3 Solutions of the Diffusion Equation

The aim of this chapter is to give the reader a feeling for properties of the diffusion equation and to acquaint her/him with frequently encountered solutions. No attempt is made to achieve completeness or full rigour. Solutions of Eq. (2.6), giving the concentration as a function of time and position, can be obtained by various means once the boundary and initial conditions have been specified. In certain cases, the conditions are geometrically highly symmetric. Then it is possible to obtain explicit analytic solutions. Such solutions comprise either Gaussians, error functions and related integrals, or they are given in the form of Fourier series.

Experiments are often designed to satisfy simple initial and boundary conditions (see Chap. 13). In what follows, we limit ourselves to a few simple cases. First, we consider solutions of steady-state diffusion for linear, axial, and spherical flow. Then, we describe examples of non-steady state diffusion in one dimension. A powerful method of solution, which is mentioned briefly, employs the Laplace transform. We end this chapter with a few remarks about instantaneous point sources in one, two, and three dimensions.

For more comprehensive treatments of the mathematics of diffusion we refer to the textbooks of CRANK [1], JOST [2], GHEZ [3] and GLICKSMAN [4]. As mentioned already, the conduction of heat can be described by an analogous equation. Solutions of this equation have been developed for many practical cases of heat flow and are collected in the book of CARSLAW AND JAEGER [5]. By replacing T with C and D with the corresponding thermal property these solution can be used for diffusion problems as well. In many other cases, numerical methods must be used to solve diffusion problems. Describing numerical procedures is beyond the scope of this book. Useful hints can be found in the literature, e.g., in [1, 3, 4, 6, 7].

3.1 Steady-State Diffusion

At steady state, there is no change of concentration with time. Steady-state diffusion is characterised by the condition

$$\frac{\partial C}{\partial t} = 0\,. \tag{3.1}$$

For the special geometrical settings mentioned in Sect. 2.2, this leads to different *stationary concentration distributions*:

For *linear flow* we get from Eqs. (2.10) and (3.1)

$$D\frac{\partial^2 C}{\partial x^2} = 0 \quad \text{and} \quad C(x) = a + Ax\,, \tag{3.2}$$

where a and A in Eq. (3.2) denote constants. A constant concentration gradient and a linear distribution of concentration is established under linear flow steady-state conditions, if the diffusion coefficient is a constant.

For *axial flow* substitution of Eq. (3.1) into Eq. (2.8) gives

$$\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = 0 \quad \text{and} \quad C(r) = B\ln r + b\,, \tag{3.3}$$

where B and b denote constants.

For *spherical flow* substitution of Eq. (3.1) into Eq. (2.9) gives

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = 0 \quad \text{and} \quad C(r) = \frac{C_a}{r} + C_b\,. \tag{3.4}$$

C_a and C_b in Eq. (3.4) denote constants.

Permeation through membranes: The passage of gases or vapours through membranes is called *permeation*. A well-known example is diffusion of hydrogen through palladium membranes. A steady state can be established in permeation experiments after a certain transient time (see Sect. 3.2.4). Based on Eqs. (3.2), (3.3), and (3.4) a number of examples are easy to formulate and are useful in permeation studies of diffusion:

Planar Membrane: If δ is the thickness, q the cross section of a planar membrane, and C_1 and C_2 the concentrations at $x = 0$ and $x = \delta$, we get from Eq. (3.2)

$$C(x) = C_1 + \frac{C_2 - C_1}{\delta}x; \quad J = qD\frac{C_1 - C_2}{\delta}\,. \tag{3.5}$$

If J, C_1, and C_2 are measured in an experiment, the diffusion coefficient can be determined from Eq. (3.5).

Hollow cylinder: Consider a hollow cylinder, which extends from an inner radius r_1 to an outer radius r_2. If at r_1 and r_2 the stationary concentrations C_1 and C_2 are maintained, we get from Eq. (3.3)

$$C(r) = C_1 + \frac{C_1 - C_2}{\ln(r_1/r_2)}\ln\frac{r}{r_1}\,. \tag{3.6}$$

Spherical shell: If the shell extends from an inner radius r_1 to an outer radius r_2, and if at r_1 and r_2 the stationary concentrations C_1 and C_2 are maintained, we get from Eq. (3.4)

$$C(r) = \frac{C_1 r_1 - C_2 r_2}{r_1 - r_2} + \frac{(C_1 - C_2)}{(\frac{1}{r_1} - \frac{1}{r_2})}\frac{1}{r}\,. \tag{3.7}$$

For the geometrical conditions treated above, it is also possible to solve the steady-state equations, if the diffusion coefficient is not a constant [8]. Solutions for concentration-dependent and position-dependent diffusivities can be found, e.g., in the textbook of JOST [2].

3.2 Non-Steady-State Diffusion in one Dimension

3.2.1 Thin-Film Solution

An initial condition at $t = 0$, which is encountered in many one-dimensional diffusion problems, is the following:

$$C(x,0) = M\,\delta(x)\,. \tag{3.8}$$

The diffusing species (diffusant) is deposited at the plane $x = 0$ and allowed to spread for $t > 0$. M denotes the number of diffusing particles per unit area and $\delta(x)$ the Dirac delta function. This initial condition is also called *instantaneous planar source.*

Sandwich geometry: If the diffusant (or diffuser) is allowed to spread into two material bodies occupying the half-spaces $0 < x < \infty$ and $-\infty < x < 0$, which have equal and constant diffusivity, the solution of Eq. (2.10) is

$$C(x,t) = \frac{M}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right). \tag{3.9}$$

Thin-film geometry: If the diffuser is deposited initially onto the surface of a sample and spreads into one half-space, the solution is

$$C(x,t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right). \tag{3.10}$$

These solutions are also denoted as *Gaussian solutions.* Note that Eqs. (3.9) and (3.10) differ by a factor of 2. Equation (3.10) is illustrated in Fig. 3.1 and some of its further properties in Fig. 3.2.

The quantity $2\sqrt{Dt}$ is a characteristic *diffusion length*, which occurs frequently in diffusion problems. Salient properties of Eq. (3.9) are the following:

1. The diffusion process is subject to the conservation of the integral number of diffusing particles, which for Eq. (3.9) reads

$$\int_{-\infty}^{+\infty} \frac{M}{2\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \mathrm{d}x = \int_{-\infty}^{+\infty} M\delta(x)\mathrm{d}x = M\,. \tag{3.11}$$

2. $C(x,t)$ and $\partial^2 C/\partial x^2$ are *even* functions of x. $\partial C/\partial x$ is an *odd* function of x.

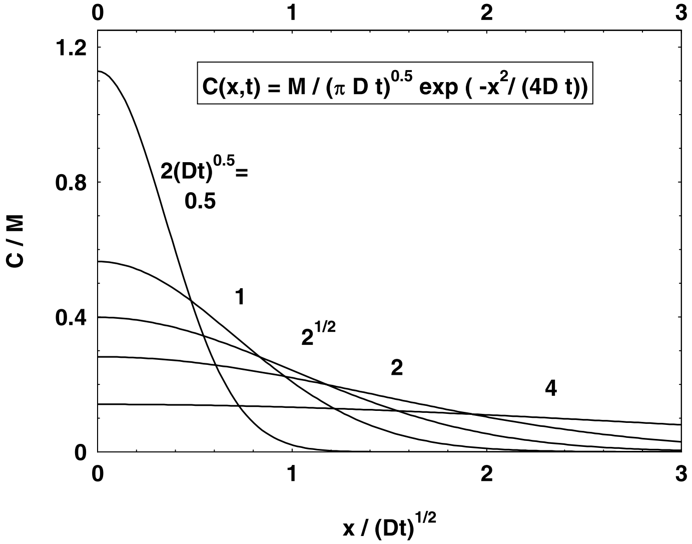

Fig. 3.1. Gaussian solution of the diffusion equation for various values of the diffusion length $2\sqrt{Dt}$

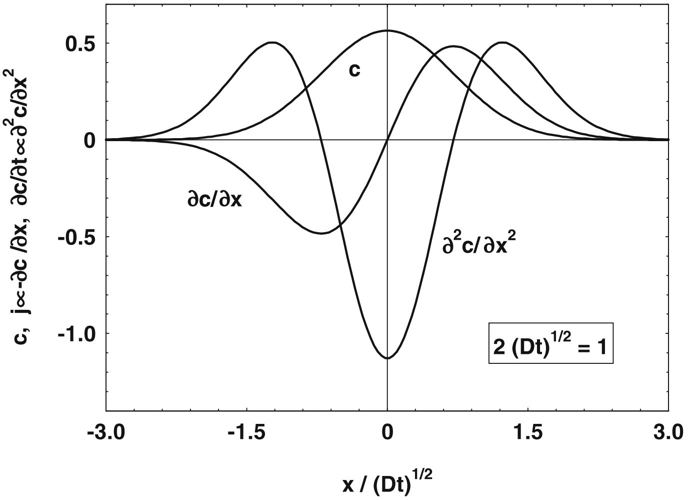

Fig. 3.2. Gaussian solution of the diffusion equation and its derivatives

3. The diffusion flux, $J = -D\partial C/\partial x$, is an *odd* function of x. It is zero at the plane $x = 0$.
4. According to the diffusion equation the rate of accumulation of the diffusing species $\partial C/\partial t$ is an *even* function of x. It is negative for small $|x|$ und positive for large $|x|$.

The tracer method for the experimental determination of diffusivities exploits these properties (see Chap. 13). The Gaussian solutions are also applicable if the thickness of the deposited layer is very small with respect to the diffusion length.

3.2.2 Extended Initial Distribution and Constant Surface Concentration

So far, we have considered solutions of the diffusion equation when the diffusant is initially concentrated in a very thin layer. Experiments are also often designed in such a way that the diffusant is distributed over a finite region. In practice, the diffusant concentration is often kept constant at the surface of the sample. This is, for example, the case during carburisation or nitridation experiments of metals. The linearity of the diffusion equation permits the use of the 'principle of superposition' to produce new solutions for different geometric arrangements of the sources. In the following, we consider examples which exploit this possibility.

Diffusion Couple: Let us suppose that the diffusant has an initial distribution at $t = 0$ which is given by:

$$C = C_0 \quad \text{for} \quad x < 0 \quad \text{and} \quad C = 0 \quad \text{for} \quad x > 0\,. \tag{3.12}$$

This situation holds, for example, when two semi-infinite bars differing in composition (e.g., a dilute alloy and the pure solvent material) are joined end to end at the plane $x = 0$ to form a diffusion couple. The initial distribution can be interpreted as a continuous distribution of instantaneous, planar sources of infinitesimal strength $\mathrm{d}M = C_0 \mathrm{d}\xi$ at position ξ spread uniformly along the left-hand bar, i.e. for $x < 0$. A unit length of the left-hand bar initially contains $M = C_0 \cdot 1$ diffusing particles per unit area. Initially, the right-hand bar contains no diffusant, so one can ignore contributions from source points $\xi > 0$. The solution of this diffusion problem, $C(x,t)$, may be thought as the sum, or integral, of all the infinitesimal responses resulting from the continuous spatial distribution of instantaneous source releases from positions $\xi < 0$. The total response occurring at any plane x at some later time t is given by the superposition

$$C(x,t) = C_0 \int\limits_{-\infty}^{0} \frac{\exp\left[-(x-\xi)^2/4Dt\right]}{2\sqrt{\pi D t}} \mathrm{d}\xi = \frac{C_0}{\sqrt{\pi}} \int\limits_{x/2\sqrt{Dt}}^{\infty} \exp(-\eta^2)\mathrm{d}\eta\,. \tag{3.13}$$

Here we used the variable substitution $\eta \equiv (x-\xi)/2\sqrt{Dt}$. The right-hand side of Eq. (3.13) may be split and rearranged as

$$C(x,t) = \frac{C_0}{2}\left[\frac{2}{\sqrt{\pi}}\int\limits_{0}^{\infty} \exp(-\eta^2)\mathrm{d}\eta - \frac{2}{\sqrt{\pi}}\int\limits_{0}^{x/2\sqrt{Dt}} \exp(-\eta^2)\mathrm{d}\eta\right]. \tag{3.14}$$

It is convenient to introduce the *error function*[1]

$$\operatorname{erf}(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2)\mathrm{d}\eta\,, \tag{3.15}$$

which is a standard mathematical function. Some properties of $\operatorname{erf}(z)$ and useful approximations are discussed below. Introducing the error function we get

$$C(x,t) = \frac{C_0}{2}\left[\operatorname{erf}(\infty) - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \equiv \frac{C_0}{2}\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{3.16}$$

where the abbreviation

$$\operatorname{erfc}(z) \equiv 1 - \operatorname{erf}(z) \tag{3.17}$$

is denoted as the *complementary error function.* Like the thin-film solution, Eq. (3.16) is applicable when the diffusivity is constant. Equation (3.16) is sometimes called the *Grube-Jedele solution.*

Diffusion with Constant Surface Concentration: Let us suppose that the concentration at $x = 0$ is maintained at concentration $C_s = C_0/2$. The Grube-Jedele solution Eq. (3.16) maintains the concentration in the midplane of the diffusion couple. This property can be exploited to construct the diffusion solution for a semi-infinite medium, the free end of which is continuously exposed to a fixed concentration C_s:

$$C = C_s \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \tag{3.18}$$

The quantity of material which diffuses into the solid per unit area is:

$$M(t) = 2C_s\sqrt{Dt/\pi}\,. \tag{3.19}$$

Equation (3.18) is illustrated in Fig. 3.3. The behaviour of this solution reveals several general features of diffusion problems in infinite or semi-infinite media, where the initial concentration at the boundary equals some constant for all time: The concentration field $C(x,t)$ in these cases may be expressed with

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[1] The *probability integral* introduced by GAUSS is defined as

$$\Phi(a) \equiv \frac{2}{\sqrt{2\pi}} \int_0^a \exp(-\eta^2/2)\mathrm{d}\eta\,.$$

The error function and the probability integral are related via

$$\operatorname{erf}(z) = \Phi(\sqrt{2}z)\,.$$

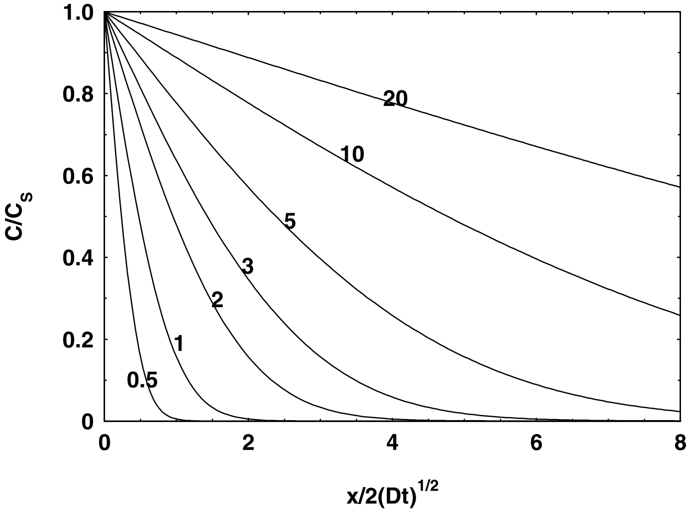

Fig. 3.3. Solution of the diffusion equation for constant surface concentration C_s and for various values of the diffusion length $2\sqrt{Dt}$

a single variable $z = x/2\sqrt{Dt}$, which is a special combination of space-time field variables. The quantity z is sometimes called a similarity variable which captures both, the spatial and temporal features of the concentration field. Similarity scaling is extremely useful in applying the diffusion solution to diverse situations. For example, if the average diffusion length is increased by a factor of ten, the product of the diffusivity times the diffusion time would have to increase by a factor of 100 to return to the same value of z.

Applications of Eq. (3.18) concern, e.g., carburisation or nitridation of metals, where in-diffusion of C or N into a metal occurs from an atmosphere, which maintains a constant surface concentration. Other examples concern in-diffusion of foreign atoms, which have a limited solubility, C_s, in a matrix.

Diffusion from a Slab Source: In this arrangement a slab of width $2h$ having a uniform initial concentration C_0 of the diffusant is joined to two half-spaces which, in an experiment may be realised as two bars of the pure material. If the slab and the two bars have the same diffusivity, the diffusion field can be expressed by an integral of the source distribution

$$C(x,t) = \frac{C_0}{2\sqrt{\pi D t}} \int\limits_{-h}^{+h} \exp\left[-\frac{(x-\xi)^2}{4Dt}\right] \mathrm{d}\xi \,. \tag{3.20}$$

This expression can be manipulated into standard form and written as

$$C(x,t) = \frac{C_0}{2}\left[\operatorname{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right] . \tag{3.21}$$

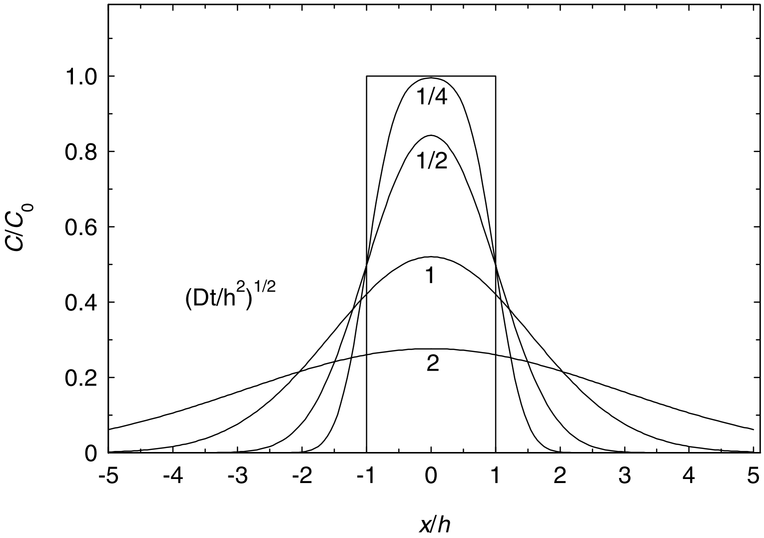

Fig. 3.4. Diffusion from a slab of width $2h$ for various values of $\sqrt{Dt}/h$

The normalised concentration field, $C(x/h, t)/C_0$, resulting from Eq. (3.21) is shown in Fig. 3.4 for various values of $\sqrt{Dt}/h$.

Error Function and Approximations: The error function defined in Eq. (3.15) is an odd function and for large arguments $|z|$ approaches asymptotically ± 1:

$$\operatorname{erf}(-z) = \operatorname{erf}(z), \quad \operatorname{erf}(\pm\infty) = \pm 1, \quad \operatorname{erf}(0) = 0\,. \tag{3.22}$$

The complementary error function defined in Eq. (3.17) has the following asymtotic properties:

$$\operatorname{erfc}(-\infty) = 2, \quad \operatorname{erfc}(+\infty) = 0, \quad \operatorname{erfc}(0) = 1\,. \tag{3.23}$$

Tables of the error function are available in the literature, e.g., in [4, 9–11].

Detailed calculations cannot be performed just relying on tabular data. For advanced computations and for graphing one needs, instead, numerical estimates for the error function. Approximations are available in commercial mathematics software. In the following, we mention several useful expressions:

1. For small arguments, $|z| < 1$, the error function is obtained to arbitrary accuracy from its Taylor expansion [10] as

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \left[z - \frac{z^3}{(3 \times 1)!} + \frac{z^5}{(5 \times 2)!} - \frac{z^7}{(7 \times 3)!} + \ldots \right]. \tag{3.24}$$

2. For large arguments, $z \gg 1$, it is approximated by its asymptotic form

$$\mathrm{erf}(z) = 1 - \frac{\exp(-z^2)}{2\sqrt{\pi}} \left(1 - \frac{1}{2z^2} + \dots\right). \tag{3.25}$$

3. A convenient rational expression reported in [11] is the following:

$$\begin{aligned}\mathrm{erf}\,(z) = 1 - &\frac{1}{(1 + 0.278393z + 0.230389z^2 + 0.000972z^3 + 0.078108z^4)^4} \\ &+ \epsilon(z)\,. \end{aligned} \tag{3.26}$$

   This expression works for $z > 0$ with an associated error $\epsilon(z)$ less than 5×10^{-4}.

3.2.3 Method of Laplace Transformation

The Laplace transformation is a mathematical procedure, which is useful for various problems in mathematical physics. Application of the Laplace transformation to the diffusion equation removes the time variable, leaving an ordinary differential equation, the solution of which yields the transform of the concentration field. This is then interpreted to give an expression for the concentration in terms of space variables and time, satisfying the initial and boundary conditions. Here we deal only with an application to the one-dimensional diffusion equation, the aim being to describe rather than to justify the procedure.

The solution of many problems in diffusion by this method calls for no knowledge beyond ordinary calculus. For more difficult problems the theory of functions of a complex variable must be used. No attempt is made here to explain problems of this kind, although solutions obtained in this way are quoted, e.g., in the chapter on grain-boundary diffusion. Fuller accounts of the method and applications can be found in the textbooks of CRANK [1], CARSLAW AND JAEGER [5], CHURCHILL [12] and others.

Definition of the Laplace Transform: The Laplace transform $\bar{f}(p)$ of a known function $f(t)$ for positive values of t is defined as

$$\bar{f}(p) = \int_0^\infty \exp(-pt) f(t) \mathrm{d}t\,. \tag{3.27}$$

p is a number sufficiently large to make the integral Eq. (3.27) converge. It may be a complex number whose real part is sufficiently large, but in the following discussion it suffices to think of it in terms of a real positive number.

Laplace transforms are common functions and readily constructed by carrying out the integration in Eq. (3.27) as in the following examples:

$$f(t) = 1, \qquad \bar{f}(p) = \int_0^\infty \exp(-pt)\mathrm{d}t = \frac{1}{p}\,, \tag{3.28}$$

$$f(t) = \exp(\alpha t), \qquad \bar{f}(p) = \int_0^\infty \exp(-pt)\exp(\alpha t)\mathrm{d}t = \frac{1}{p-\alpha}\,, \tag{3.29}$$

$$f(t) = \sin(\omega t), \qquad \bar{f}(p) = \int_0^\infty \exp(-pt)\sin(\omega t)\mathrm{d}t = \frac{\omega}{p^2+\omega^2}\,. \tag{3.30}$$

Semi-infinite Medium: As an application of the Laplace transform, we consider diffusion in a semi-infinite medium, $x > 0$, when the surface is kept at a constant concentration C_s. We need a solution of Fick's equation satisfying this boundary condition and the initial condition $C = 0$ at $t = 0$ for $x > 0$. On multiplying both sides of Fick's second law Eq. (2.6) by $\exp(-pt)$ and integrating, we obtain

$$D\int_0^\infty \exp(-pt)\frac{\partial^2 C}{\partial x^2}\mathrm{d}t = \int_0^\infty \exp(-pt)\frac{\partial C}{\partial t}\mathrm{d}t\,. \tag{3.31}$$

By interchanging the orders of differentiation and integration, the left-hand term is then

$$D\int_0^\infty \exp(-pt)\frac{\partial^2 C}{\partial x^2}\mathrm{d}t = D\frac{\partial^2}{\partial x^2}\int_0^\infty C\exp(-pt)\mathrm{d}t = D\frac{\partial^2 \bar{C}}{\partial x^2}\,. \tag{3.32}$$

Integrating the right-hand term of Eq. (3.31) by parts, we have

$$\int_0^\infty \exp(-pt)\frac{\partial C}{\partial t}\mathrm{d}t = \left[C\exp(-pt)\right]_0^\infty + p\int_0^\infty C\exp(-pt)\mathrm{d}t = p\bar{C}\,, \tag{3.33}$$

since the term in brackets vanishes by virtue of the initial condition and through the exponential factor. Thus Fick's second equation transforms to

$$D\frac{\partial^2 \bar{C}}{\partial x^2} = p\bar{C}\,. \tag{3.34}$$

The Laplace transformation reduces Fick's second law from a partial differential equation to the ordinary differential equation Eq. (3.34). By treating the boundary condition at $x = 0$ in the same way, we obtain

$$\bar{C} = \int_0^\infty C_s\exp(-pt)\mathrm{d}t = \frac{C_s}{p}\,. \tag{3.35}$$

The solution of Eq. (3.34), which satisfies the boundary condition and for which $\bar{C}$ remains finite for large x is

$$\bar{C} = \frac{C_s}{p} \exp\left(\sqrt{\frac{p}{D}}\right) x \,. \tag{3.36}$$

Reference to a table of Laplace transforms [1] shows that the function whose transform is given by Eq. (3.36) is the complementary error function

$$C = C_s \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) . \tag{3.37}$$

We recognise that this is the solution given already in Eq. (3.16).

3.2.4 Diffusion in a Plane Sheet – Separation of Variables

Separation of variables is a mathematical method, which is useful for the solution of partial differential equations and can also be applied to diffusion problems. It is particularly suitable for solutions of Fick's law for finite systems by assuming that the concentration field can be expressed in terms of a periodic function in space and a time-dependent function. We illustrate this method below for the problem of diffusion in a plane sheet.

The starting point is to strive for solutions of Eq. (2.10) trying the 'Ansatz'

$$C(x,t) = X(x)T(t) \,, \tag{3.38}$$

where $X(x)$ and $T(t)$ separately express spatial and temporal functions of x and t, respectively. In the case of linear flow, Fick's second law Eq. (2.10) yields

$$\frac{1}{DT}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} \,. \tag{3.39}$$

In this equation the variables are separated. On the left-hand side we have an expression depending on time only, while the right-hand side depends on the distance variable only. Then, both sides must equal the same constant, which for the sake of the subsequent algebra is chosen as $-\lambda^2$:

$$\frac{1}{DT}\frac{\partial T}{\partial t} = \frac{1}{X}\frac{\partial^2 X}{\partial^2 x} \equiv -\lambda^2 \,. \tag{3.40}$$

We then arrive at two ordinary linear differential equations: one is a first-order equation for $T(t)$, the other is a second-order equation for $X(x)$. Solutions to each of these equations are well known:

$$T(t) = T_0 \exp\left(-\lambda^2 Dt\right) \tag{3.41}$$

and

$$X(x) = a\ \sin(\lambda x)\ +\ b\cos(\lambda x) \,, \tag{3.42}$$

where T_0, a, and b are constants. Inserting Eqs. (3.41) and (3.42) in (3.38) yields a particular solution of the form

$$C(x,t) = [A\sin(\lambda x) + B\cos(\lambda x)]\exp(-\lambda^2 Dt)\,, \tag{3.43}$$

where $A = aT_0$ and $B = bT_0$ are again constants of integration. Since Eq. (2.10) is a linear equation its general solution is obtained by summing solutions of the type of Eq. (3.43). We get

$$C(x,t) = \sum_{n=1}^{\infty}[A_n\sin(\lambda_n x) + B_n\cos(\lambda_n x)]\exp(-\lambda_n^2 Dt)\,, \tag{3.44}$$

where A_n, B_n and λ_n are determined by the initial and boundary conditions for the particular problem. The separation constant $-\lambda^2$ cannot be arbitrary, but must take discrete values. These *eigenvalues* uniquely define the eigenfunctions of which the concentration field $C(x,t)$ is composed.

Out-diffusion from a plane sheet: Let us consider out-diffusion from a plane sheet of thickness L. An example provides out-diffusion of hydrogen from a metal sheet during degassing in vacuum. The diffusing species is initially distributed with constant concentration C_0 and both surfaces of the sheet are kept at zero concentration for times $t > 0$:

Initial condition $C = C_0$, for $0 < x < L$ at $t = 0$
Boundary condition $C = 0$, for $x = 0$ and $x = L$ at $t > 0$.

The boundary conditions demand that

$$B_n = 0 \quad \text{and} \quad \lambda_n = \frac{n\pi}{L}\,, \quad \text{where} \quad n = 1,2,3,\ldots \tag{3.45}$$

The numbers λ_n are the eigenvalues of the plane-sheet problem. Inserting these eigenvalues, Eq. (3.44) reads

$$C(x,t) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi}{L}x\right)\exp\left(-\frac{n^2\pi^2 D}{L^2}t\right). \tag{3.46}$$

The initial conditions require that

$$C_0 = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi}{L}x\right). \tag{3.47}$$

By multiplying both sides of Eq. (3.47) by $\sin(p\pi x/L)$ and integrating from 0 to L we get

$$\int_0^L \sin\left(\frac{p\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\mathrm{d}x = 0 \tag{3.48}$$

for $n \neq p$ and $L/2$ for $n = p$. Using these orthogonality relations all terms vanish for which n is even. Thus

$$A_n = \frac{4C_0}{n\pi}; \quad n = 1, 3, 5, \ldots \tag{3.49}$$

The final solution of the problem of out-diffusion from a plane sheet is

$$C(x,t) = \frac{4C_0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left[\frac{(2j+1)\pi}{L} x\right] \exp\left[-\frac{(2j+1)^2 \pi^2 D}{L^2} t\right], \tag{3.50}$$

where for convenience $2j + 1$ was substituted for n so that j takes values $0, 1, 2, \ldots$. Each term in Eq. (3.50) corresponds to a term in the *Fourier series* (here a trigonometrical series) by which for $t = 0$ the initial distribution Eq. (3.47) can be represented. Each term is also characterised by a relaxation time

$$\tau_j = \frac{L^2}{(2j+1)^2 \pi^2 D}, \quad j = 0, 1, 2, \ldots \tag{3.51}$$

The relaxation times decrease rapidly with increasing j, which implies that the series Eq. (3.50) converges satisfactorily for moderate and large times.

Desorption and Absorption: It is sometimes of interest to consider the average concentration in the sheet, $\bar{C}$, defined as

$$\bar{C}(t) = \frac{1}{L} \int_0^L C(x,t) dx \,. \tag{3.52}$$

Inserting Eq. (3.50) into Eq. (3.52) yields

$$\frac{\bar{C}(t)}{C_0} = \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\frac{t}{\tau_j}\right). \tag{3.53}$$

We recognise that for $t \gg \tau_1$ the average concentration decays exponentially with the relaxation time

$$\tau_0 = \frac{L^2}{\pi^2 D} \,. \tag{3.54}$$

Direct applications of the solution developed above concern degassing of a hydrogen-charged metal sheet in vacuum or decarburisation of a sheet of steel. If we consider the case $t \gg \tau_1$, we get

$$C(x,t) \approx \frac{4C_0}{\pi} \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{t}{\tau_0}\right). \tag{3.55}$$

The diffusion flux from both surfaces is then given by

$$|J| = 2D \left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{8DC_0}{L} \exp\left(-\frac{t}{\tau_0}\right). \tag{3.56}$$

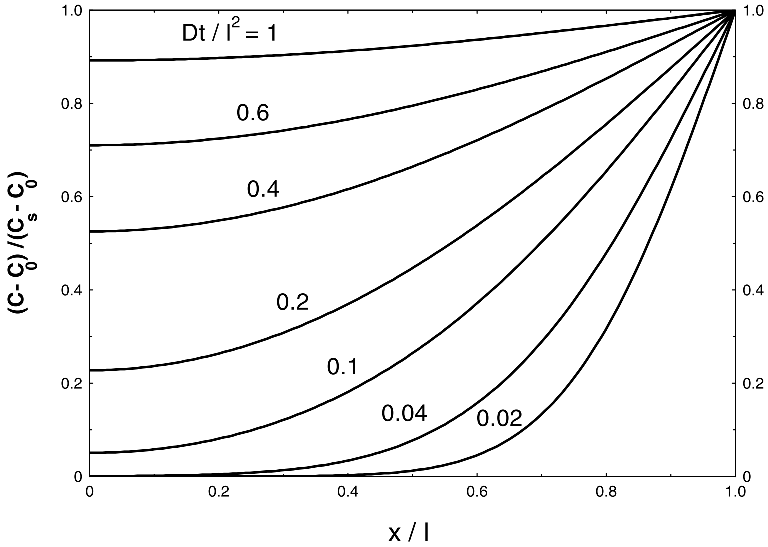

Fig. 3.5. Absorption/desorption of a diffusing species of/from a thin sheet for various values of Dt/l^2

An experimental determination of $|J|$ and/or of the relaxation time τ_0 can be used to measure D.

The solution for a plane sheet with constant surface concentration maintained at C_s and uniform initial concentration C_0 inside the sheet (region $-l < x < +l$) is a straightforward generalisation of Eq. (3.50). We get

$$\frac{C - C_0}{C_s - C_0} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{(-1)^j}{2j+1} \cos\left[\frac{(2j+1)\pi}{2l} x\right] \exp\left[-\frac{(2j+1)^2 \pi^2 D}{4l^2} t\right] . \tag{3.57}$$

For $C_s < C_0$ this solution describes *desorption* and for $C_s > C_0$ *absorption.* It is illustrated for various normalised times Dt/l^2 in Fig. 3.5.

3.2.5 Radial Diffusion in a Cylinder

We consider a long circular cylinder, in which the diffusion flux is radial everywhere. Then the concentration is a function of radius r and time t, and the diffusion equation becomes

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right) . \tag{3.58}$$

Following the method of separation of the variables, we see that for constant D

$$C(r,t) = u(r) \exp(-D\alpha^2 t) \tag{3.59}$$

is a solution of Eq. (3.58), provided that u satisfies

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \alpha^2 u = 0\,, \tag{3.60}$$

which is the *Bessel equation* of order zero. Solutions may be obtained in terms of *Bessel functions*, suitably chosen so that the initial and boundary conditions are satisfied.

Let us suppose that the surface concentration is constant and that the initial distribution of the diffusant is $f(r)$. For a cylinder of radius R, the conditions are:

$$\begin{aligned} &C = C_0, && r = R, && t \geq 0\,; \\ &C = f(r), && 0 < r < R, && t = 0\,. \end{aligned}$$

The solution to this problem is [1]

$$\begin{aligned} C(r,t) &= C_0\left[1 - \frac{2}{R}\sum_{n=1}^{\infty}\frac{1}{\alpha_n}\frac{J_0(r\alpha_n)}{J_1(R\alpha_n)}\exp(-D\alpha_n^2 t)\right] \\ &+\frac{2}{R^2}\sum_{n=1}^{\infty}\exp(-D\alpha_n^2 t)\frac{J_0(r\alpha_n)}{J_1^2(R\alpha_n)}\int rf(r)J_0(r\alpha_n)\mathrm{d}r\,. \end{aligned} \tag{3.61}$$

In Eq. (3.61) J_0 is the Bessel function of the first kind and order zero and J_1 the Bessel function of first order. The α_n are the positive roots of $J_0(R\alpha_n) = 0$.

If the concentration is initially uniform throughout the cylinder, we have $f(r) = C_1$ and Eq. (3.61) reduces to

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{R}\sum_{n=1}^{\infty}\frac{\exp(-D\alpha_n^2 t)J_0(\alpha_n r)}{\alpha_n J_1(\alpha_n R)}\,. \tag{3.62}$$

If $M(t)$ denotes the quantity of diffusant which has entered or left the cylinder in time t and $M(\infty)$ the corresponding quantity at infinite time, we have

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=1}^{\infty}\frac{4}{\alpha_n^2 R^2}\exp(-D\alpha_n^2 t)\,. \tag{3.63}$$

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3.2.6 Radial Diffusion in a Sphere

The diffusion equation for a constant diffusivity and radial flux takes the form

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right)\,. \tag{3.64}$$

By substituting

$$u(r,t) = C(r,t)r\,, \tag{3.65}$$

Eq. (3.64) becomes

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial r^2}\,. \tag{3.66}$$

This equation is analogous to linear flow in one dimension. Therefore, solutions of many problems of radial flow in a sphere can be deduced from those of the corresponding linear flow problems.

If we suppose that the sphere is initially at a uniform concentration C_1 and the surface concentration is maintained constant at C_0, the solution is [1]

$$\frac{C - C_1}{C_0 - C_1} = 1 + \frac{2R}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi r}{R}\right)\exp(-Dn^2\pi^2 t/R^2)\,. \tag{3.67}$$

The concentration at the centre is given by the limit $r \to 0$, that is by

$$\frac{C - C_1}{C_0 - C_1} = 1 + 2\sum_{n=1}^{\infty}(-1)^n\exp(-Dn^2\pi^2 t/R^2)\,. \tag{3.68}$$

If $M(t)$ denotes the quantity of diffusant which has entered or left the sphere in time t and $M(\infty)$ the corresponding quantity at infinite time, we have

$$\frac{M(t)}{M(\infty)} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-Dn^2\pi^2 t/R^2)\,. \tag{3.69}$$

The corresponding solutions for small times are

$$\frac{C - C_1}{C_0 - C_1} = \frac{R}{r}\sum_{n=0}^{\infty}\left[\operatorname{erfc}\frac{(2n+1) - r}{2\sqrt{Dt}} - \operatorname{erfc}\frac{(2n+1) + r}{2\sqrt{Dt}}\right] \tag{3.70}$$

and

$$\frac{M(t)}{M(\infty)} = 6\sqrt{\frac{Dt}{R^2}}\left[\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}\operatorname{ierfc}\frac{nR}{\sqrt{Dt}}\right] - 3\frac{Dt}{R^2}\,, \tag{3.71}$$

where ierfc denotes the inverse of the complementary error function.

3.3 Point Source in one, two, and three Dimensions

In the previous section, we have dealt with one-dimensional solutions of the linear diffusion equation. As examples for diffusion in higher dimensions, we consider now diffusion from instantaneous sources in two- and three-dimensional media.

The diffusion response for a point source in three dimensions and for a line source in two dimensions differs from that of the thin-film source in one dimension given by Eq. (3.9). Now we ask for particular solutions of

Fick' second law under spherical or axial symmetry conditions described by Eqs. (2.12) and (2.11). Let us suppose that in the case of spherical flow a point source located at $|\boldsymbol{r}_3| = 0$ releases at time $t = 0$ a fixed number N_3 of diffusing particles into an infinite and isotropic medium. Let us also suppose that in the case of axial flow a line source located at $|\boldsymbol{r}_2| = 0$ releases N_2 diffusing particles into an infinite and isotropic medium. The diffusion flow will be either spherical or axisymmetric, respectively. The concentration fields that develop around instantaneous plane-, line-, and point-sources in one, two, three dimensions, can all be expressed in homologous form by

$$C(\boldsymbol{r}_d, t) \;=\; \frac{N_d}{(4\pi Dt)^{d/2}} \exp\left(-\frac{|\boldsymbol{r}_d|^2}{4Dt}\right) \quad (d = 1, 2, 3). \tag{3.72}$$

In Eq. (3.72) $\boldsymbol{r}_d$ denotes the d-component vector extending from the source located at $\boldsymbol{r}_d = 0$ to the field point, $\boldsymbol{r}_d$, of the concentration field. If the source strength N_d denotes the number of particles in all three dimensions, the diffusion fields predicted by Eq. (3.72) must be expressed in dimensionality-compatible concentration units. These are [*number per length*] for $d = 1$, [*number per length*^{2}] for $d = 2$, and [*number per length*^{3}] for $d = 3$. We note that the source solutions are all linear, in the sense that the concentration response is proportional to the initial source strength.

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