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Chapter 2

Brownian motion, random walks, and the diffusion equation

Diffusion is a process by which atoms move through solids, liquids or gases. In both the liquid and gaseous states, diffusion is rapid in comparison to the solid state diffusion because of the openness of their structures, which means that entropic effects counteract the effects of interatomic forces. In solids, the rigid packing of atoms resulting from the dominance of the interatomic forces causes diffusion to be a much slower process because, whatever the mechanism for atomic motion, interatomic bonds must be deformed. Phase transformations, in particular, are often accompanied by the transport of matter that is mediated by diffusion of atoms through the solid. The effectiveness of solid state diffusion depends on factors such as the size of the atom in relation to the host, steric constraints determined by the local environment of the mobile atom, the microstructure of the host, and the temperature.

In this chapter, we begin our discussion of diffusion in solids by developing the diffusion equation. This equation provides the mathematical description of how the concentration of mobile species evolves in various geometries and spatial dimensions. The factors that affect diffusion are subsumed into a coefficient called the diffusion constant. The determination of the diffusion constant either from direct experimental measurement or from first-principles calculations is a central concern in the kinetics of materials.

Our discussion starts with a brief summary of Brownian motion, which was the experimental impetus for the theoretical foundation of diffusion. Brownian motion will then be abstracted into the random walk, the prototypical random process, which will be used to derive the diffusion equation in one spatial dimension. This will provide the basis for our discussion of atomic diffusion mechanisms in solids, which is the subject of the next chapter. We then consider a more macroscopic development of diffusion based on Fick's laws. This is a more direct route to the diffusion equation, but is essentially phenomenological, and has only a tenuous

relation to the underlying microscopic processes. We conclude with a derivation of the fundamental solution of the diffusion equation and consider some examples of diffusion in various geometries.

2.1 Random walks and Brownian motion

2.1.1 Brownian motion

In 1827, the Scottish botanist Robert Brown used a microscope to observe the random motion of pollen immersed in water. Albert Einstein (1956), in papers published between 1905 and 1908, pointed out that this motion is caused by the random bombardment of the pollen by thermally excited water molecules (which are invisible under the microscope) and put forward a theory to account for these observations. In fact, the theory of Brownian motion was set out five years earlier by the French mathematician Louis Bachelier in his thesis on price fluctuations in financial markets. But this work went largely unnoticed until the 1960s, when the mathematical theory of finance was being developed and the significance of Bachelier's work was finally appreciated.

Figure 2.1(a) shows the trajectory of a test particle in a two-dimensional simulation of Brownian motion based on a system of particles with only contact interactions and whose collisions are elastic. Most evident from this figure is the erratic motion of the particle, showing both long paths between collisions as well as periods during which the collisions are more frequent. The collision frequency depends on factors such as the temperature, the density of the gas, and the relative sizes of the test and gas particles, but the basic phenomenology has been observed for a broad range of systems and conditions.

To develop a theory of Brownian motion, we consider the basic experimental observations modeled in figure 2.1(a). Each particle in a Brownian environment undergoes random collisions resulting in the erratic motion noted above. There are also periods where a particle experiences no collisions, during which the motion of
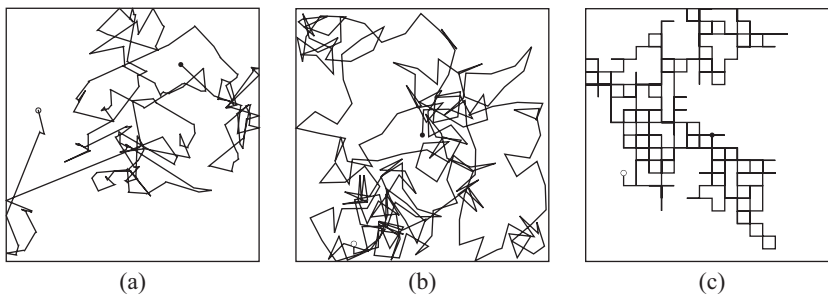

(a)   (b)   (c)

Figure 2.1. (a) Simulation of Brownian motion showing the trajectory of a test particle in a gas. There are only contact interactions between the gas particles and the collisions between particles are elastic. (b) Two-dimensional random walk in which the step length is fixed, but the angle of the next step is chosen randomly. (c) Two-dimensional random walk on a square lattice, where motion along the x- and y-directions are chosen by separate trials whose outcomes are each ± 1 lattice spacing. Reflecting boundary conditions are used in all simulations. The initial position is indicated by a filled circle, and the final position by an unfilled circle.

the particle is ballistic. This tells us that we must abandon Newtonian mechanics as the fundamental equation of the motion of the system as a whole, but instead must rely on a statistical description. Newton's equation of motion can, however, be used to describe the trajectories of individual particles, including collisions and trajectories. In the limit of long-times, entropy is maximized and the Maxwell speed distribution is obtained.

Figure 2.1(b) shows a random walk in which successive steps are the same length, but with a direction selected randomly from the range $(0, 2\pi]$. Any apparent similarities between this random walk and Brownian motion is due to the particular realization. What may appear as a ballistic or near-ballistic trajectory results from a particular choice of angles. Figure 2.1(c) shows a random walk on a two-dimensional square lattice. Each trial indicates the direction of a step whose length is the lattice spacing, either forward or backward along the x-direction, and similarly along the y-direction. This model is appropriate for the motion of atoms within the crystal structure of another material, as will be discussed in the next chapter.

2.1.2 The random walk and the diffusion equation

We will develop a model of Brownian motion based on the **random walk**, a common starting point for descriptions of physical phenomena that involve an element of randomness (Chandrasekhar 1943), and the simplest model for Brownian motion. To illustrate the methodology, we will restrict our development to one spatial dimension. Analogous results can be obtained in higher dimensions, but with a corresponding increase in algebraic complexity. An example of a random walk is the cumulative result of a succession of coin flips. For each flip, called a trial, the coin lands either face up ('heads') or face down ('tails'). Each trial is an independent and fair event, in that the likelihood of heads or tails is the same for every coin flip, independent of the results of previous trials. For a sequence of successive trials, a quantity S is defined, such that for every result of heads, we add one to S and, for every result of tails, we subtract one from S. Initially, $S = 0$, so the sum at the end of the sequence equals the number of heads in excess of the number of tails (if S is positive) or the number of tails in excess of the number of heads (if S is negative). The name 'random walk' is derived from the fact that a point moved one position to the right (resp., left) for every result of heads (resp., tails) executes a 'walk,' with S representing the net displacement to the right or to the left from its starting position, which is usually taken as the origin. The random walk is the simplest random process in that the underlying source of the randomness does not change with time, a property known as **stationarity**, and the likelihood of the outcomes of a trial is independent of the results of previous trials, which is called the **Markov** property.

Based on these considerations, the central quantity in the description of a random walk is the probability $p(na, k\tau)$ that, beginning at the origin, the walker is at position na after k trials. We have taken the distance of each step to be a and the trial frequency as τ^{-1}, so that every τ seconds a trial determines if the walker moves to the left or to the right by a distance a. Both a and τ will play important roles in the description of atomic diffusion in solids. There are two ways we can proceed.

The first is to explicitly construct $p(na, k\tau)$ by enumerating the possible sequences of outcomes. This approach, which is discussed at length by Reif (1985), has the advantage of being exact, but can become cumbersome for complex geometries. The alternative, which we will follow here, is a systematic approximation of the discrete random walk by a continuous process. The important advantage of this approach is that the continuum formulation benefits from the wealth of analytic and numerical methods for solving the diffusion equation. In fact, the triumvirate consisting of the diffusion equation, the wave equation, and Laplace's equation are the basis for essentially all discussions about the properties and methods of solution of the equations of mathematical physics.

Consider the probability $p(na, k\tau)$ of the walker being at position na after k trials. How did the walker arrive at this position? Since the probability of moving to the left or to the right is the same for every time step, there are two possibilities: at time $(k-1)\tau$ the walker was (i) at position $(n-1)a$ and moved to the right with probability $\frac{1}{2}$, or (ii) at position $(n+1)a$ and moved to the left, also with probability $\frac{1}{2}$. Each of these terms is shown in figure 2.2. Since moves to the left and right are equally likely and independent of time, we obtain:

$$p(na, k\tau) = \tfrac{1}{2}p((n-1)a, (k-1)\tau) + \tfrac{1}{2}p((n+1)a, (k-1)\tau). \qquad (2.1)$$

This type of equation is called a **recursion relation** because we can write analogous equations with $p((n \pm 1)a, (k-1)\tau)$ on the left-hand side and continue this process back to the initial time. This would, in principle, enable us to solve for $p(na, k\tau)$. But a more expedient route to a solution is obtained by examining this equation in the limit that a and τ approach zero, whereupon the original *discrete* random walk

$$p(na, k\tau)$$

$$(n-2)a \quad (n-1)a \quad na \quad (n+1)a \quad (n+2)a$$

$$p((n-1)a, (k-1)\tau)$$

$$(n-2)a \quad (n-1)a \quad na \quad (n+1)a \quad (n+2)a$$

$$p((n+1)a, (k-1)\tau)$$

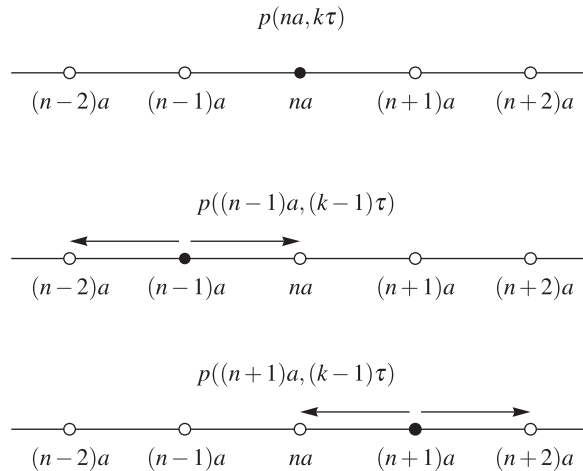$$(n-2)a \quad (n-1)a \quad na \quad (n+1)a \quad (n+2)a$$

Figure 2.2. Pictorial representation of the recursion relation (2.1) for the random walk. The left-hand side of (2.1) is represented by the top panel, the first and second terms on the right-hand side by the center and bottom panels, respectively. Filled circles indicate occupied sites and unfilled circles unoccupied sites.

becomes a *continuous* process. The outcome of this procedure is that the *difference* equation (2.1) is transformed to a *differential* equation in which the position *na* becomes the continuous position x and the time $k\tau$ becomes the continuous time t. The first step is to expand the quantities $p((n \pm 1)a, (k-1)\tau)$ on the right-hand side in (2.1) in a Taylor series in the two variables:

$$p(x \pm a, t - \tau) = p(x, t) + \frac{\partial p}{\partial x}\bigg|_{na,k\tau}(\pm a) + \frac{\partial p}{\partial t}\bigg|_{na,k\tau}(-\tau) + \frac{1}{2}\frac{\partial^2 p}{\partial x^2}\bigg|_{na,k\tau}(\pm a)^2$$
$$+ \frac{\partial^2 p}{\partial x \partial t}\bigg|_{na,k\tau}(\pm a)(-\tau) + \frac{1}{2}\frac{\partial^2 p}{\partial t^2}\bigg|_{na,k\tau}(-\tau)^2 + \cdots. \tag{2.2}$$

After substitution of this expansion into (2.1), we obtain,

$$p(x, t) = p(x, t) - \frac{\partial p}{\partial t}\tau + \frac{1}{2}\frac{\partial^2 p}{\partial x^2}a^2 + \frac{1}{2}\frac{\partial^2 p}{\partial t^2}\tau^2 + \cdots. \tag{2.3}$$

The terms that contain odd-order spatial derivatives of p have canceled, so only even-order spatial derivatives appear on the right-hand side of this equation. A simple rearrangement of this equation yields

$$\frac{\partial p}{\partial t} - \frac{1}{2}\frac{\partial^2 p}{\partial t^2}\tau + \cdots = \frac{a^2}{2\tau}\frac{\partial^2 p}{\partial x^2} + \cdots. \tag{2.4}$$

There are infinitely many derivatives on either side in this equation. To make this a tractable equation for further analytic study, we must eliminate higher-order derivatives in a systematic manner to obtain a finite-order partial differential equation. To accomplish this, we take a judicious limit: $a \to 0$ and $\tau \to 0$, with the proviso that

$$\lim_{a \to 0, \tau \to 0} \left(\frac{a^2}{2\tau}\right) \equiv D \tag{2.5}$$

is finite. To see the effect of this limit, consider a general term in the Taylor series expansion of $p(x, t)$ with $2r$ space derivatives ($r = 1, 2, \ldots$) and s time derivatives ($s = 1, 2, \ldots$):

$$\frac{\partial^{2r+s}p}{\partial x^{2r}\,\partial t^s}(\pm a)^{2r}(-1)^s\tau^{s-1} = (-1)^s\frac{\partial^{2r+s}p}{\partial x^{2r}\,\partial t^s}\left(\frac{a^2}{\tau}\right)a^{2(r-1)}\tau^s, \tag{2.6}$$

in which we have divided by τ, as required in the passage to (2.4). If we suppose that the partial derivative remains finite as $a \to 0$ and $\tau \to 0$, then, since the factor a^2/τ has a finite limit, the only terms that survive in this limit are those with $s = 1$ and $r = 0$, i.e.

$$-\frac{\partial p}{\partial t}, \tag{2.7}$$

and those with $s = 0$ and $r = 1$, i.e.

$$\frac{a^2}{\tau}\frac{\partial^2 p}{\partial x^2}. \tag{2.8}$$

All other terms have additional factors of a and/or τ that are not balanced as in (2.5) and, hence, vanish. We are left with

$$\boxed{\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}, \quad D = \frac{a^2}{2\tau},} \tag{2.9}$$

which is the classical **diffusion equation**, also known as the **heat equation** which, as we have already note, is one of the standard partial differential equations of mathematical physics. There are several noteworthy aspects of this equation and its relation to the random walk:

1. The diffusion equation is a *linear* equation, which means that classical methods such as the separation of variables and Green's functions, which rely on the superposition principle, can be used to obtain solutions.
2. This equation is first order in time and second order in space. Thus, to obtain unique solutions of particular problems, we must specify an initial condition, usually at $t = 0$, and two spatial conditions, either at finite boundaries or at infinity.
3. The quantity D, called the **diffusion constant**, embodies the step length a and time step τ from the original random walk. In this sense, our derivation serves as a prototype for multiscale modeling strategies in that we have a coarse-grained description of the original system that retains the characteristic parameters of the original microscopic process.
4. Our derivation began with the simplest case of a random walk—unbiased in one spatial dimension. More general examples that include bias, waiting times, and higher spatial dimensions are also amenable to the approach we have described (Chandrasekhar 1943). Some of these will be taken up in the exercises.
5. The diffusion equation appears in other contexts, such as thermal diffusion, where it is called the **heat equation**, with D being the thermal diffusivity.

Before we examine solutions of the diffusion equation, we will derive this equation from a macroscopic perspective using Fick's laws.

2.2 Fick's laws and the diffusion equation

2.2.1 Fick's first law

Diffusion is the physical process by which a physical quantity, such as matter or heat, moves from a region of high concentration to one of lower concentration.

In general, any spatial variation of a diffusing physical quantity will, over time, become homogeneous, resulting in a cessation of the net flow of that quantity. The mathematical framework of these observations was established by Adolf Fick in the mid-1800s. With variations in a concentration $c(\boldsymbol{x}, t)$ determined by the gradient ∇c, **Fick's first law** for the diffusive flux $\boldsymbol{J}$ is

$$\boldsymbol{J} = -D\nabla c. \tag{2.10}$$

The constant of proportionality D—the diffusion constant—is the same as that in (2.9). The negative sign indicates that the flux vector points in the direction of decreasing concentration. With $L \equiv$ length, and $T \equiv$ time, the dimensions of D are $L^2 T^{-1}$ and, in three dimensions, the dimensions of concentration are L^{-3}. Hence, the dimensions of $\boldsymbol{J}$ are those of flux: $L^{-2}T^{-1}$.

The form of Fick's law in (2.10) appears in other contexts. The relationship between the electrical current density $\boldsymbol{j}$ and the applied electric field $\boldsymbol{E}$ is given by **Ohm's law**:

$$\boldsymbol{j} = \sigma \boldsymbol{E}, \tag{2.11}$$

where σ is the electrical conductivity. The relationship between the heat flow q in the presence of variations of temperature T is expressed by **Fourier's law**:

$$\boldsymbol{q} = -C\nabla T, \tag{2.12}$$

where C is the coefficient of thermal conductivity. The coefficient C may vary with the temperature and position, and varies from one substance to another, but it is always a *positive* constant. In each of these equations, the current is directed in the direction of the gradient of a scalar function, which defines the direction of maximum change of that function.

2.2.2 The continuity equation

For a vector field $\boldsymbol{J}$, the divergence theorem states that

$$\iint_S \boldsymbol{J} \cdot \boldsymbol{n} \, dA = \iiint_V \nabla \cdot \boldsymbol{J} \, dV, \tag{2.13}$$

in which the volume V is enclosed by the surface S whose area element is dA with *outward* normal $\boldsymbol{n}$. If $\boldsymbol{J}$ represents a mass flux, then in the absence of any sources or sinks within V, the left-hand side of this equation is the rate of material leaving the volume (if this quantity is positive) or entering the volume (if this quantity is negative). Denoting by $c(\boldsymbol{x}, t)$ the mass concentration at position $\boldsymbol{x}$ at time t, we have

$$-\frac{d}{dt} \iiint_V c \, dV = -\iiint_V \frac{\partial c}{\partial t} \, dV = \iint_S \boldsymbol{J} \cdot \boldsymbol{n} \, dS.$$

Combining this result with (2.13), we obtain

$$\iiint_V \frac{\partial c}{\partial t} \, dV + \iiint_V \nabla \cdot \boldsymbol{J} \, dV = \iiint_V \left(\frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{J} \right) dV = 0.$$

Since the volume is arbitrary, this equality implies the equality of the integrands, which yields the **continuity equation**:

$$\frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{J} = 0. \tag{2.14}$$

This is a partial differential equation that describes the transport of any conserved quantity, e.g. mass, charge, and, in quantum mechanics, probability density.

2.2.3 Fick's second law and the diffusion equation

The continuity equation is completely general, but to find a solution for the evolution of the concentration, we need an expression for $\boldsymbol{J}$, i.e. we need a **constitutive relation**. This is provided by Fick's first law (2.10), but we should be aware that this is only a phenomenological expression and there may be other forms that are appropriate for particular systems. Substitution of (2.10) into (2.14) yields

$$\frac{\partial c}{\partial t} = \nabla(D\nabla c) = (\nabla D) \cdot (\nabla c) + D\nabla^2 c.$$

This is the general form of **Fick's second law**. If the diffusion constant is independent of position, then we arrive at

$$\frac{\partial c}{\partial t} = D\nabla^2 c, \tag{2.15}$$

which is the diffusion equation, also sometimes called Fick's second law.

The assumption of a diffusion constant with no spatial dependence merits some discussion. Near a phase boundary, D is likely to be different in the two phases on either side of the boundary and, indeed, near the boundary itself. In that case, the solution is obtained within each region, and the solutions are then matched near the boundary by requiring the concentration and the mass current to be continuous across the boundary. For other situations, where D cannot be regarded as being piece-wise constant, other methods will be required.

2.3 Fundamental solution of the diffusion equation

There are several ways of solving the diffusion equation. The most elementary way is based on the separation of variables method, which then leads to Fourier series in one dimension and to other orthogonal function expansions in higher dimensions. In this section, we will derive a solution of the diffusion equation called the 'fundamental solution.' We will illustrate the methodology for the one-dimensional form of the equation,

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{2.16}$$

where the solution is required over the entire real line and the initial condition is

$$c(x, 0) = c_0(x). \tag{2.17}$$

This corresponds to the physical situation where there is a finite concentration of mass within a region of space which is then dispersed under the action of diffusion.

2.3.1 Differential equation for Fourier components

Our first step is to obtain a differential equation for the Fourier transform $\tilde{c}(k, t)$ of $c(x, t)$ with respect to x:

$$\tilde{c}(k, t) = \int_{-\infty}^{\infty} c(x, t)\, e^{ikx}\, dx. \tag{2.18}$$

We multiply both sides of (2.16) by e^{ikx} and integrate x over $(-\infty, \infty)$:

$$\int_{-\infty}^{\infty} \frac{\partial c}{\partial t}\, e^{ikx}\, dx = D \int_{-\infty}^{\infty} \frac{\partial^2 c}{\partial x^2}\, e^{ikx}\, dx. \tag{2.19}$$

The left-hand side of this equation is

$$\int_{-\infty}^{\infty} \frac{\partial c}{\partial t}\, e^{ikx}\, dx = \frac{\partial}{\partial t}\left[\int_{-\infty}^{\infty} c(x, t)\, e^{ikx}\, dx\right] = \frac{\partial \tilde{c}(k, t)}{\partial t}. \tag{2.20}$$

The right-hand side of can be evaluated by two applications of integration by parts. Recall that this method of integration is derived from the derivative of the product of two functions $u(x)$ and $v(x)$,

$$\frac{d(uv)}{dx} = \frac{du}{dx}v + u\frac{dv}{dx}, \tag{2.21}$$

which is then integrated between limits a and b:

$$\int_a^b \frac{d(uv)}{dx}\, dx = uv\Big|_a^b = \int_a^b \frac{du}{dx}v\, dx + \int_a^b u\frac{dv}{dx}\, dx. \tag{2.22}$$

A simple rearrangement yields the integration by parts method in its standard form:

$$\int_a^b \frac{du}{dx}v\, dx = uv\Big|_a^b - \int_a^b u\frac{dv}{dx}\, dx. \tag{2.23}$$

Applying this method twice to the right-hand side of (2.19), with $v = e^{ikx}$ and u equal to derivatives of c, yields

$$\int_{-\infty}^{\infty} \frac{\partial^2 c}{\partial x^2}\, e^{ikx}\, dx = e^{ikx}\frac{\partial c}{\partial x}\Big|_{-\infty}^{\infty} - ik \int_{-\infty}^{\infty} \frac{\partial c}{\partial x}\, e^{ikx}\, dx$$
$$= \frac{\partial c}{\partial x}\, e^{ikx}\Big|_{-\infty}^{\infty} - ikc\, e^{ikx}\Big|_{-\infty}^{\infty} - k^2 \int_{-\infty}^{\infty} c(x, t)e^{ikx}\, dx. \tag{2.24}$$

Since we are restricting ourselves to solutions whose integral over the real line is finite, we must require that the solution and its derivative vanish as $x \to \pm\infty$ for all times:

$$\lim_{x \to \pm\infty} c(x, t) = 0 \qquad \text{and} \qquad \lim_{x \to \pm\infty} c_x(x, t) = 0. \qquad (2.25)$$

Thus, the boundary terms in (2.24) vanish, leaving

$$\int_{-\infty}^{\infty} \frac{\partial^2 c}{\partial x^2} \, e^{ikx} \, dx = -k^2 \int_{-\infty}^{\infty} c(x, t) \, e^{ikx} \, dx = -k^2 \tilde{c}(k, t). \qquad (2.26)$$

The second derivative of c with respect to x is seen to be replaced by a multiplication of $\tilde{c}$ by the square of the transformation variable, k. This is a general result and illustrates one of the central reasons why Fourier transforms are useful for solving differential equations, namely, that derivatives are replaced by multiplication by the transformation variable. Combining (2.20) and (2.26), we obtain the differential equation for the Fourier transform $\tilde{c}(k, t)$ of the concentration:

$$\frac{\partial \tilde{c}(k, t)}{\partial t} = -Dk^2 \tilde{c}(k, t). \qquad (2.27)$$

We are thus left with solving a first-order equation involving derivatives of only one of the original variables. The initial condition $\tilde{c}(k, 0)$ for this equation is

$$\tilde{c}(k, 0) = \int_{-\infty}^{\infty} c(x, 0) \, e^{ikx} \, dx = \int_{-\infty}^{\infty} c_0(x) \, e^{ikx} \, dx \equiv \tilde{c}_0(k), \qquad (2.28)$$

where $\tilde{c}_0(k)$ is the Fourier transform of the initial function $c_0(x)$ in (2.17). The solution of (2.27) is now a straightforward matter and we obtain

$$\tilde{c}(k, t) = \tilde{c}_0(k) \, e^{-Dk^2 t}, \qquad (2.29)$$

so the solution to (3.8) and (3.19) is obtained by inverting the Fourier transform:

$$c(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{c}_0(k) \, e^{-Dk^2 t} \, e^{-ikx} \, dk. \qquad (2.30)$$

This expression is the solution to the initial-value problem of the diffusion equation for any initial function $c_0(x)$.

2.3.2 The fundamental solution

To carry out the integral on the right-hand side of (2.30) we need an explicit functional form for c_0. We first consider the special choice where $\tilde{c}_0(k) = 1$ for all k, in which case our solution reduces to

$$c(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(Dk^2 t + ikx)} \, dk. \qquad (2.31)$$

This integral can be evaluated by first completing the square in the argument of the exponential,

$$Dk^2t + ikx = \left(k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}\right)^2 + \frac{x^2}{4Dt}, \tag{2.32}$$

which yields

$$c(x, t) = \frac{e^{-x^2/4Dt}}{2\pi} \int_{-\infty}^{\infty} \exp\left[-\left(k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}\right)^2\right] dk. \tag{2.33}$$

Then, by introducing a new integration variable s,

$$s = k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}, \tag{2.34}$$

which also requires that

$$ds = \sqrt{Dt}\, dk, \tag{2.35}$$

we obtain

$$\begin{aligned} c(x, t) &= \frac{e^{-x^2/4Dt}}{2\pi\sqrt{Dt}} \int_{-\infty+ix/2\sqrt{Dt}}^{\infty+ix/2\sqrt{Dt}} e^{-s^2}\, ds \\ &= \frac{e^{-x^2/4Dt}}{2\pi\sqrt{Dt}} \underbrace{\int_{-\infty}^{\infty} e^{-s^2}\, ds}_{\sqrt{\pi}} = \frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}}. \end{aligned} \tag{2.36}$$

The second equality is justified by contour integration. The details are worked out in the appendix to this chapter. The last equality is the **fundamental solution** of the diffusion equation:

$$\boxed{c(x, t) = \frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}}.} \tag{2.37}$$

The reason for this name is that initial-value problems of the diffusion equation (section 2.3.3) and solutions of inhomogeneous diffusion equations can be expressed as convolutions of the fundamental solution. Moreover, absorbing and reflecting boundaries in semi-infinite and finite domains can also be expressed as convolutions of a fundamental solution that has been modified by the presence of boundaries by using a generalized method of images.

There are several properties of this solution that are immediately apparent. The Gaussian probability density $p_G(x)$ is expressed in terms of the mean μ and variance σ^2 (where σ is the standard deviation) as

$$p_G(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]. \tag{2.38}$$

Comparing this expression with (2.37) shows that the fundamental solution is a Gaussian probability density with $\mu = 0$ and $\sigma^2 = 2Dt$ (figure 2.4). As time

increases, the diffusing species can explore increasingly more distant regions of the real line, resulting in an increased variance. Additionally, since the diffusion equation was derived from the general form of the continuity equation (2.14), we expect the concentration to be a conserved quantity. We can show this by integrating the diffusion equation over the real line:

$$\int_{-\infty}^{\infty} \frac{\partial c}{\partial t}\, dx = \frac{\partial}{\partial t}\left[\int_{-\infty}^{\infty} c(x)\, dx\right] = \int_{-\infty}^{\infty} \frac{\partial^2 c}{\partial x^2}\, dx = \frac{\partial c}{\partial x}\bigg|_{-\infty}^{\infty} = 0, \qquad (2.39)$$

where we have used the fact that the current at $\pm\infty$ vanishes. Hence, the total concentration does not change with time.

The behavior of this solution as $t \to 0$ is also revealing (figure 2.3). If $x \neq 0$, then the exponential dominates and the solution vanishes. If $x = 0$, then the exponential reduces to unity, and the solution becomes unbounded. Thus,

$$\lim_{t \to 0} c(x, t) = \begin{cases} 0, & \text{if } x \neq 0; \\ \infty, & \text{if } x = 0. \end{cases} \qquad (2.40)$$
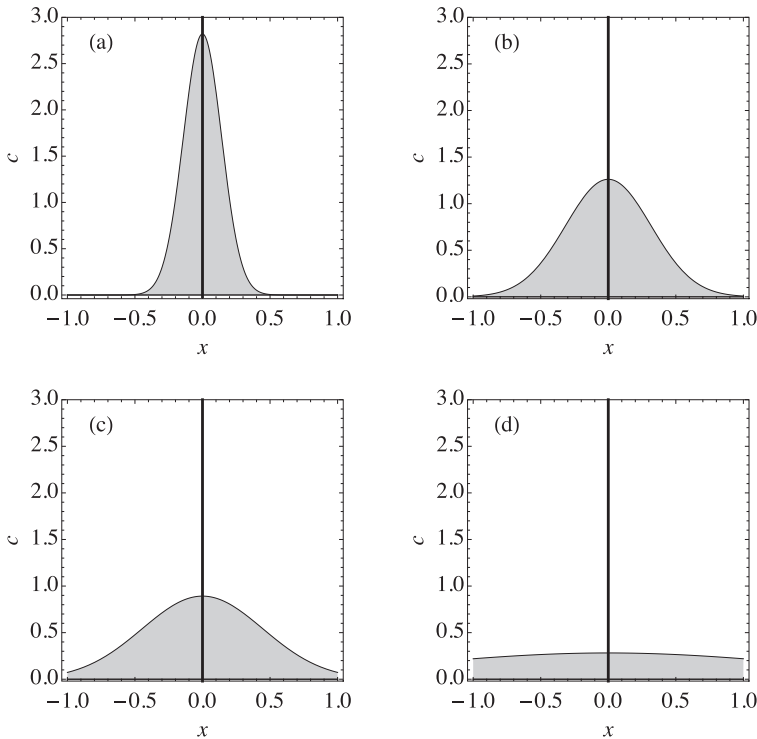

Figure 2.3. The evolution of the fundamental solution of the diffusion equation in (2.37) at times (a) $Dt = 0.01$, (b) $Dt = 0.05$, (c) $Dt = 0.1$, (d) $Dt = 1$. The initial condition, a delta-function at $x = 0$ (shown in bold), unfolds into successively broader distributions while maintaining the area under each curve (shown shaded) constant.

In fact, the solution in this limit is the **Dirac delta-function**, which is denoted by $\delta(x)$, a result which stems from our requiring that the Fourier coefficients of the initial function are all equal to unity. Thus, from (2.31), we have that

$$c(x, 0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \, dk = \delta(x). \tag{2.41}$$

During the time-development of the fundamental solution (figure 2.3), the initially sharp peak at $x = 0$ (shown in bold) is broadened into a normal distribution whose width increases with time. Because the integrated area must remain constant and because there are no boundaries, the value of the solution at any point, and at the origin, in particular, decreases monotonically with time.

2.3.3 Solution of the initial-value problem

Equation (2.30) is the Fourier transform of the solution to the initial-value problem for the diffusion equation. An expression for this solution in terms of the original variables is obtained by applying the convolution theorem (exercise 5), which states that, for the Fourier transforms $\tilde{f}(k)$ and $\tilde{g}(x)$ of functions $f(x)$ and $g(x)$, respectively,

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(k)\tilde{g}(k)e^{-ikx} \, dk = \int_{-\infty}^{\infty} f(x')g(x - x') \, dx'. \tag{2.42}$$

Referring to (2.30), identifying

$$\tilde{f}(k) = \tilde{c}_0(k), \qquad \tilde{g}(k) = e^{-Dk^2 t}, \tag{2.43}$$

and using the fact that the Fourier transform of $\tilde{f}(k)$ is given by the fundamental solution (2.37), we obtain

$$\boxed{c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} c_0(x') \exp\left[-\frac{(x - x')^2}{4Dt}\right] dx'.} \tag{2.44}$$

The interpretation of this solution is that, at $t = 0$, there is a fundamental solution associated with every point x' whose amplitude is $c_0(x')$. The evolution of the concentration from this initial condition is obtained by allowing each of these fundamental solutions to evolve independently, with the value of the concentration at any later time obtained by integrating the fundamental solutions. The linearity of the diffusion equation guarantees that this use of the superposition principle yields the correct solution. Hence, (2.44) is the integral representation of the initial-value problem of the diffusion equation. In particular, at $t = 0$, we have

$$\lim_{t \to 0} c(x, t) = \int_{-\infty}^{\infty} c_0(x')\delta(x - x') \, dx' = c_0(x). \tag{2.45}$$

2.4 Examples

To illustrate the use of (2.44) to solve a particular initial-value problem, we consider an initial concentration with the following profile:

$$c_0(x) = \begin{cases} 1, & \text{if } x \leqslant 0; \\ 0, & \text{if } x > 0. \end{cases} \tag{2.46}$$

This profile evolves as the diffusing species moves into the region $x > 0$. This is a one-dimensional version of the interdiffusion of one species into a region occupied by a different material. The substitution of this initial concentration into (2.44) yields

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{0} \exp\left[-\frac{(x - x')^2}{4Dt}\right] dx'. \tag{2.47}$$

This integral can be simplified by changing the integration variable from x' to

$$s = \frac{x - x'}{\sqrt{4Dt}}, \tag{2.48}$$

in which case the integration element becomes

$$dx' = -ds\sqrt{4Dt}, \tag{2.49}$$

and the limits of integration change from $x' \to \infty$ and $x' = 0$ to $s \to \infty$ and $s = x/\sqrt{4Dt}$, respectively. The transformed solution is

$$c(x, t) = \frac{1}{\sqrt{\pi}} \int_{x/\sqrt{4Dt}}^{\infty} e^{-s^2} ds. \tag{2.50}$$

A more compact solution can be obtained by using the definition of the error function, $\mathrm{erf}(x)$ and the complementary error function $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$[1]:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt, \tag{2.51}$$

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} dt. \tag{2.52}$$

Hence, the solution (2.50) can be written as

$$\boxed{c(x, t) = \frac{1}{2}\,\mathrm{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right].} \tag{2.53}$$

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[1] The motivation for the names 'error function' and 'complementary error function' can be understood as follows. For data that are described by a normal distribution with standard deviation σ, $\mathrm{erf}(a/(\sigma\sqrt{2}))$ is the probability that the error of a single measurement lies between $-a$ and a, and $\mathrm{erfc}(a/(\sigma\sqrt{2}))$ is the probability that the data lie outside of this range.
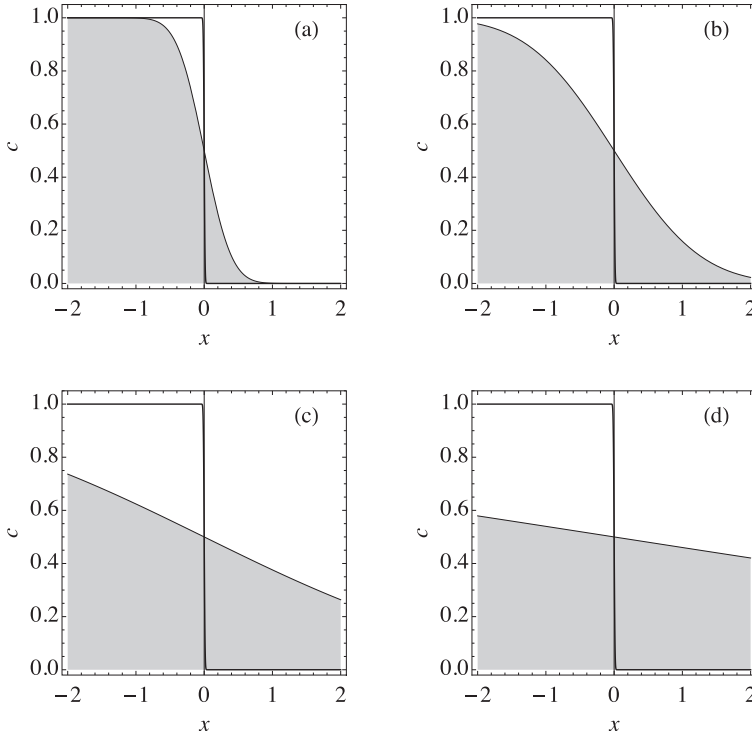
Figure 2.4. The solution of the diffusion equation from the initial condition (2.46) for times (a) $Dt = 0.01$, (b) $Dt = 1$, (c) $Dt = 100$, (d) $Dt = 10^4$. The initial condition is shown by bold lines in each panel.

The evolution of this solution is shown in figure 2.4. Note how the abrupt change in concentration at the origin is rapidly smoothed out. The value $c(0, t) = \frac{1}{2}$ is maintained for all times and can be used to fixed the concentration of the diffusing species at the origin.

As another example, consider the heat equation for a temperature distribution $T(x, t)$,

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial x^2}, \tag{2.54}$$

where K is the thermal diffusion constant. Suppose that the initial temperature distribution $T_0(x) \equiv T(x, 0)$ is

$$T_0(x) = \begin{cases} T_2, & \text{if } |x| \leqslant 1; \\ T_1, & \text{if } |x| > 1. \end{cases} \tag{2.55}$$

To solve this initial-value problem, we introduce the new variable $u \equiv T - T_1$, in terms of which the initial-value problem is expressed as

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2}, \tag{2.56}$$

with $u_0(x) \equiv u(x, 0)$ given by

$$u_0(x) = \begin{cases} T_2 - T_1 & \text{if } |x| \leqslant 1; \\ 0, & \text{if } |x| > 1. \end{cases} \tag{2.57}$$

The substitution of this initial concentration into (2.44) yields

$$u(x, t) = \frac{T_2 - T_1}{\sqrt{4\pi Dt}} \int_{-1}^{1} \exp\left[-\frac{(x - x')^2}{4Dt}\right] dx'. \tag{2.58}$$

Proceeding as above, the solution is obtained as

$$u(x, t) = \frac{T_2 - T_1}{2}\left[\text{erf}\left(\frac{x + 1}{\sqrt{4Dt}}\right) - \text{erf}\left(\frac{x - 1}{\sqrt{4Dt}}\right)\right]. \tag{2.59}$$

The evolution of this solution is shown in figure 2.5. The edges of the distribution are smoothed out very quickly because the second derivative of the concentration is greatest at these points. Near inflection points, which in figure 2.5(a) and (b) are near the edges of the initial temperature distribution, the reduction in temperature is comparatively slower. In terms of a Fourier series representation of this solution, the
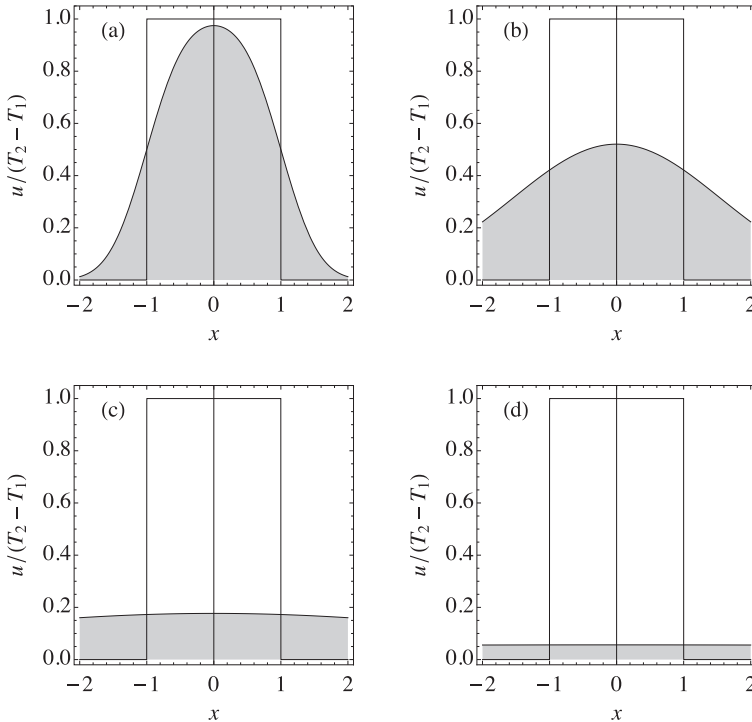

Figure 2.5. The evolution of the solution (2.59) of the heat equation from the initial condition (2.57) at times (a) $Dt = 0.1$, (b) $Dt = 1$, (c) $Dt = 10$, (d) $Dt = 100$. The initial condition is shown by bold lines in each panel.

edges of the distribution correspond to high-k components with large decay rates. The distribution away from the edges retains its form for longer at times, because such features correspond to lower-k components, with smaller decay rates. Only at much later times do these features smooth out, as the heat equation eliminates all but the uniform solution corresponding to $u = 0$, i.e. $T = T_1$.

2.5 Summary

We have derived this equation from opposing starting points: as a continuum equation from the random walk, and as a continuity equation supplemented by Fick's first law. The connection with the random walk shows the microscopic basis for diffusion, while the connection to Fick's law shows that diffusion is a homogenization process that drives the system towards a uniform distribution of mass. The combination of the continuity equation and the absence of any energy input into driving diffusion, results in a slow process, even in liquids and gases.

We have obtained solutions of the diffusion in terms of the fundamental solution, but there are methods of solution which are useful for particular problems:

   (i) Separation of variables and expansions in orthogonal functions for finite geometries. The fundamental solution may also prove useful here if there are discontinuities in the initial concentration, such as (2.55), for which the Fourier series fails to converge, exhibiting instead the **Gibbs phenomena**.

 (ii) Laplace transforms, which are transforms in time for initial-value problems, are useful for constant-flux boundary conditions and time-dependent boundary conditions.

(iii) Numerical methods for complex geometries, concentration-dependent diffusion constants, time-dependent boundary conditions, and other cases where analytic solutions are not easily obtained.

Further reading

The diffusion equation (also known as the heat equation) has a long and distinguished history from its introduction by Joseph Fourier in the early 1800s. A historical summary has been given by Narasimhan (2009). Comprehensive presentations of solutions to the diffusion equation may be found in the classic texts by Carslaw and Jaeger (1959) and by Crank (1956). The classic review by Chandrasekhar (1943) includes random walks and diffusion equations in various dimensions and geometries. Reif (1965) develops Brownian motion from the Langevin equation, which is based on Newton's equation supplemented by a random force due the fluctuating environment of the diffusing particle.

Further reading from recommended texts:

    Cottrell (1967): Chapter 12.
    Porter and Easterling (2004): Chapter 2.
    Balluffi, Allen, and Carter (2005): Chapters 3–5.
    Christian (2002): sections 40, 41.

Exercises

1. Consider a random walk in which the probability of movement ℓ to the left and r to the right are unequal, but still satisfy $\ell + r = 1$. As in section 2.1.2, we suppose that the walker occupies sites na on a one-dimensional lattice (where n is an integer) and the step frequency is τ^{-1}. Beginning with the recursion relation

$$p(na, k\tau) = rp((n - 1)a, (k - 1)\tau) + \ell p((n + 1)a, (k - 1)\tau)$$

for the probability of the walker occupying site na at time $k\tau$, take appropriate limits to obtain the **diffusion equation with drift**:

$$\frac{\partial p}{\partial t} = -u\frac{\partial p}{\partial x} + D\frac{\partial^2 p}{\partial x^2}.$$

Here, the drift u and diffusion constant D are given in terms of the parameters of this biased random walk.

2. Suppose we have a solution $c(x, t)$ to the one-dimensional diffusion equation,

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

By using an appropriate change of variables, show how a solution to the diffusion equation with drift can be obtain from $c(x, t)$.

3. The entropy S of a distribution $p(x)$ is

$$S = -k_B \int p(x) \ln[p(x)] \, dx,$$

in which k_B is Boltzmann's constant. Show that the entropy associated with solutions of the diffusion equation $c_t = Dc_{xx}$ on the infinite domain $(-\infty, \infty)$ (i.e. no boundaries),

$$S(t) = -k_B \int c(x, t) \ln[c(x, t)] \, dx,$$

has the property that

$$\frac{dS}{dt} \geqslant 0.$$

Provide a physical explanation of this result.

4. Show that, for a solution $c(x, t)$ of the diffusion equation,

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

on the infinite domain $(-\infty, \infty)$ with the initial condition $c(x, 0) = \delta(x)$, the mean displacement $\langle x \rangle$ and the root mean square displacement $\langle x^2 \rangle^{1/2}$ are

$$\langle x \rangle = 0, \qquad \langle x^2 \rangle^{1/2} = \sqrt{2Dt}.$$

5. Consider the Fourier transform,

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(k)\tilde{g}(k)e^{-ikx}dk,$$

in which $\tilde{f}(k)$ and $\tilde{g}(k)$ are the Fourier transforms of functions $f(x)$ and $g(x)$:

$$\tilde{f}(k) = \int_{-\infty}^{\infty} f(x)e^{ikx}dx, \qquad \tilde{g}(k) = \int_{-\infty}^{\infty} g(x)e^{ikx}dx.$$

Show that

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(k)\tilde{g}(k)e^{-ikx}\, dk = \int_{-\infty}^{\infty} f(x')g(x - x')dx'.$$

This is the **convolution theorem**. Use this theorem to deduce that the solution of the initial-value problem of the diffusion equation for $-\infty \leqslant x \leqslant \infty$ is

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} c_0(x')\, e^{-(x-x')^2/4Dt}\, dx'.$$

6. The procedure followed in section 2.3 for deriving the fundamental solution over the real line can be adapted to account for the presence of boundaries. The steps are as follows:

   (a) Begin by Fourier-transforming the diffusion equation, with the integral performed only over the semi-infinite line $0 \leqslant x \leqslant \infty$, to obtain

   $$\frac{\partial \tilde{c}(k, t)}{\partial t} = -D\frac{\partial c}{\partial x}\bigg|_{x=0} + iDkc\bigg|_{x=0} - Dk^2\tilde{c}(k, t). \tag{2.60}$$

   (b) Show that the real and imaginary parts of (2.60) are

   $$\frac{\partial \tilde{c}_r}{\partial t} = -D\frac{\partial c}{\partial x}\bigg|_{x=0} - Dk^2\tilde{c}_r(k, t),$$

   $$\frac{\partial \tilde{c}_i}{\partial t} = Dkc\bigg|_{x=0} Dk^2\tilde{c}_i(k, t),$$

   where $\tilde{c}_r$ and $\tilde{c}_i$ are the real and imaginary parts of $\tilde{c}$. Use the fact that

   $$e^{ikx} = \cos kx + i \sin kx$$

   to express the Fourier transforms $\tilde{c}_r$ and $\tilde{c}_i$ as integrals over the appropriate functions and over the appropriate domain. Determine the solutions of these equations if there is (i) an absorbing boundary

at $x = 0$, i.e. $c(0, t) = 0$, and (ii) a reflecting boundary at $x = 0$, i.e. $c_x(0, t) = 0$.

(c) The solution for the case of a reflecting boundary is given by the inverse transform

$$c(x, t) = \frac{2}{\pi} \int_0^\infty \tilde{c}_r(k, 0)\, e^{-Dk^2 t} \cos kx\, dk. \tag{2.61}$$

Determine the Fourier components for the initial condition $c(x, 0) = \delta(x - x')$. Carry out the resulting integral in (2.61) to obtain

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - x')^2}{4Dt}\right] + \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x + x')^2}{4Dt}\right].$$

Provide a physical interpretation of this solution.

Hint: The following trigonometric identity proves useful for the evaluation of (2.61):

$$\cos a \cos b = \tfrac{1}{2}\left[\cos(a - b) + \cos(a + b)\right].$$

7. Consider a film of thickness d consisting of A atoms on a semi-infinite substrate of B atoms. The diffusing species is A and complete solubility of A in B is assumed. The top surface of the film is at $x = 0$ and no matter flows through this surface. If all A atoms are initially found only in the thin film, show that the concentration $c(x, t)$ of A atoms is given by

$$c(x, t) = \frac{1}{2}\left[\mathrm{erf}\left(\frac{x + d}{\sqrt{4Dt}}\right) - \mathrm{erf}\left(\frac{x - d}{\sqrt{4Dt}}\right)\right],$$

in which $\mathrm{erf}(x)$ is the error function:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt.$$

8. Determine the solution of the one-dimensional diffusion equation,

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

for the semi-infinite region $0 \leqslant x < \infty$ such that $c(x, 0) = 0$ and $c(0, t) = c_0$, i.e. the initial concentration is zero in the physical region and the concentration at $x = 0$ is maintained at c_0 for $t > 0$. Proceed by defining a new function $u(x, t) = c(x, t) - c_0$ and solving the corresponding problem for u to obtain

$$c(x, t) = c_0 \left[1 - \text{erf}\left(\frac{x}{\sqrt{4Dt}} \right) \right].$$

Plot this solution for different 'times' Dt and comment on the important features of its evolution.

9. Our derivation of the diffusion equation from the random walk indicates that the combination x^2/t is a key variable. Accordingly, consider a solution $\phi(\xi)$, for $\xi(x, t) = x/\sqrt{t}$, over the infinite domain $-\infty \leqslant x \leqslant \infty$. The normalization of ϕ is

$$\int_{-\infty}^{\infty} \phi(\xi) \, d\xi = \frac{1}{\sqrt{t}} \int_{-\infty}^{\infty} \phi\left(\frac{x}{\sqrt{t}} \right) dx = 1.$$

An explicit functional form for this solution is obtained as follows:

(a) Substitute

$$c(x, t) = \frac{1}{\sqrt{t}} \phi\left(\frac{x}{\sqrt{t}} \right)$$

into the diffusion equation and show that the resulting equation for ϕ can be written as

$$\frac{d}{d\xi} \left(2D \frac{d\phi}{d\xi} + \xi\phi \right) = 0.$$

(b) By integrating this equation and imposing the normalization above, obtain the fundamental solution

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right).$$

10. Consider isotropic diffusion in two spatial dimensions, for which the characteristic variable is $(x^2 + y^2)/t = r^2/t$, where $0 \leqslant r < \infty$ is the distance from the origin. For a solution $\phi(\xi)$, with $\xi = r/\sqrt{t}$, the normalization in polar coordinates is

$$\int \phi(\xi) \, d\xi = \frac{2\pi}{t} \int_{0}^{\infty} \phi\left(\frac{r}{\sqrt{t}} \right) r \, dr = 1.$$

Substitute

$$c(r, t) = \frac{1}{t} \phi\left(\frac{r}{\sqrt{t}} \right)$$

into the two-dimensional diffusion equation in polar coordinates and, by following steps similar to those in problem 9, obtain the fundamental solution

$$c(r, t) = \frac{1}{4\pi Dt} \exp\left(-\frac{r^2}{4Dt}\right).$$

11. Show that fundamental solution obtained in problem 10, can be written as the product of one-dimensional fundamental solutions along the x- and y-axes, with $r^2 = x^2 + y^2$. What conclusions can you draw from this construction? The fundamental solution for isotropic diffusion in d dimensions is

$$c(r, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right).$$

Provide a physical explanation for the qualitative behavior of the decay rate of the fundamental solution as a function of the spatial dimension.

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