Last Time

Electromigration

Anisotropy and Onsager Coefficients

The Diffusion Equation

The Diffusion Equation for Uniform Diffusivity

The Steady-State Condition

3.21 Spring 2002: Lecture 7

Scaling and the Diffusion Equation

Note that the diffusivity has units (number×cm^2)/s; therefore, Dt/x^2 is dimensionless. Introduce a dimensionless variable η:

$$\eta \equiv \frac{x}{\sqrt{4Dt}} \tag{7-1}$$

Suppose for a particular problem, that the boundary and initial conditions are also invariant to this scaling implied by η, in other words, if the length scale is tripled (yards instead of feet) then the time scale for the boundary conditions is multiplied by a factor of nine. Or, under the scaling,

$$\bar{x} = \lambda x \quad \bar{t} = \lambda^2 t \quad \text{then: } \bar{\eta} = \eta \tag{7-2}$$

the boundary conditions can be written entirely in terms of the one dimensionless variable η.

An example of such a problem would be the "step-function" initial conditions with either Dirichlet or zero-flux Neumann boundary conditions at $\pm\infty$:

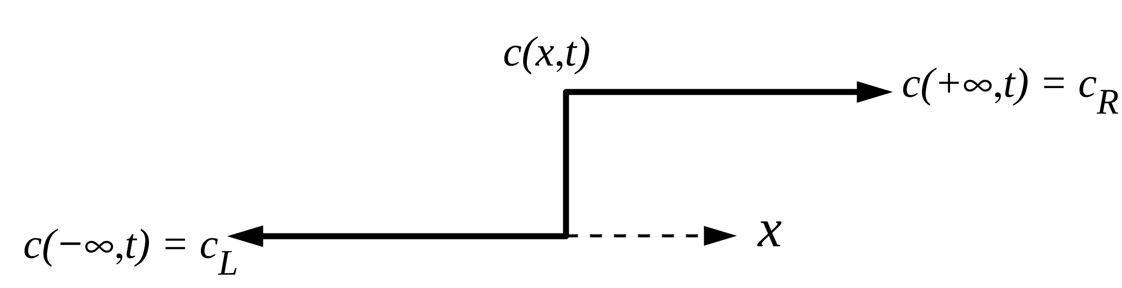

Figure 7-1: Spatially-dependent function for the initial condition of the step-function.

Initial conditions:

$$c(x, t = 0) = \begin{cases} C_L & -\infty < x < 0 \\ C_R & 0 < x < \infty \end{cases} \tag{7-3}$$

or

$$c(\eta = \infty) = C_R \quad c(\eta = -\infty) = C_L \tag{7-4}$$

with boundary conditions:

$$c(x = +\infty, t) = (\eta = +\infty) = C_R \quad \text{or} \quad \frac{\partial c(x,t)}{\partial x}\bigg|_{x=+\infty} = \frac{dc(\eta)}{d\eta}\bigg|_{\eta=\infty} = 0 \tag{7-5}$$

and

$$c(x = -\infty, t) = c(\eta = -\infty) = C_L \quad \text{or} \quad \frac{\partial c(x,t)}{\partial x}\bigg|_{x=-\infty} = \frac{dc(\eta)}{d\eta}\bigg|_{\eta=-\infty} = 0 \tag{7-6}$$

Using the definition for η:

$$\frac{\partial}{\partial t} = \frac{\partial \eta}{\partial t}\frac{\partial}{\partial \eta} \qquad \frac{\partial}{\partial x} = \frac{\partial \eta}{\partial x}\frac{\partial}{\partial \eta} \tag{7-7}$$

The diffusion equation becomes:

$$-2\eta \frac{\partial c}{\partial \eta} = \frac{\partial^2 c}{\partial \eta^2} \tag{7-8}$$

Because everything in the above equation depends only on η, the partial differential equation becomes an ordinary differential equation ($\partial \to d$) that can be integrated without too much difficulty.

Let

$$q \equiv \frac{dc}{d\eta} \tag{7-9}$$

so that

$$-2\eta q = \frac{dq}{d\eta} \tag{7-10}$$

which can be integrated

$$\frac{dc}{d\eta} = b_0 e^{-\eta^2} \tag{7-11}$$

where b_0 is an integration constant and this can be integrated again

$$c(\eta) - c(\eta = \eta_0) = b_0 \int_{\eta_0}^{\eta} e^{-\zeta^2} d\zeta \tag{7-12}$$

Let $\eta_0 = -\infty$ and with the step-function initial conditions, $c(\eta = -\infty) = C_L$,

$$c(\eta) = C_L + b_0 (\int_{-\infty}^{0} e^{-\zeta^2} d\zeta + \int_{0}^{\eta} e^{-\zeta^2} d\zeta) \tag{7-13}$$

or, by introducing another constant for b_0,

$$c(\eta) = C_L + a_0 \left(\frac{2}{\sqrt{\pi}} \int_{-\infty}^{0} e^{-\zeta^2} d\zeta + \frac{2}{\sqrt{\pi}} \int_{0}^{\frac{x}{\sqrt{4Dt}}} e^{-\zeta^2} d\zeta \right) \tag{7-14}$$

The integral with an argument is just some function with a peculiar name:

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-\zeta^2} d\zeta \tag{7-15}$$

that has the properties: $\text{erf}(0) = 0$, $\text{erf}(\infty) = 1$ (this is where the $\sqrt{\pi}$ comes from), $\text{erf}(-z) = -\text{erf}(z)$

So, the solution to the one-dimensional step function IC uniform diffusion equation is:

$$c(x,t) = \frac{C_R + C_L}{2} + \frac{C_R - C_L}{2}\text{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{7-16}$$

or

$$c(x,t) = \langle C \rangle + \frac{\Delta C}{2}\text{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{7-17}$$

Short Distances, Long Times

An additional and useful property of the error function is that $\text{erf}(z) \approx z$ for $z \ll 1$

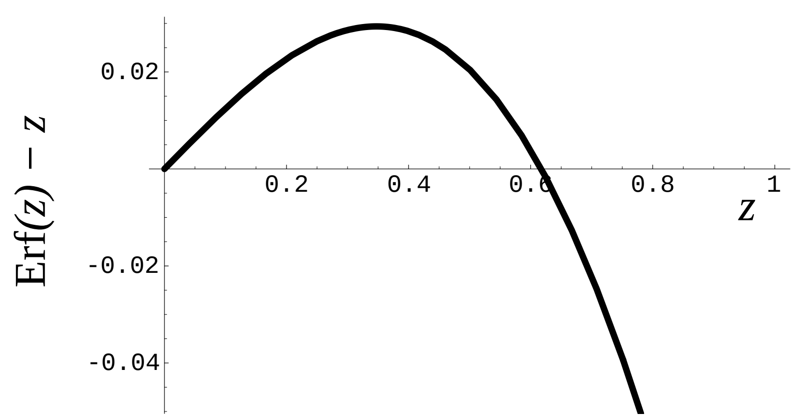

Figure 7-2: The *difference* between the error function $\text{erf}(z)$ and its argument z. Up to values of about $z = 0.9$, the difference is less than 13%.

Because the scaling parameter $\eta \equiv \frac{x}{\sqrt{4Dt}}$ is small for long times $t \gg \tau_D$ where τ_D is the characteristic diffusion time:[14]

$$\tau_D \equiv \frac{x^2}{4D} \tag{7-18}$$

[14]Note that *long times* must be specified in terms of some characteristic time that depends on a diffusivity and a length. A similar comment applies to any limiting value of a physical parameter.

or for *short* distances $x \ll \chi_D$ where χ_D is the characteristic diffusion length:

$$\chi_D \equiv \sqrt{4Dt} \tag{7-19}$$

the solution of the step-function IC becomes:

$$c(x,t) = \langle c \rangle + \frac{\Delta C}{2} \frac{x}{\sqrt{4Dt}} \tag{7-20}$$

The flux at the origin varies as,

$$J(x=0,t) = -\Delta C \sqrt{\frac{D}{4\pi t}} \tag{7-21}$$

The total amount of material that flows past the origin (per unit area) up to a time τ goes as $\sqrt{\tau}$:

$$J_{cumulative}(x=0,\tau) = -\Delta C \sqrt{\frac{D\tau}{\pi}} \tag{7-22}$$

Superposition Example

The simple solution that was developed above can be used with the method of superposition to develop a large number of solutions.

For example, suppose the initial conditions are changed so that there is a finite source of material diffusing into an infinite material and the finite source is confined to slab of with Δx in the x-direction but extending infinitely in the y- and z-directions.[15]

[15] This is effectively a one dimensional problem in the x-spatial variable.

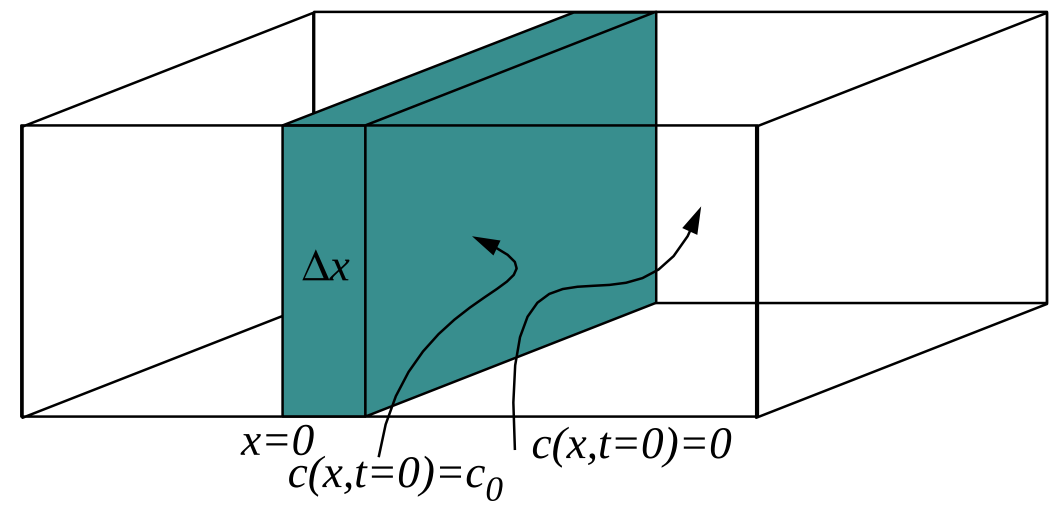

Figure 7-3: Initial conditions for the one dimensional finite square source initial conditions.

These initial conditions can be obtained by summing two known solutions, i.e. those for the initial conditions:

$$c(x, t=0) = \begin{cases} 0 & -\infty < x < 0 \\ c_0 & 0 < x < \infty \end{cases} \tag{7-23}$$

and

$$c(x, t=0) = \begin{cases} 0 & -\infty < x < \Delta x \\ -c_0 & \Delta x < x < \infty \end{cases} \tag{7-24}$$

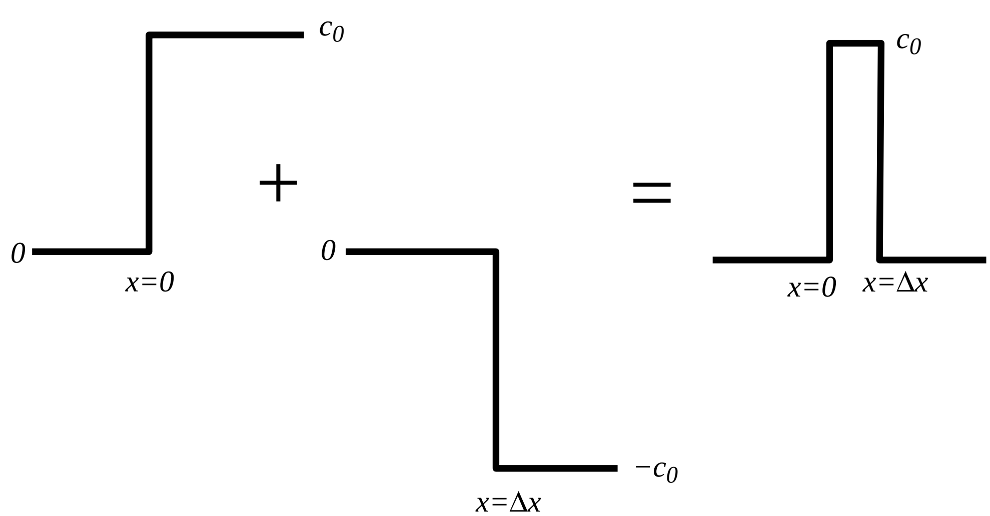

Figure 7-4: Graphical representation of the method of superposition.

The solution is just the sum:

$$c(x,t) = \frac{c_0}{2} + \frac{c_0}{2}\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{\sqrt{4Dt}}} e^{-\zeta^2} d\zeta - \frac{c_0}{2} - \frac{c_0}{2}\frac{2}{\sqrt{\pi}}\int_0^{\frac{x-\Delta x}{\sqrt{4Dt}}} e^{-\zeta^2} d\zeta \tag{7-25}$$

$$c(x,t) = \frac{c_0}{2}\left[\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) - \mathrm{erf}\left(\frac{x-\Delta x}{\sqrt{4Dt}}\right)\right] \tag{7-26}$$

It will be beneficial to reflect on what kinds of problems (i.e. which initial and boundary conditions) will admit solutions from scaling and then subsequent summing of solutions. First for the scaling solution, the boundary and initial conditions had to be invariant under the scale factor $\eta \equiv \frac{x}{\sqrt{4Dt}}$—this is usually the case for infinite domains with zero flux conditions at $|\vec{r}| = \infty$. Second, the summing method works when each solution that is to be summed also satisfies scaling—therefore the initial conditions for the particular problem must also be invariant. Typically, these methods are useful in the infinite domain.

The One-Dimensional Fundamental Solution

The solution for "point-source" initial conditions will prove to be quite useful for cases when the addition of a large number of solutions generate the initial conditions for a particular problem. The solution obtained in Eq. 7-26 can be used to obtain the fundamental solution. Expanding in powers of small $dx = \Delta x$:[16]

$$c(x,t) = \frac{c(x=0,t=0)dx}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{7-27}$$

This is the fundamental solution for a point source in a 1D infinite domain.

Many other solutions by summing point source solutions,

[16] It is fairly easy to show that $\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}(z - \frac{z^3}{3} + \mathcal{O}(z^5))$.

In general,[17] for almost any initial conditions $c(x, t = 0) = c_{ic}(x)$ on the 1D infinite domain with zero flux at $x = \pm\infty$,

$$c(x,t) = \int_{-\infty}^{\infty} \frac{c_{ic}(\zeta) e^{-\frac{(x-\zeta)^2}{4Dt}}}{\sqrt{4\pi Dt}} d\zeta \tag{7-28}$$

Otherwise known as the the Green's function solution.[18]

Other Fundamental Solutions

The same method can be used to find fundamental solutions for cases where the finite source is a object of a given dimensionality embedded in an infinite space of larger dimension. This is called the "co-dimension" and it is the dimensionality of the infinite region minus the dimensionality of the embedded object.

All the pertinent examples are contained in the following table:

Co-dimension	Example	Symmetric Part of ∇^2	Fundamental Solution
1	Point on Line Line on Plane Plane in 3D	$\frac{\partial^2}{\partial x^2}$	$\frac{c(x=0,t=0)dx}{\sqrt{4\pi Dt}} e^{\left(-\frac{x^2}{4Dt}\right)}$
2	Point in Plane Line in 3D	$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)$	$\frac{c(x=0,t=0)2\pi r dr}{4\pi Dt} e^{\left(-\frac{r^2}{4Dt}\right)}$
3	Point in 3D	$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$	$\frac{c(x=0,t=0)4\pi r^2 dr}{(4\pi Dt)^{3/2}} e^{\left(-\frac{r^2}{4Dt}\right)}$

[17] There are some technical restrictions on the class of initial conditions are fairly easy to guess.
[18] Or the "Son of York Trick"....