Solutions to the Diffusion Equation

Solutions to Fick's Laws

- Fick's second law, isotropic one-dimensional diffusion, *D* independent of concentration

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

Figure removed due to copyright restrictions.
See Figure 4.1 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter. *Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Linear PDE; solution requires one initial condition and two boundary conditions.

Steady-State Diffusion

- When the concentration field is independent of time and D is independent of c, Fick's second law is reduced to Laplace's equation, $\nabla^2 c = 0$

  For simple geometries, such as permeation through a thin membrane, Laplace's equation can be solved by integration.

- Examples of steady-state profiles

(a) Diffusion through a flat plate

Figure removed due to copyright restrictions.
See Figure 5.1 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

(b) Diffusion through a cylindrical shell

Figure removed due to copyright restrictions.
See Figure 5.2 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Error function solution...

- Interdiffusion in two semi-infinite bodies

Solution can be obtained by a “scaling” method that involves a single variable, $\eta \equiv x/\sqrt{4Dt}$

$$c(\eta) = c\left(\frac{x}{\sqrt{4Dt}}\right) = \bar{c} + \frac{\Delta c}{2}\,\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

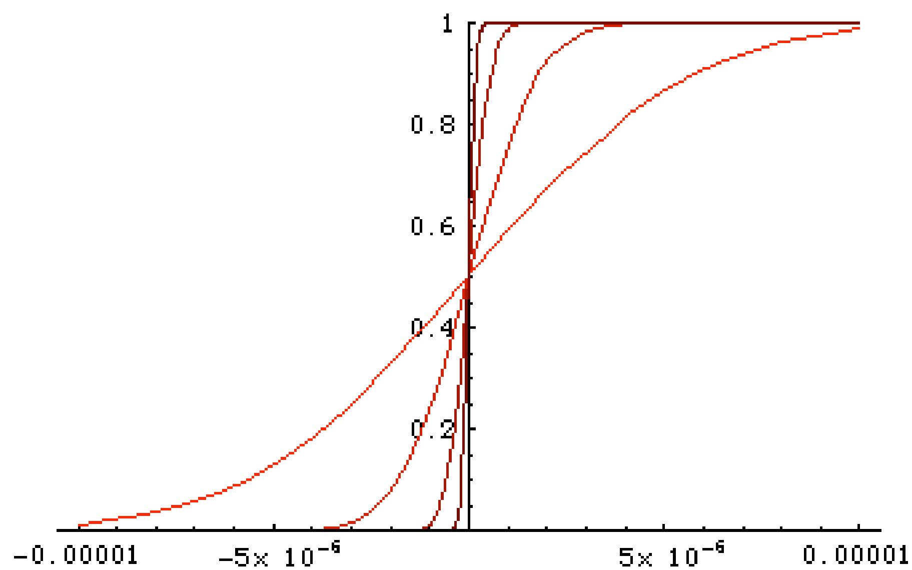
- erf (x) is known as the *error function* and is defined by

$$\mathrm{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x e^{-\zeta^2} d\zeta$$

- An example:

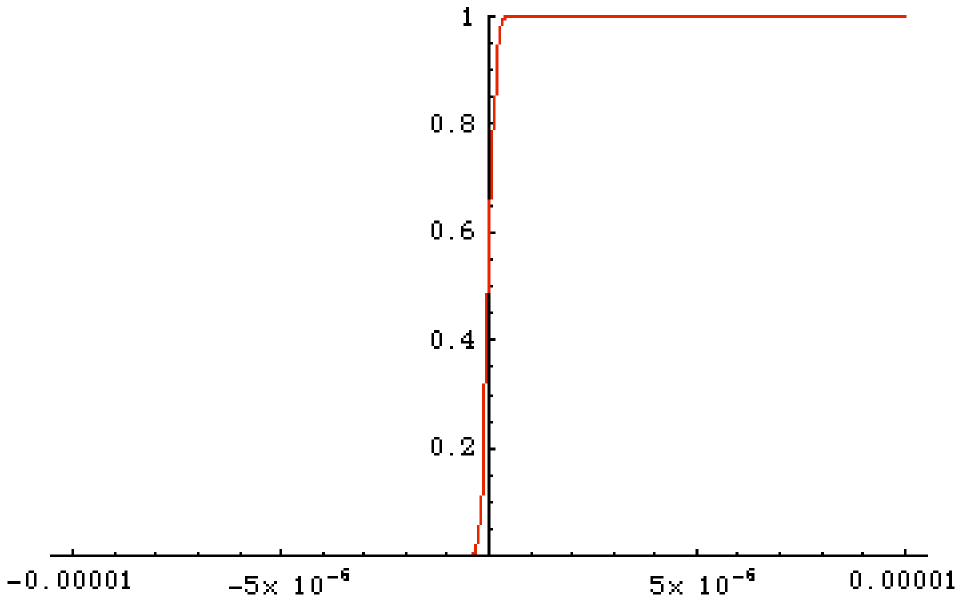
$$c(x<0,0)=0; c(x>0,0)=1; c(-\infty,t)=0; \; c(\infty,t)=1; \; D=10^{-16}$$

$t = 10^2, 10^3, 10^4, 10^5$



- Application to problems with fixed c at surface

- Movie showing time dependence of erf solution…



Superposition of solutions

- When the diffusion equation is linear, *sums of solutions are also solutions*. Here is an example that uses superposition of error-function solutions:

Two step functions, properly positioned, can be summed to give a solution for *finite layer* placed between two semi-infinite bodies.

- Superposed error functions, cont'd

The two step functions (moved left/right by $\Delta x/2$):

$$c_{\text{left}} = \frac{c_0}{2}\left[1 + \text{erf}\left(\frac{x + \Delta x/2}{\sqrt{4Dt}}\right)\right]$$

$$c_{\text{right}} = -\frac{c_0}{2}\left[1 + \text{erf}\left(\frac{x - \Delta x/2}{\sqrt{4Dt}}\right)\right]$$

and their sum

$$c_{\text{layer}} = \frac{c_0}{2}\left[\text{erf}\left(\frac{x + \Delta x/2}{\sqrt{4Dt}}\right) - \text{erf}\left(\frac{x - \Delta x/2}{\sqrt{4Dt}}\right)\right]$$

- Superposed error functions, cont'd

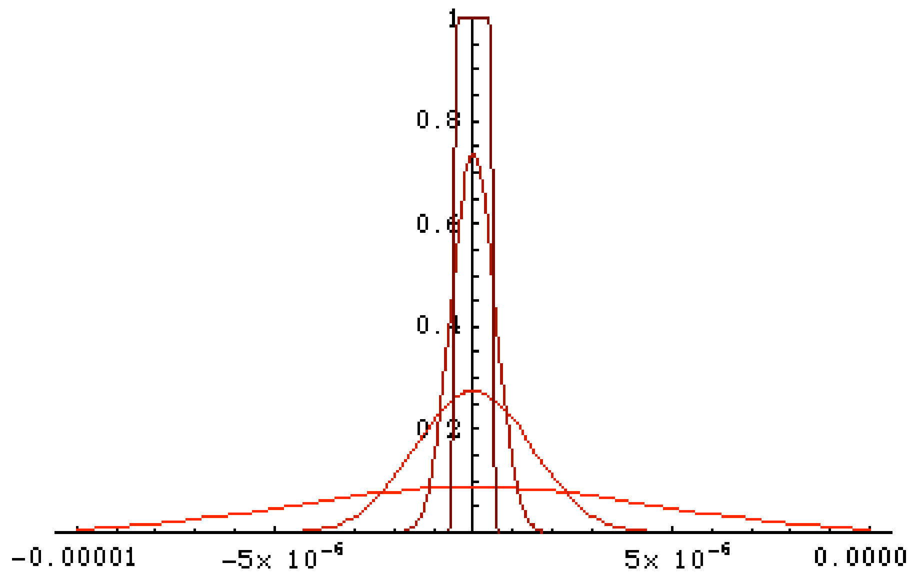
An example:

$$c(-\infty,t)=0;\ c(\infty,t)=0;\ c(x\le-\Delta x/2,0)=0;\ c(-\Delta x/2<x<\Delta x/2)=1;$$

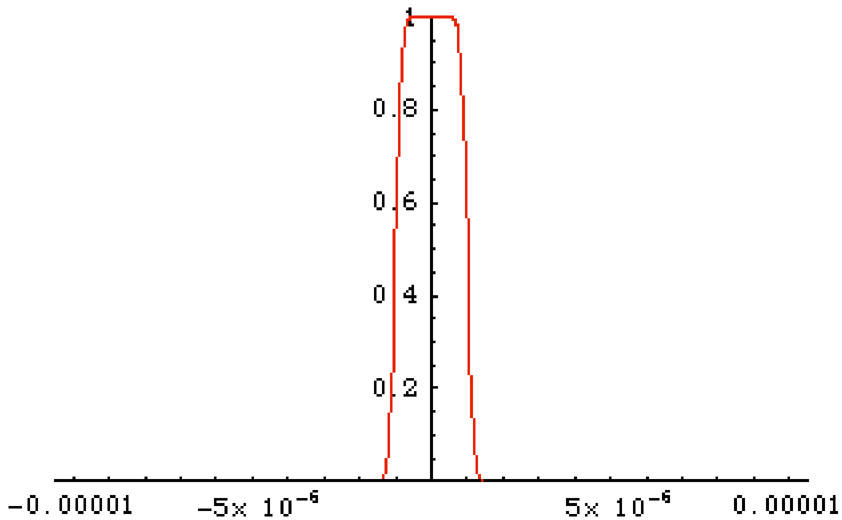
$$c(x\ge\Delta x/2,0)=0;\ \Delta x=2\times10^{-6};\ D=10^{-16}$$

$t = 10^1, 10^3, 10^4, 10^5$

- Application to problems with *zero-flux plane* at surface $x = 0$



- Movie showing time dependence of superimposed erf solutions…



The "thin-film" solution

- The "thin-film" solution can be obtained from the previous example by looking at the case where Δx is very small compared to the diffusion distance, x, and the thin film is initially located at $x = 0$:

$$c(x,t) = \frac{N}{\sqrt{4\pi Dt}} e^{-x^2/(4Dt)}$$

where N is the number of "source" atoms per unit area initially placed at $x = 0$.

Diffusion in finite geometries

- Time-dependent diffusion in finite bodies can soften be solved using the *separation of variables* technique, which in cartesian coordinates leads to trigonometric-series solutions.
  A solution of the form

$$c(x,y,z,t) = X(x)\cdot Y(y)\cdot Z(z)\cdot T(t)$$

is sought.

- Substitution into Fick's second law gives two ordinary-differential equations for one-dimensional diffusion:

$$\frac{dT}{dt} = -\lambda DT$$

$$\frac{d^2 X}{dx^2} = -\lambda X$$

where λ is a constant determined from the boundary conditions.

- Example: degassing a thin plate in a vacuum

$$c(0 < x < L, 0) = c_0;\ c(0,t) = c(L,t) = 0$$

The function $X(x)$ turns out to be the Fourier series representation of the initial condition—in this case, it is a Fourier sine-series representation of a constant, c_0:

$$X_n(x) = \sum_{n=1}^{\infty} a_n \sin\left(n\pi \frac{x}{L}\right)$$

with

$$a_n = \frac{2c_0}{L} \int_0^L \sin\left(n\pi \frac{\xi}{L}\right) d\xi$$

- degassing a thin plate, cont'd

The function $T(t)$ must have the form:

$$T_n(t) = T_n^{\circ} \exp\left(-\frac{n^2\pi^2}{L^2} Dt\right)$$

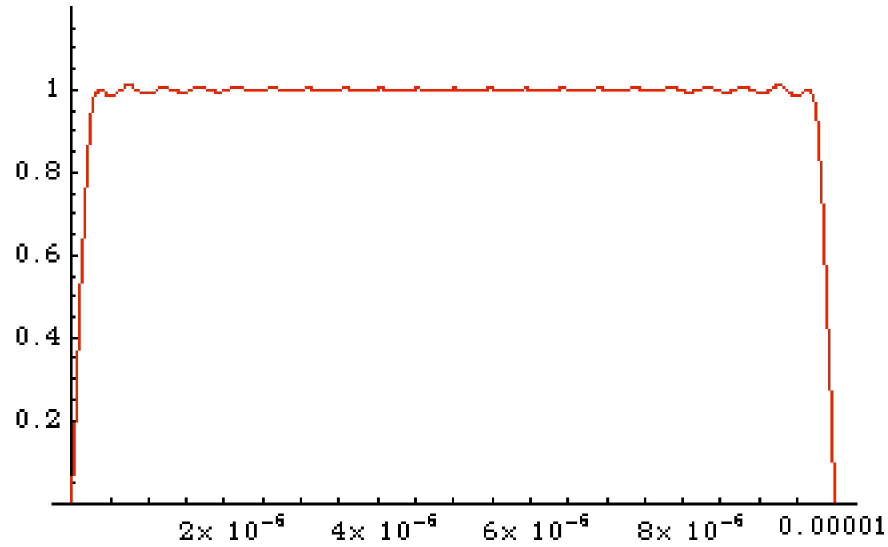
and thus the solution is given by *KoM* Eq. 5.47:

$$c(x,t) = \frac{4c_0}{\pi}\sum_{j=0}^{\infty}\left(\frac{1}{2j+1}\sin\left[(2j+1)\pi\frac{x}{L}\right]\exp\left[-\frac{(2j+1)^2\pi^2}{L^2}Dt\right]\right)$$

- degassing a thin plate, cont'd

Example: $c(0,t)=0;\ c(L,t)=0;\ c(0<x<L,0)=1$

$$L=10^{-5};\ D=10^{-16}$$



Other useful solution methods

- Estimation of diffusion distance from $x \approx \sqrt{4Dt}$
- Superposition of point-source solutions to get solutions for arbitrary initial conditions $c(x,0)$
- Method of Laplace transforms
  Useful for constant-flux boundary conditions, time-dependent boundary conditions
- Numerical methods
  Useful for complex geometries, $D = D(c)$, time-dependent boundary conditions, etc.