small perturbations of the interface. When the liquid is constitutionally supercooled, the morphological instability takes on some new characteristics, which we discuss here in broad terms.

1. As in the case of the Stefan problem, the thermal field has a stabilizing influence on the interface (Figure 8a). Isotherms are compressed near peaks in the interface, enhancing the heat flux at those points, and rarefied near troughs, suppressing the heat flux. The heat flux inhibits the growth of ice at the peaks, while reinforcing it at the troughs, stabilizing the interface.

2. The compositional field, which was not present in our original Stefan problem, is destabilizing (Figure 8b). Like isotherms, surfaces of constant concentration are compressed near peaks, enhancing the flux of solute away from the interface. Thus, the

Figure 7: Temperature and compositional field on the equilibrium phase diagram.
ice can grow more quickly at peaks because the solute, which inhibits growth, can diffuse away more quickly, leading to instability.

3. As we saw in the problem of crystal growth into a supercooled liquid, surface energy is stabilizing (Figure 8c) A divergent normal on a curved interface lowers the equilibrium temperature near peaks and raises it at troughs, giving rise to a heat flux from the troughs to the peaks. As in the case of the thermal field, this stabilizes the interface.

These three mechanisms operate on three different lengthscales: in decreasing order they are the thermal diffusion lengthscale, the compositional diffusion lengthscale, and the capillary lengthscale. Thus, the interface is conditionally unstable: the interface may be unstable, marginally stable, or completely unstable, depending upon the precise lengthscales involved.

The condition for instability can be translated into a critical solidification rate, as shown in the neutral stability curve in Figure 9. Likewise, we can plot the critical solidification rate $V_C$ as a function of the initial composition of the melt $C_0$(Figure 10). For a given value of $C_0$, the interface is stable for sufficiently low solidification rates (typically around $1 \mu \text{ms}^{-1}$), but as we increase the solidification rate, the interface can go unstable. If we

Figure 8: Mechanisms contributing to the morphological instability in sea ice.
increase the solidification rate more, to say 1ms⁻¹, the interface can be stable again. Such rapid solidification is generally not of interest in ice studies, but is relevant to spot welding.

Student Problem

Consider a lump of sea ice floating in the ocean. Both the ice and the sea water are at uniform temperature $T_0 = -2^\circ C$, say, such that, $T_0$ is greater than the liquidus temperature of the far field concentration $C_0$. There is no gravity, so convection does not play a role. What happens, and how quickly?

Solution:
By solving the diffusion equation for the concentration field, we get

$$C = C_0 + (C_i - C_0) \frac{\text{erfc}(x/2\sqrt{Dt})}{\text{erfc}(a/2\sqrt{Dt})} \quad (x > a),$$

(26)
where $D$ is the diffusion coefficient of the concentration field. On the other hand, we have the concentration conservation:

$$-C_i \dot{a} = D \frac{\partial C}{\partial x} \bigg|_{a=0}$$  \hspace{2cm} (27)

Therefore,

$$\dot{a} = \frac{C_i - C_0}{C_i} \sqrt{\frac{D}{\pi t}} \text{erfc} \left( \frac{a}{2\sqrt{Dt}} \right) e^{-a^2/4Dt}$$  \hspace{2cm} (28)

Because $C_0 > C_i$, $\dot{a} < 0$: the ice is dissolving. Because of the absorption of the latent heat, the system cannot be isothermal: the temperature is depressed at the phase boundary.