5

Diffusion: basic theory

Summary
In this chapter the basic equation of molecular diffusion and simple applications are developed.

5.1 Basic equations

The basic diffusion of matter, also called molecular diffusion, is described by Fick's law, first stated by Fick (1855). Fick's law states that the transfer rate of mass across an interface normal to the x-direction and in a quiescent fluid varies directly as the coefficient of molecular diffusion D_m and the negative gradient of solute concentration. For a one-dimensional process:

$$\dot{m} = -D_m \frac{\partial C_m}{\partial x} \tag{5.1}$$

where $\dot{m}$ is the solute mass flux and C_m is the mass concentration of matter in liquid. The coefficient of proportionality D_m is called the *molecular diffusion coefficient*. Equation (5.1) implies a mass flux from a region of high mass concentration to one of smaller concentration. An example is the transfer of atmospheric gases at the free surface of a water body. Dissolution of oxygen from the atmosphere to the water yields some re-oxygenation.

The continuity equation (i.e. conservation of mass) for the contaminant states that spatial rate of change of mass flow rate per unit area equals minus the time rate of change of mass:

$$\frac{\partial \dot{m}}{\partial x} + \frac{\partial C_m}{\partial t} = 0 \tag{5.2}$$

Replacing into equation (5.1), it yields:

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} \tag{5.3a}$$

For diffusion in a three-dimensional system, the combination of equations (5.1) and (5.2) gives:

$$\frac{\partial C_m}{\partial t} = D_m \left(\frac{\partial^2 C_m}{\partial x^2} + \frac{\partial^2 C_m}{\partial y^2} + \frac{\partial^2 C_m}{\partial z^2} \right) \tag{5.3b}$$

Equations (5.3a) and (5.3b) are called the *diffusion equations*. It may be solved analytically for a number of basic boundary conditions. Mathematical solutions of the diffusion equation (and heat equation) were addressed in two classical references (Crank 1956, Carslaw and Jaeger 1959). Since equations (5.3a) and (5.3b) are linear, the *theory of superposition* may be used to build up solutions with more complex problems and boundary conditions: e.g. spreading of mass caused by two successive slugs.

Discussion: theory of superposition

If the functions ϕ_1 and ϕ_2 are solutions of the diffusion equation subject to the respective boundary conditions $B_1(\phi_1)$ and $B_2(\phi_2)$, any linear combination of these solutions, $(a\phi_1 + b\phi_2)$, satisfies the diffusion equation and the boundary conditions $aB_1(\phi_1) + bB_2(\phi_2)$. This is the principle of superposition for homogeneous differential equations.

Figure 5.1(a) and (b) illustrates a simple example. Figure 5.1(a) shows the solution of diffusion equation for the sudden injection of mass slug at the origin. By adding an uniform velocity (current), the solution is simply the superposition of Fig. 5.1(a) plus the advection of the centre of mass (Fig. 5.1(b)).

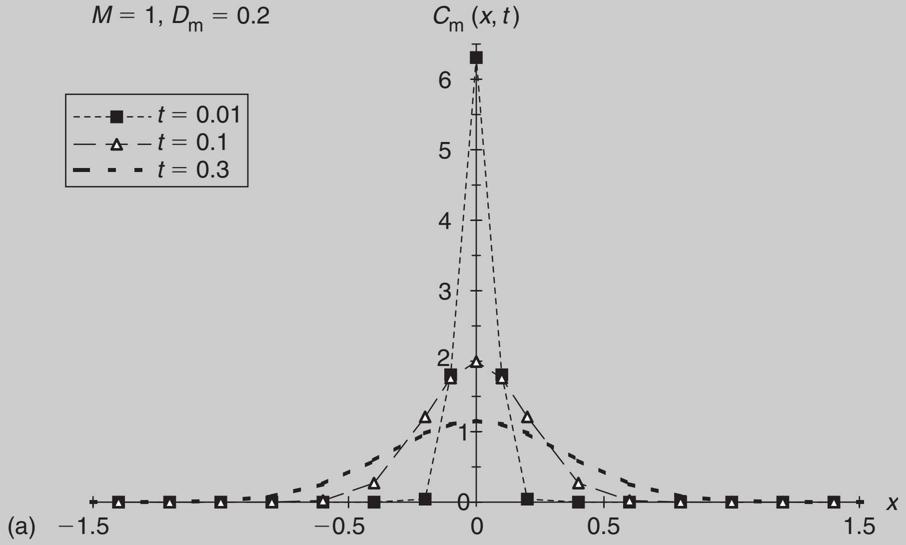

Fig. 5.1 (a) Application of the theory of superposition. (a) Diffusion downstream a sudden mass slug injection. Gaussian distribution solutions of equation (5.4) for $M = 1$ and $D_m = 0.2$.

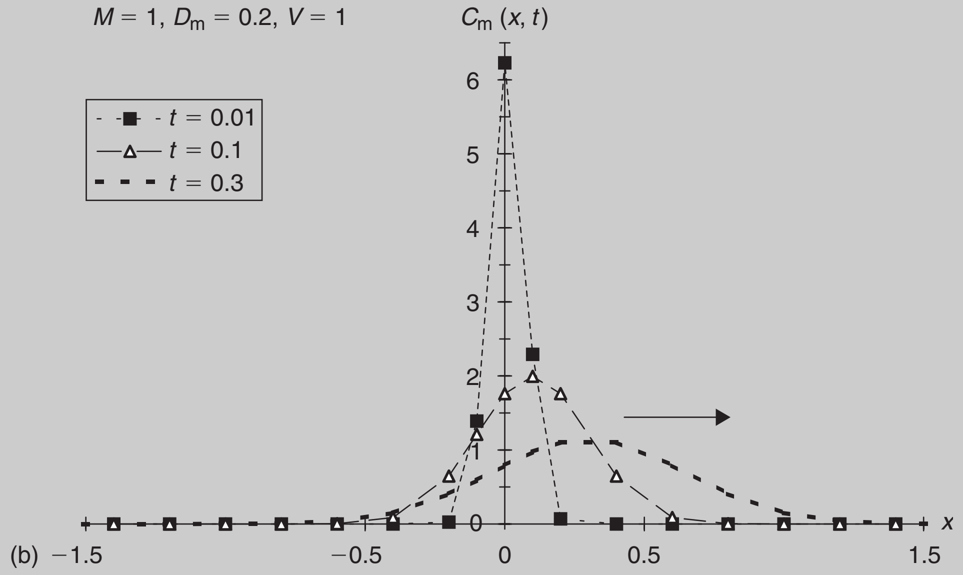

Fig. 5.1 (b) Advection downstream a sudden mass slug injection for $M = 1$, $D_m = 0.2$, $V = 1$ – equation (6.5).

Notes

1. Adolf Eugen Fick was a 19th Century German physiologist who applied Fourier's (1822) law of heat flow to molecular diffusion process.
2. Typical values of molecular diffusion coefficients for solutes in water are in the range 5×10^{-10} to $2 \times 10^{-9}\,m^2/s$. D_m is a property of the fluid. For a given solvent (i.e. fluid), solute (i.e. tracer), concentration and temperature, D_m is a constant.
3. Turbulent enhances mixing drastically. Turbulent diffusion may be described also by equations (5.1)–(5.3) in which the molecular diffusion D_m is replaced by a turbulent diffusion coefficient that is a function of the flow conditions (Chapter 7).
4. The theory of superposition may be applied to the diffusion equations (5.3a) and (5.3b) because it is linear.

5.2 Applications

5.2.1 *Initial mass slug*

Initial mass slug introduced at t = 0 *and* x = 0

A simple example is the one-dimensional spreading of a mass M of contaminant introduced suddenly at $t = 0$ at the origin ($x = 0$) in an infinite (one-dimensional) medium with zero contaminant concentration. The fluid is at rest everywhere (i.e. $V = 0$). The fundamental solution of the diffusion equation (5.3a) is:

$$C_m(x,t) = \frac{M}{\sqrt{4\pi D_m t}} \exp\left(-\frac{x^2}{4D_m t}\right) \qquad \text{for } t > 0 \tag{5.4}$$

Equation (5.4) is called a *Gaussian distribution* or random distribution. The mean equals zero and the standard deviation σ equals $\sqrt{2D_m t}$. In the particular case of $M = 1$, it is known as the normal distribution. Equation (5.4) is plotted in Fig. 5.1(a). The curve has a bell shape.

DISCUSSION

The Gaussian distribution is given by:

$$C_m = C_{max} \exp\left(-\frac{1}{2}\left(\frac{x-m}{\sigma}\right)^2\right)$$

where m is the mean and σ is the standard deviation.

For a Gaussian distribution of tracers, the standard deviation σ may be used as a characteristic length scale of spreading. Ninety-five per cent of the total mass is spread between $(m - 2\sigma)$ and $(m + 2\sigma)$, where m is the mean. Hence an adequate estimate of the width of a dispersing cloud is about 4σ (Fischer *et al*. 1979, p. 41).

For an initial mass slug, the length of contaminant cloud at a time t is $4\sigma = 4\sqrt{2D_m t}$.

Initial mass slug introduced at t = 0 *and* x = x$_o$

Considering an initial mass slug introduced at $t = 0$ and $x = x_o$, the analytical solution of the diffusion equations (5.3a) and (5.3b) is:

$$C_m(x,t) = \frac{M}{\sqrt{4\pi D_m t}} \exp\left(-\frac{(x-x_o)^2}{4D_m t}\right) \qquad \text{for } t > 0 \tag{5.5}$$

Two initial mass slug introduced at t = 0

Considering two separate slugs (mass M_1 and M_2) introduced at $t = 0$, $x = x_1$ and $x = x_2$ respectively (Fig. 5.2), the solution of the diffusion equation is:

$$C_m(x,t) = \frac{M_1}{\sqrt{4\pi D_m t}} \exp\left(-\frac{(x-x_1)^2}{4D_m t}\right) + \frac{M_2}{\sqrt{4\pi D_m t}} \exp\left(-\frac{(x-x_2)^2}{4D_m t}\right) \qquad \text{for } t > 0 \tag{5.6}$$

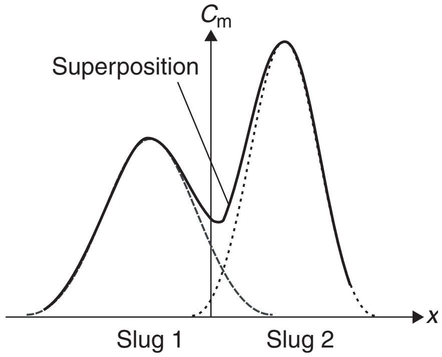

Fig. 5.2 Application of the theory of superposition: diffusion downstream a sudden injection of two mass slugs.

The solution is based upon the assumption that the mass slugs diffuse independently because of the fundamental premise that the motion of individual particles is independent of the concentration of other particles (Fischer *et al*. 1979, p. 42).

5.2.2 Initial step function $C_m(x, 0)$

Considering a sudden increase (i.e. step) in mass concentration at $t = 0$, the boundary conditions are:

$$C_m(x, t < 0) = 0 \qquad \text{everywhere for } t < 0$$
$$C_m(x, 0) = 0 \qquad x < 0$$
$$C_m(x, 0) = C_o \qquad \text{for } x > 0$$

The solution of the diffusion equation may be resolved as a particular case of superposition integral. It yields:

$$C_m(x, t) = \frac{C_o}{2}\left(1 + \text{erf}\left(\frac{x}{\sqrt{4D_m t}}\right)\right) \quad \text{for } t > 0 \tag{5.7}$$

where the *error function* erf is defined as:

$$\text{erf}(u) = \frac{2}{\sqrt{\pi}}\int_0^u \exp(-\tau^2)\,d\tau$$

Equation (5.7) is shown in Fig. 5.3. Details of the error function erf are given in Appendix A (Section 5.3).

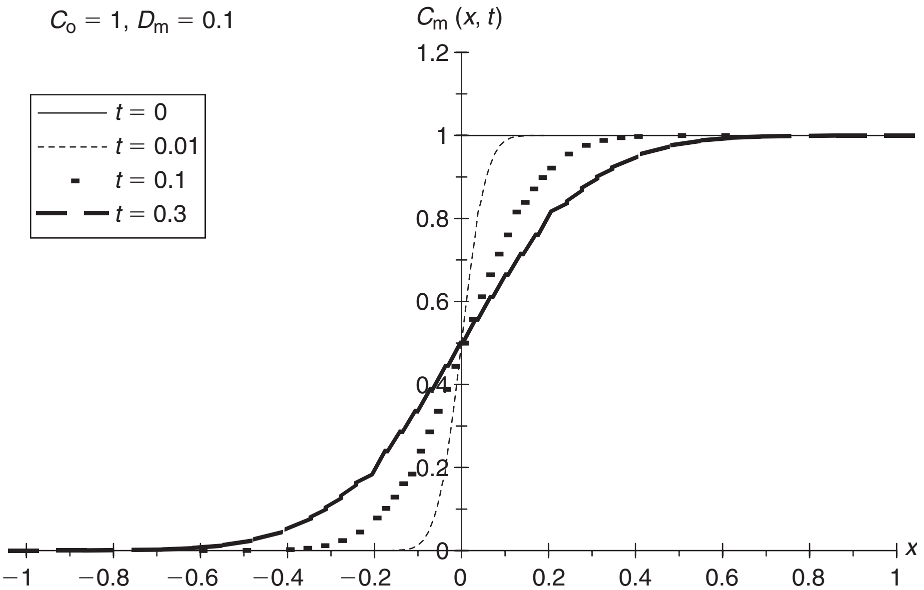

Fig. 5.3 Contaminant diffusion for an initial step distribution, solutions of equation (5.7) for $C_o = 1$ and $D_m = 0.1$.

Note
At the origin, the mass concentration becomes a constant for $t > 0$: $C_m(x = 0, t > 0) = C_o/2$.

5.2.3 Sudden increase in mass concentration at the origin

The concentration is initially zero everywhere. At the initial time $t = 0$, the concentration is suddenly raised to C_o at the origin $x = 0$ and held constant: $C_m(0, t \geqslant 0) = C_o$. The analytical solution of the diffusion equations (5.3a) and (5.3b) is:

$$C_m(x,t) = C_o\left(1 - \mathrm{erf}\left(\frac{x}{\sqrt{4D_m t}}\right)\right) \qquad \text{for } x > 0 \tag{5.8}$$

Equation (5.8) is that of an advancing front (Fig. 5.4). At the limit $t = +\infty$, $C_m = C_o$ everywhere.

The result may be extended, using the theory of superposition, when the mass concentration at the origin C_o varies with time. The solution of the diffusion equation is:

$$C_m(x,t) = \int_{-\infty}^{t} \frac{\partial C_o(\tau)}{\partial \tau}\left(1 - \mathrm{erf}\left(\frac{x}{\sqrt{4D_m(t-\tau)}}\right)\right) d\tau \qquad \text{for } x > 0 \tag{5.9}$$

DISCUSSION
The step function (Section 5.2.2) is a limiting of the sudden increase in mass concentration at the origin with constant mass concentration at the origin. In Section 5.2.2, the mass concentration at the origin was $C_m(x = 0, t > 0) = C_o/2$.

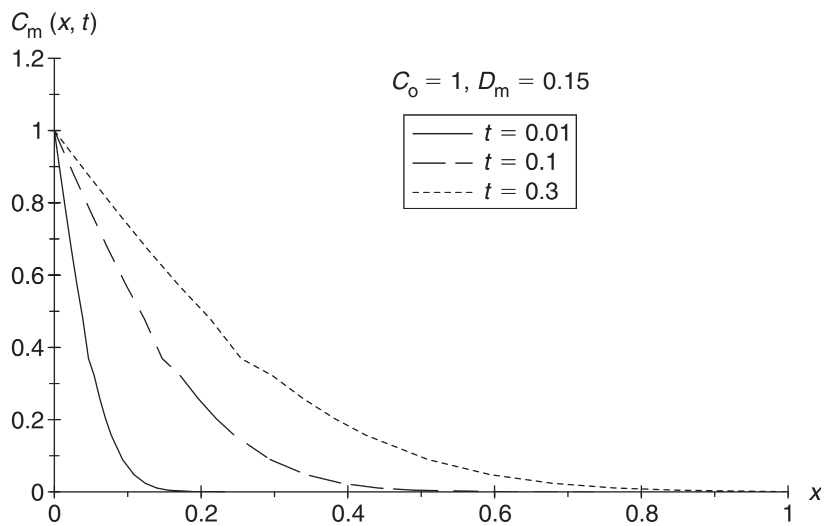

Fig. 5.4 Spread of a sudden concentration increase at the origin, solutions of equation (5.8) for $C_o = 1$ and $D_m = 0.15$.

5.2.4 Effects of solid boundaries

When the spreading (e.g. of a mass slug) is restricted by a solid boundary, the principle of superposition and the *method of images* may be used. The spreading pattern resulting from a combination of two mass slugs of equal strength includes a line of zero concentration gradient midway between them (Fig. 5.5). Since the mass flux is zero according to Fick's law (equation (5.1)), it can be considered as a boundary wall[1] without affecting the other half of the diffusion pattern.

A simple example is the spreading of a mass slug introduced at $x = 0$ and $t = 0$, with a wall at $x = -L$ (Fig. 5.5). At the wall there is no transport through the boundary. That is, the concentration gradient must be zero at the wall:

$$\dot{m}(x = -L, t) = -D_{\mathrm{m}} \frac{\partial C_{\mathrm{m}}}{\partial x} = 0 \qquad \text{Boundary condition at the wall: } x = -L$$

In order to ensure no mass transport at the wall, a *mirror image* of mass slug, with mass M injected at $x = -2L$, is superposed to the real mass slug of mass M injected at $x = 0$. The flow due to the mirror image of the mass slug is superposed onto that due to the mass slug itself. It yields:

$$C_{\mathrm{m}}(x,t) = \frac{M}{\sqrt{4\pi D_{\mathrm{m}} t}} \left(\exp\left(-\frac{x^2}{4D_{\mathrm{m}} t} \right) + \exp\left(-\frac{(x + 2L)^2}{4D_{\mathrm{m}} t} \right) \right) \qquad \text{for } t > 0 \qquad (5.10)$$

Equation (5.10) is the solution of the superposition of two mass slugs of equal mass injected at $x = -2L$ and $x = 0$. It is also the solution of a mass slug injected at $x = 0$ with a solid boundary at $x = -L$.

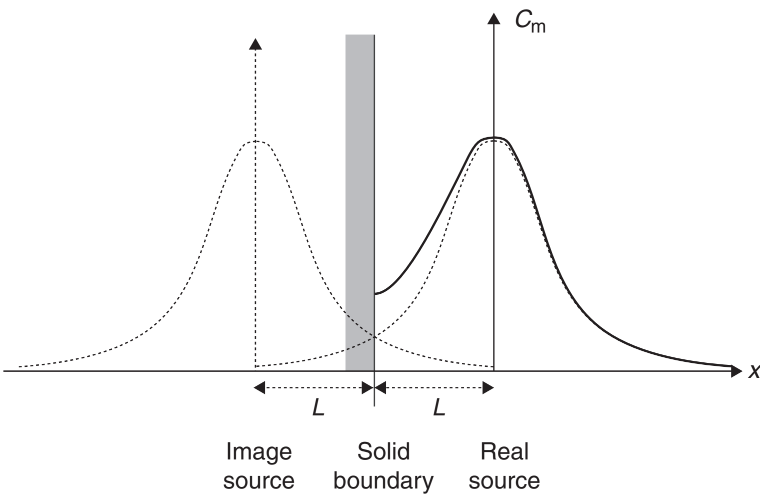

Fig. 5.5 Spread of a sudden concentration increase at the origin with one boundary.

[1] There is no mass flux through a wall and any solid boundary.

Problems involving straight or circular boundaries can be solved by the method of images. Considering a mass slug injected at the origin in between two solid walls located at $x = -L$ and $x = +L$, the solution of the problem is:

$$C_{\mathrm{m}}(x,t) = \frac{M}{\sqrt{4\pi D_{\mathrm{m}} t}} \sum_{i=-\infty}^{+\infty} \exp\left(-\frac{(x+2iL)^2}{4D_{\mathrm{m}}t}\right) \qquad \text{for } t > 0 \tag{5.11}$$

The solution is obtained by adding an infinity of mass slug source on both positive and negative axis (Fischer *et al*. 1979, pp. 47–48).

> ### *Note*
> The method of images is a tool by which straight solid boundaries are treated as symmetry lines. The problem is solved analytically by combining the method of images with the theory of superposition.
>
> In Fig. 5.5, the real slug is located at $x = 0$. The solid boundary is located at $x = -L$. Hence the image slug (or mirror slug) must be located at $x = -2L$ to verify zero mass flux at $x = -L$. (Remember: there is no transport through the boundary.)

5.3 Appendix A – Mathematical aids

Differential operators

Gradient:

$$\overrightarrow{\mathrm{grad}}\ \Phi(x,y,z) = \nabla\Phi(x,y,z) = \vec{\mathbf{i}}\frac{\partial\Phi}{\partial x} + \vec{\mathbf{j}}\frac{\partial\Phi}{\partial y} + \vec{\mathbf{k}}\frac{\partial\Phi}{\partial z} \quad \text{Cartesian coordinate}$$

Divergence:

$$\mathrm{div}\ \vec{\mathrm{F}}(x,y,z) = \nabla\ \vec{\mathrm{F}}(x,y,z) = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$$

Curl:

$$\overrightarrow{\mathrm{curl}}\ \vec{\mathrm{F}}(x,y,z) = \nabla \wedge \vec{\mathrm{F}}(x,y,z) = \vec{\mathbf{i}}\left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}\right) + \vec{\mathbf{j}}\left(\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x}\right) + \vec{\mathbf{k}}\left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right)$$

Laplacian operator:

$$\Delta\Phi(x,y,z) = \nabla \times \nabla\Phi(x,y,z) = \mathrm{div}\ \overrightarrow{\mathrm{grad}}\ \Phi(x,y,z) = \frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial y^2} + \frac{\partial^2\Phi}{\partial z^2}$$

Laplacian of scalar

$$\Delta\ \vec{\mathrm{F}}(x,y,z) = \nabla \times \nabla\ \vec{\mathrm{F}}(x,y,z) = \vec{\mathbf{i}}\ \Delta F_x + \vec{\mathbf{j}}\ \Delta F_y + \vec{\mathbf{k}}\ \Delta F_z \quad \text{Laplacian of vector}$$

Table 5A.1 Values of the error function erf

u	erf(u)	u	erf(u)
0	0	1	0.8427
0.1	0.1129	1.2	0.9103
0.2	0.2227	1.4	0.9523
0.3	0.3286	1.6	0.9763
0.4	0.4284	1.8	0.9891
0.5	0.5205	2	0.9953
0.6	0.6309	2.5	0.9996
0.7	0.6778	3	0.99998
0.8	0.7421	$+\infty$	1
0.9	0.7969		

Error function

The Gaussian error function, or function erf, is defined as:

$$\mathrm{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp(-t^2)\,\mathrm{d}t$$

Tabulated values are given in Table 5A.1. Basic properties of the function are:

$$\mathrm{erf}(0) = 0$$

$$\mathrm{erf}(+\infty) = 1$$

$$\mathrm{erf}(-u) = -\mathrm{erf}(u)$$

$$\mathrm{erf}(u) = \frac{1}{\sqrt{\pi}}\left(u - \frac{u^3}{3\times 1!} + \frac{u^5}{5\times 2!} - \frac{u^7}{7\times 3!} + \cdots\right)$$

$$\mathrm{erf}(u) \approx 1 - \frac{\exp(-u^2)}{\sqrt{\pi}u}\left(1 - \frac{1}{2u^2} - \frac{1\times 3}{\left(2x^2\right)^2} - \frac{1\times 3\times 5}{\left(2x^2\right)^3} + \cdots\right)$$

where $n! = 1 \times 2 \times 3 \times \cdots \times n$.

The complementary Gaussian error function erfc is defined as:

$$\mathrm{erfc}(u) = 1 - \mathrm{erf}(u) = \frac{2}{\sqrt{\pi}} \int_u^{+\infty} \exp(-t^2)\,\mathrm{d}t$$

Note

In first approximation, the function erf(u) may be correlated by:

$$\mathrm{erf}(u) \approx u(1.375511 - 0.61044u + 0.088439u^2) \qquad 0 \le u < 2$$

$$\mathrm{erf}(u) \approx \tanh(1.198787u) \qquad -\infty < u < +\infty$$

with a normalized correlation coefficient of 0.99952 and 0.9992 respectively. In many applications, the above correlations are not accurate enough, and Table 5A.1 should be used.

Notation

x, y, z	Cartesian coordinates
r, θ, z	polar coordinates
$\partial/\partial x$	partial differentiation with respect to the x-coordinate
$\partial/\partial y$, $\partial/\partial z$	partial differential (Cartesian coordinate)
$\partial/\partial r$, $\partial/\partial\theta$	partial differential (polar coordinate)
$\partial/\partial t$	partial differential with respect to time t
$\mathrm{D}/\mathrm{D}t$	absolute derivative
$N!$	N-factorial: $N! = 1 \times 2 \times 3 \times 4 \times \cdots \times (N-1) \times N$

Constants

e	constant such as $\mathrm{Ln(e)} = 1$: $\mathrm{e} = 2.718\,281\,828\,459\,045\,235\,360\,287$
π	$\pi = 3.141\,592\,653\,589\,793\,238\,462\,643$
$\sqrt{2}$	$\sqrt{2} = 1.414\,213\,562\,373\,095\,048\,8$
$\sqrt{3}$	$\sqrt{3} = 1.732\,050\,807\,568\,877\,293\,5$

Mathematical bibliography

Beyer, W.H. (1982). *CRC Standard Mathematical Tables*. (CRC Press Inc.: Boca Raton, Florida, USA).

Korn, G.A. and Korn, T.M. (1961). *Mathematical Handbook for Scientist and Engineers*. (McGraw-Hill Book Comp.: New York, USA).

Spiegel, M.R. (1968). *Mathematical Handbook of Formulas and Tables*. (McGraw-Hill Inc.: New York, USA).

5.4 Exercises

1. A 3.1 kg mass of dye is injected in the centre of large pipe. In the absence of flow and assuming molecular diffusion only, calculate the time at which the mass concentration equals 0.1 g/L at the injection point. *Assume* $\mathrm{D}_m = 0.89 \times 10^{-2}\,m^2/s$.
2. Considering a one-dimensional semi-infinite reservoir bounded at one end by a solid boundary (e.g. a narrow dam reservoir), a 5 kg mass slug of contaminant ($D_\mathrm{m} = 1.1 \times 10^{-2}\,\mathrm{m^2/s}$) is injected 12 m from the straight boundary (e.g. concrete dam wall). Calculate the tracer concentration at the boundary 5 min after injection. Estimate the maximum tracer concentration at the boundary and the time (after injection) at which it occurs.
3. A 10 km long pipeline is full of fresh water. At one end of the pipeline, a contaminant is injected in such a fashion that the contaminant concentration is kept constant and equals 0.14 g/L. Assuming $D_\mathrm{m} = 1.4 \times 10^{-3}\,\mathrm{m^2/s}$ and an infinitely long pipe, calculate the time at which the pollutant concentration exceeds 0.007 and 0.01 g/L at 4.2 km from the injection point.

5.5 Exercise solutions

1. $t = 8500$ s (2 h 21 min).
2. (a) $C_\mathrm{m} = 2.8 \times 10^{-5}\,\mathrm{kg/m^3}$ and (b) $C_\mathrm{m} = 0.2\,\mathrm{kg/m^3}$ and $t = 6480$ s (1.8 h).
3. (a) $t = 18\,900$ days (0.007 g/L) and (b) $t = 22\,000$ days (0.01 g/L).