

Chapter 1

Fick's Laws and Macroscopic Diffusion

1.1 Introduction

In the first part of this course we will discuss diffusion, which is the fundamental process for atomic transport in solid state transformations and reactions. We start with a mathematical description of diffusion due to a concentration gradient. We see that random atomic jumps act to smooth out spatially varying concentrations, with an atomic flux which is proportional to the concentration gradient. Later in the course we show that this behavior is a special case, and that, more generally, the atomic flux will be proportional to a gradient in chemical potential.

1.2 Fick's Laws

1.2.1 Fick's First Law

We first examine a simple one-dimensional model of diffusion. We consider diffusion of a trace amount of an impurity (or tracer) in a single-phase alloy. If the planer density of impurities at a position z is given by $\sigma(z)$ (measured in atoms/cm²), and if the spacing between adjacent planes is Δz , then the volume concentration of impurities $c(z)$ is given by:

$$c(z) = \frac{\sigma(z)}{\Delta z}$$

Further, we assume that we have one-dimensional random nearest neighbor jumps, and the diffusing atoms are chemically identical to, but distinguishable from the host atoms. This is the case for radioactive isotope tracers, for example. We define J_+ to be the flux of atoms to the right from the plane at z to the one at $z + \Delta z$. This is given by:

$$J_+ = \frac{1}{2}\Gamma\sigma(z)$$

where Γ is the mean jump frequency, and the factor of $1/2$ accounts for the jumps being able to go in either the plus or minus z direction. We can also define J_- as the flux of atoms to the left from the plane at $z + \Delta z$ to the one at z , and we find:

$$J_- = \frac{1}{2}\Gamma\sigma(z + \Delta z)$$

If we assume that Γ is not a function of concentration, then the net flux J is given by:

$$\begin{aligned} J &= J_+ - J_- \\ &= -\frac{1}{2}\Gamma [\sigma(z + \Delta z) - \sigma(z)] \\ &= -\frac{1}{2}\Gamma\Delta z [c(z + \Delta z) - c(z)] \\ &= -\frac{1}{2}\Gamma (\Delta z)^2 \frac{c(z + \Delta z) - c(z)}{\Delta z} \\ &\approx -\frac{1}{2}\Gamma (\Delta z)^2 \frac{\partial c}{\partial z} \\ &= -D \frac{\partial c}{\partial z} \end{aligned} \tag{1.1}$$

where in the last step we have assigned:

$$D = \frac{1}{2}\Gamma (\Delta z)^2$$

The quantity D is known as the diffusivity, and for the three-dimensional case we find:

$$D = \frac{1}{6}\Gamma (\Delta z)^2$$

Equation 1.1 which relates the concentration gradient to the flux is known as Fick's first law. As we go into this course, we will find that Fick's first

law does not always hold, but it is in fact a special case of the more general statement that a flux will be driven by a gradient in chemical potential. In many cases, the gradient in chemical potential is proportional to the gradient in concentration.

Let's discuss units. In the cgs system, the various quantities have the units:

$$J \left(\frac{\text{atoms}}{\text{cm}^2\text{s}} \right) = -D \left(\frac{\text{cm}^2}{\text{s}} \right) \frac{\partial c}{\partial z} \left(\frac{\text{atoms}}{\text{cm}^4} \right)$$

Actually, the flux is a vector quantity in that you might want to know the direction as well as magnitude of the atomic flow. Hence, Fick's first law can be written as a vector equation:

$$\mathbf{J} = -D\nabla c$$

where ∇ is the gradient operator.

1.2.2 The Conservation Equation

In practice, atomic fluxes are often a difficult quantity to measure. In solids, it is more typical to measure concentration profile changes which result from thermal treatment. Hence it is helpful to have an expression to describe how a flux will change a concentration profile. Consider the situation in Fig. 1.1, where we have a bar with concentration profile $c(z)$, giving rise to flux $J(z) = -D\partial c/\partial z$. We consider the volume element $A\Delta z$ where A is the cross section area. If there is curvature in $c(z)$ then the fluxes at z and $z + \Delta z$ are not equal. We will have a flux into our volume element given by $J(z)$ and a flux going out of $J(z + \Delta z)$. Thus the rate of change in concentration in the volume element due to fluxes is:

$$\frac{\partial c}{\partial t} = \frac{J(z) - J(z + \Delta z)}{\Delta z}$$

so in the limit of small Δz we have

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial z}$$

In three-dimensions the vectorial relationship is:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} \tag{1.2}$$

where the quantity $\nabla \cdot \mathbf{J}$ is known as the divergence of \mathbf{J} , and where now the flux is represented by a vector \mathbf{J} which contains information on the direction and magnitude of the atomic flux.

Equation 1.2 is known as the conservation equation, and it holds if the species we are considering is neither being created or destroyed. If the species is not conserved, then we must add a source term to Eqn. 1.2. For example, we are sometimes interested in the diffusion of vacancies which can be created or destroyed at a surface or interior defect. If $p(\mathbf{r}, t)$ represents the rate of production of the species of interest as a function of position and time then the conservation equation becomes:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} + p(\mathbf{r}, t)$$

It is important to recognize that the conservation equation will hold even when Fick's first law does not.

1.2.3 Fick's Second Law

If we combine Fick's first law

$$\mathbf{J} = -D\nabla c$$

with the conservation equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}$$

we find:

$$\frac{\partial c}{\partial t} = \nabla \cdot D\nabla c \quad (1.3)$$

Equation 1.3 is known as Fick's second law. We will frequently consider the situation where the diffusivity D is independent of concentration, and hence position, so that Fick's second law becomes:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \quad (1.4)$$

where ∇^2 is known as the Laplacian operator. In a Cartesian coordinate system the Laplacian is:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

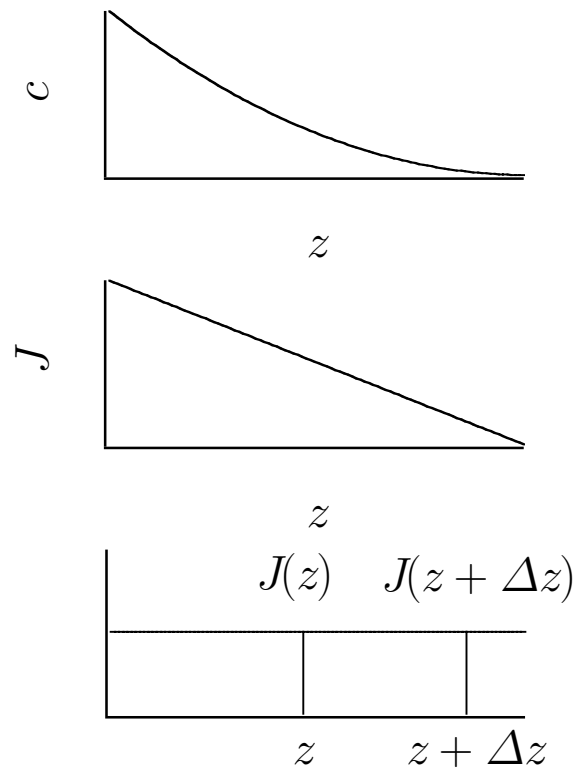


Figure 1.1: Schematic of concentration and flux as a function of position near a volume element.

The form of the Laplacian and other vector operators for different coordinate systems are summarized in a handout from MSE 205.

Equation 1.4 is a partial differential equation which is second order in the spatial coordinate and first order in time. Hence a unique solution will be characterized by a statement of the initial state of the system and two boundary conditions.

1.2.4 Cylindrical Example Using Fick's First Law

For the first example we consider diffusion through a pipe. This is a common experimental situation for determining diffusion rate and its compositional dependence. We have a pipe of inner radius r_1 and outer radius r_2 (Fig. 1.2). We somehow conspire to maintain a constant concentration c_1 on the inner pipe wall at $r = r_1$. This can be done, for example, by maintaining a constant chemical potential in the gas inside of the pipe. We also assume that the pipe is long enough so that there are no end effects, and that we have waited a long time, so the concentration in the pipe is not changing, i.e.

$$\frac{\partial c}{\partial t} = 0$$

This later assumption is known as a steady-state condition and with it the concentration becomes independent of time, i.e. $c(\mathbf{r}, t) \rightarrow c(\mathbf{r})$.

It is natural to use cylindrical coordinates for this problem, and due to the symmetry of the geometry and boundary condition Fick's first law becomes:

$$\mathbf{J} = -D \frac{dc}{dr} \hat{\mathbf{r}}$$

where now we take the total derivative since we are at steady-state, so the concentration is not a function of time, and the symmetry of the problem (ignoring end effects) dictates that it is also not a function of spatial coordinates other than the radius.

A steady-state flux within the cylinder will give rise to a mass flow outside the cylinder. In the experimental situation, we measure the rate at which atoms appear outside the cylinder \dot{m} (atoms/s). If, inside our pipe, we draw an imaginary cylinder with radius $r_1 < r < r_2$ we see that the total number of atoms passing through this cylinder must be the same for any value of r within this range. That is, the flux times the area must be \dot{m} . This yields:

$$\dot{m} = (-D \nabla c) (2\pi r h)$$

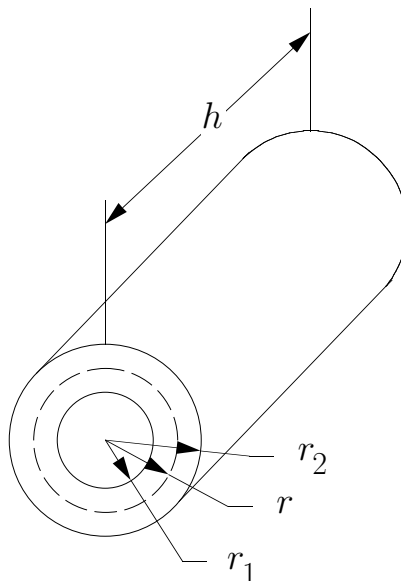


Figure 1.2: Schematic of pipe showing length h , inner radius r_1 , and outer radius r_2 .

$$= -2\pi r h D \frac{\partial c}{\partial r}$$

If $D \neq D(c)$ we can integrate to find:

$$\begin{aligned} \int_{c_1}^c dc &= \int_{r_1}^r -\frac{\dot{m}}{2\pi r h D} dr \\ c - c_1 &= -\frac{\dot{m}}{2\pi h D} \int_{r_1}^r \frac{dr}{r} \\ &= -\frac{\dot{m}}{2\pi h D} \ln \frac{r}{r_1} \end{aligned}$$

We see that a plot of $c(r)$ versus $\ln r$ will give a straight line. By measuring the mass flow \dot{m} and the concentration at two different r -values, we can obtain D . For example if we measure c_1 and c_2 , the concentration at the inner and outer radii of the cylinder, we obtain:

$$D = \frac{-\dot{m}}{2\pi h(c_2 - c_1)} \ln \frac{r_2}{r_1}$$

In the case that the diffusivity depends on concentration ($D = D(c)$), we

cannot perform the integration as above. We have:

$$\dot{m} = -2\pi r h D(c) \frac{\partial c}{\partial r}$$

which can be solved for $D(c)$ to find:

$$D(c) = -\frac{\dot{m}}{2\pi r h \frac{\partial c}{\partial r}} = -\frac{\dot{m}}{2\pi h \frac{\partial c}{\partial \ln r}}$$

This gives us a way to determine $D(c)$. We measure the concentration $c(r)$ as a function of radius r . If D depends on concentration a plot of c versus $\ln r$ will not yield a straight line, but from the slope of the line we can determine $D(r)$ which can be transformed to $D(c)$. This is shown schematically in Fig. 1.3.

1.3 The Thin Film Solution

The next example we consider is the solution of Fick's second law with the initial condition of an infinitely thin film placed between two semi-infinite media. This is often a good approximation to real situations, and it forms the basis for constructing solutions to more complex situations. The boundary conditions are that the composition must go to zero at $z = \pm\infty$. The solution is:

$$c(z, t) = \frac{m_B}{\sqrt{4\pi Dt}} \exp\left(-\frac{z^2}{4Dt}\right) \quad (1.5)$$

where m_B is the total amount per area of the diffusing species, D is the composition-independent diffusivity, and z is the distance from the original interface. It can be shown by direct substitution that Eqn. 1.5 solves Fick's second law (Eqn. 1.4):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$

The solution in Eqn. 1.5 also has the correct normalization, that is, the total amount of diffusing material is m_B :

$$\int_{-\infty}^{\infty} c(z, t) dz = m_B$$

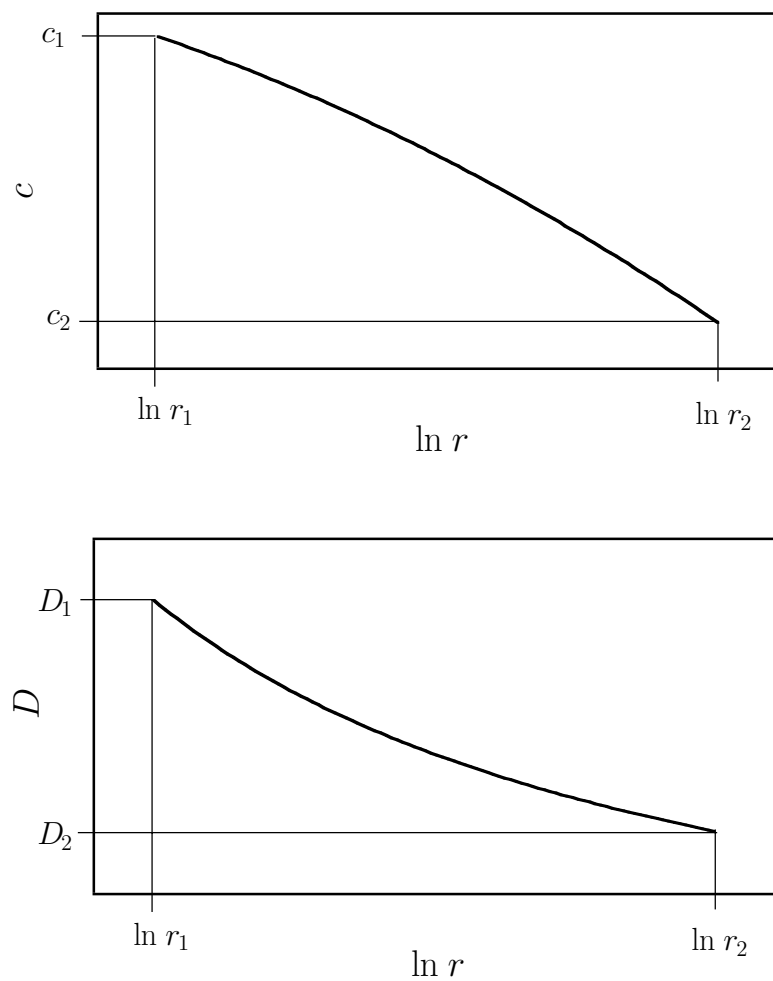


Figure 1.3: Schematic showing concentration as a function of $\ln r$ resulting from a steady state cylindrical diffusion experiment, and the position-dependent diffusivity $D(r)$ which can be extracted.

Furthermore, we match the boundary conditions, and, at $t = 0$, our solution has the values:

$$\begin{aligned} &\text{for } |z| > 0, \quad c \rightarrow 0 \quad \text{as } t \rightarrow 0 \\ &\text{for } z = 0, \quad c \rightarrow \infty \quad \text{as } t \rightarrow 0 \end{aligned}$$

which states that initially we have a finite amount of material in an infinitely narrow band. This is the initial condition for the problem we set out to solve.

The concentration has a Gaussian spatial profile, with width w (distance between inflection points) given by:

$$w = 2\sqrt{2Dt}$$

This width is a measure of the diffusion distance. The concentration at the origin ($z = 0$) is given by:

$$c(0, t) = \frac{m_B}{\sqrt{4\pi Dt}}$$

which decreases linearly with $1/\sqrt{t}$.

It is instructive to examine the behavior of this solution relative to Fick's laws. In Fig. 1.4 the composition, flux, and time rate of change of composition are plotted as a function of distance at some fixed time. In region where the slope of the concentration is positive, the flux, given by:

$$J = -D \frac{\partial c}{\partial z},$$

is negative, so that material is moving to the left. The opposite is true where the slope of the concentration is negative. The diffusing atoms move down the concentration gradient. By Fick's second law (Eqn. 1.4), the rate of accumulation of material is proportional to the second derivative of the concentration with respect to position. Thus, where the curvature of the concentration is positive, diffusing atoms are accumulating. The opposite is true where the curvature is negative.

1.4 Solutions Based on the Thin-Film Solution

There are a class of solutions based on the thin film solution which are examples of the general problem solving method known as Green's Functions. The general recipe is:

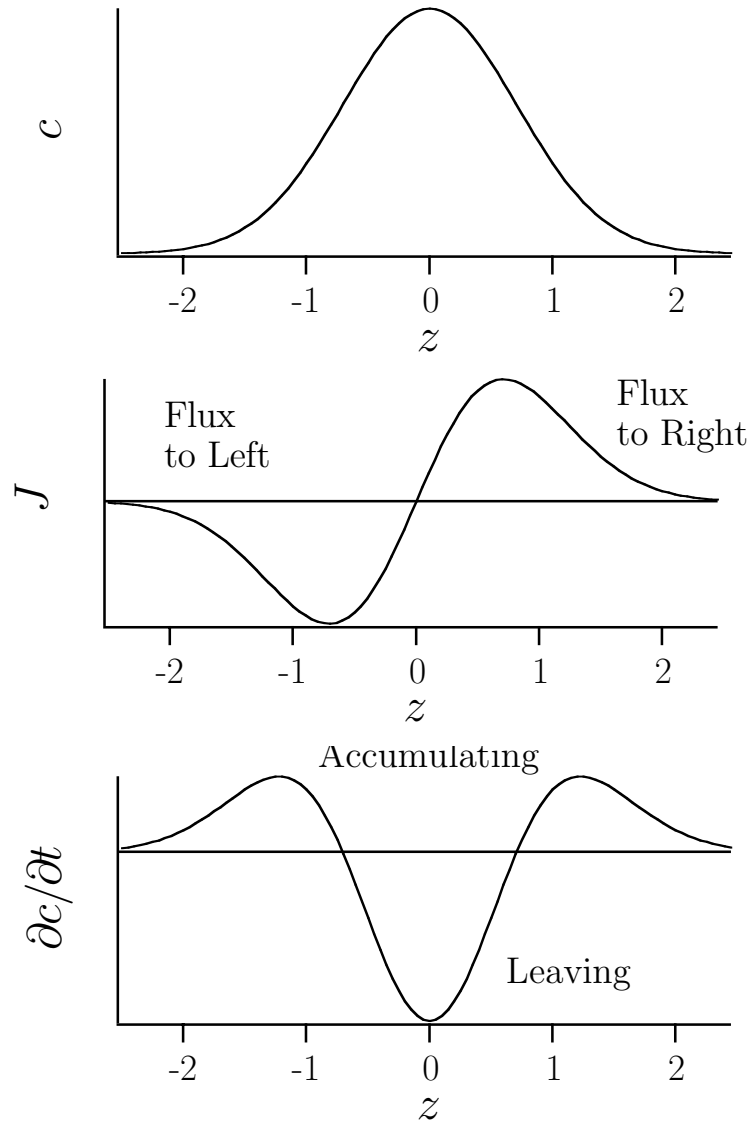


Figure 1.4: Composition, flux, and time rate of change of composition for the thin film solution.

- Find the response of the system to a delta function input. In the case of the diffusion equation this amounts to solving Fick's second law for the infinitely thin film with unit total material ($m_B = 1$).
- Integrate this response over actual input. In the case of the diffusion equation, this amounts to integrating over the initial composition.

This technique can be applied to cases when the problem can be framed with an infinite system. In a homework problem, you will show that:

$$c(z, t) = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} f(z') \exp \left[\frac{-(z - z')^2}{4Dt} \right] dz'$$

solves the diffusion equation, where $f(z)$ is the initial distribution for an infinite system, i. e. :

$$f(z) = c(z, 0)$$

and the diffusivity is not a function of composition ($D \neq D(c)$).

As an example of the use of this method, we consider the situation of a pair of semi-infinite solids which initially have different composition. We arbitrarily set the composition in one equal to 0 and the other equal to c_0 , so that the initial condition is:

$$c(z, 0) = \begin{cases} 0 & z < 0 \\ c_0 & z \geq 0 \end{cases}$$

The solution is then:

$$\begin{aligned} c(z, t) &= \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} f(z') \exp \left[\frac{-(z - z')^2}{4Dt} \right] dz' \\ &= \frac{c_0}{\sqrt{4\pi Dt}} \int_0^{\infty} \exp \left[\frac{-(z - z')^2}{4Dt} \right] dz' \end{aligned}$$

We can cast this integral into a standard form with the variable substitution:

$$\eta = \frac{z - z'}{\sqrt{4Dt}}$$

so that

$$d\eta = \frac{-dz'}{\sqrt{4Dt}}$$

and the solution becomes:

$$\begin{aligned} c(z, t) &= \frac{c_0}{\sqrt{4\pi Dt}} \int_{z/\sqrt{4Dt}}^{-\infty} e^{-\eta^2} (-\sqrt{4Dt}) d\eta \\ &= \frac{c_0}{\sqrt{\pi}} \left[\int_0^{\infty} e^{-\eta^2} d\eta + \int_0^{z/\sqrt{4Dt}} e^{-\eta^2} d\eta \right] \end{aligned}$$

This can be represented as a special function known as the error function $\text{erf}(y)$ defined as:

$$\text{erf}(y) \equiv \frac{2}{\sqrt{\pi}} \int_0^y e^{-\eta^2} d\eta$$

This function has the properties:

$$\begin{aligned} \text{erf}(0) &= \frac{2}{\sqrt{\pi}} \int_0^0 e^{-\eta^2} d\eta = 0 \\ \text{erf}(\infty) &= \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\eta^2} d\eta = 1 \end{aligned}$$

In terms of these definitions, the solution is:

$$c(z, t) = \frac{c_0}{2} \left[1 + \text{erf} \left(\frac{z}{\sqrt{4Dt}} \right) \right]$$

It is interesting to consider what we have done using this solution method. We have used a collection of infinitely thin slabs to represent a semi-infinite solid, and have let the material in each slab diffuse into a Gaussian profile in a manner predicted by the thin film solution. The composition profile is then a sum of these Gaussians. This is illustrated schematically in Fig. 1.5.

It is also interesting to consider the time evolution of this solution. The value of the composition at the origin for all times is $c_0/2$, as is the value at infinite time at all positions. That is:

$$\begin{aligned} c(0, t) &= \frac{c_0}{2} \\ c(z, \infty) &= \frac{c_0}{2} \end{aligned}$$

The composition profile spreads as a function of time. For a homework problem you show that the points z_1 and z_2 defined by:

$$\begin{aligned} c(z_1, t) &= \frac{c_0}{4} \\ c(z_2, t) &= \frac{3c_0}{4} \end{aligned}$$

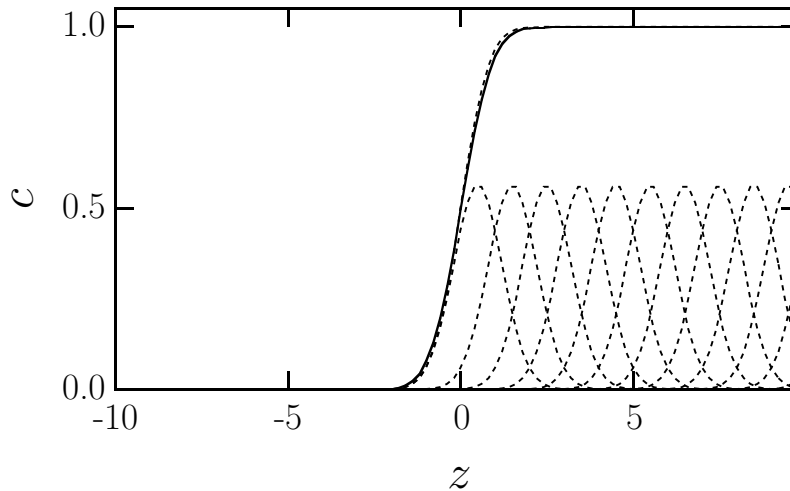


Figure 1.5: Schematic of solution to the step composition profile. Dotted lines are the solutions for thin slabs, and the sum of these solutions, solid line is the actual error function solution.

spread apart with the distance between them being proportional to the square root of time. So again, we find that the diffusion distance is proportional to \sqrt{Dt} .

We can generalize the error function solution for other cases. The function:

$$c(z, t) = A + B \operatorname{erf} \left(\frac{z}{\sqrt{4Dt}} \right)$$

solves the diffusion equation. If we can choose constants A and B to meet the initial condition and boundary conditions, we have a solution.

Before leaving this solution method we make some general comments. First of all, we have assumed that the diffusivity is not a function of composition ($D \neq D(c)$). This is often a bad assumption if there are large composition differences in the problem. However this solution is often used to estimate the behavior of a system assuming some average diffusion constant. Furthermore, we have also assumed that the system is infinite. This assumption can also lead to trouble as explored in one of the exercises. In general this solution is valuable for the case that the diffusion distances are small relative to the dimensions of the system.