

CHEM2024 - Week 25 Lecture 1 - Partial differential equations

Chapter 14 of Steiner, "The Chemistry Maths Book", 2nd edition.

1. Partial differential equations – a chemical example

Consider a liquid solution in which the concentration of the substance is not uniform. *Fick's first law of diffusion* tells us that the flux $\vec{j}(\vec{r}, t)$ of the substance at each point $\vec{r} = [x \ y \ z]$ is proportional to the gradient of its concentration $c(\vec{r}, t)$:

$$\vec{j}(\vec{r}, t) = -D \left[\frac{\partial c}{\partial x} \ \frac{\partial c}{\partial y} \ \frac{\partial c}{\partial z} \right] = -D \vec{\nabla} c(\vec{r}, t) \quad (1)$$

where D is the *diffusion coefficient*, the gradient operator is defined in the usual way:

$$\vec{\nabla} = \left[\frac{\partial}{\partial x} \ \frac{\partial}{\partial y} \ \frac{\partial}{\partial z} \right] \quad (2)$$

and the minus sign appears because the substance moves down the gradient – any sharp variations in concentration are being smoothed rather than amplified.

The flux must obey the conservation of matter – the total change in concentration at a particular point must be equal to how much the flux has added or taken out:

$$\frac{\partial}{\partial t} c(\vec{r}, t) = - \left[\frac{\partial j_x}{\partial x} + \frac{\partial j_y}{\partial y} + \frac{\partial j_z}{\partial z} \right] = -\text{div}[\vec{j}(\vec{r}, t)] \quad (3)$$

The operator summing the derivatives of the Cartesian components of a vector is called *divergence*:

$$\text{div}[\vec{f}] = \frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z} \quad (4)$$

The minus sign is again necessary because a positive divergence of the flux leads to a reduction in local concentration. After putting the two equations together and simplifying, we obtain:

$$\frac{\partial}{\partial t} c(\vec{r}, t) = D \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] c(\vec{r}, t) \quad \Leftrightarrow \quad \frac{\partial c}{\partial t} = D \Delta c \quad (5)$$

where Δ is the already familiar *Laplace operator*:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (6)$$

Equation (5) is a simple form of the *diffusion equation* that also governs the transport of heat.

2. Classification of partial differential equations

The *order* of a PDE is defined in the same way as for ODEs – it is the order of the highest derivative occurring in the equation. The PDE is called *linear* if the unknown function enters linearly. Second order PDEs occur particularly often and have their own classification. A PDE of the following general form

$$\sum_{nk} a_{nk} \frac{\partial^2 f}{\partial x_n \partial x_k} + \text{lower order terms} = 0 \quad (7)$$

is called:

elliptic – if the eigenvalues of \mathbf{A} are all of the same sign. A common example is Poisson's equation connecting the electrostatic potential $\varphi(\vec{r})$ with the charge density $\rho(\vec{r})$:

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \varphi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon_0} \quad (8)$$

parabolic – if the eigenvalues of \mathbf{A} are all of the same sign and one is zero. A common example is the diffusion equation in which the second derivative with respect to time does not occur:

$$\frac{\partial}{\partial t} c(\vec{r}, t) = D \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] c(\vec{r}, t) \quad \Leftrightarrow \quad \frac{\partial c}{\partial t} = D \Delta c \quad (9)$$

hyperbolic – if the eigenvalues of \mathbf{A} are all of the same sign, except for one that has the opposite sign. A common example is the wave equation describing strings and membranes:

$$\frac{\partial^2}{\partial t^2} u(\vec{r}, t) = c^2 \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] u(\vec{r}, t) \quad (10)$$

where c is the speed at which the waves propagate.

ultrahyperbolic – if more than one eigenvalue of \mathbf{A} has the sign that is different from the rest of the eigenvalues, and the equation does not belong to any of the classes listed above. Ultrahyperbolic equations are rare in physics because their structure implies multiple time variables.

PDEs often come with *boundary conditions* – prescriptions on how the unknown function and its derivatives must behave on the boundary of the region of interest (zero potential for conductive walls, absorptive or reflective walls for diffusion and wave mechanics, etc.). If the equation involves a time variable, *initial conditions*, specifying the function at time zero may also be supplied.

3. Variable separation method

We shall state without proof that a sufficiently well-behaved complex function $\psi(x, y, \dots)$ of real variables may be represented in the following way:

$$\psi(x, y, \dots) = \sum_{n, k, \dots} \alpha_{n, k, \dots} [f_n(x) g_k(y) \dots] \quad (11)$$

where $\{f_n(x)\}$ is a complete basis set on the space of all well behaved functions of x , $\{g_k(y)\}$ is a complete basis set on the space of all well behaved functions of y , and so on. The expansion coefficients $\alpha_{n, k, \dots}$ are complex numbers. For example, a function of three variables may be expanded as:

$$\psi(x, y, z) = \sum_{nkm} \alpha_{nkm} f_n(x) g_k(y) h_m(z) \quad (12)$$

that is to say, $\{f_n(x) g_k(y) h_m(z)\}$ is the basis of the solution space and α_{nkm} are the expansion coefficients. Such representations are useful for solving partial differential equations because they convert them into sequences of ordinary differential equations that are easier to solve. The procedure consists in substituting $[f_n(x) g_k(y) \dots]$ as a trial solution, obtaining those systems of functions individually, and then using the initial and boundary conditions to find the expansion coefficients in Equation (11).

4. Example: diffusion equation in one dimension

The procedure is best illustrated using the practical example of the diffusion equation in one dimension. With only one spatial coordinate, the diffusion equation in Equation (5) becomes:

$$\frac{\partial}{\partial t} c(x, t) = D \frac{\partial^2}{\partial x^2} c(x, t) \quad (13)$$

For the boundary conditions, let us take impermeable glass walls at $x = -1$ and $x = +1$. The flux at the wall is zero, and therefore (by Fick's first law) the gradient of the concentration must also be zero:

$$\left. \frac{\partial}{\partial x} c(x, t) \right|_{x=\pm 1} = 0 \quad (14)$$

The initial condition shall be a squared cosine bell centred at the origin:

$$c(x, 0) = \cos^2(\pi x/2) \quad (15)$$

As suggested by Equation (11), we will be looking for a general solution of the following form:

$$c(x, t) = f(x) g(t) \quad (16)$$

After plugging this solution into Equation (13), we obtain:

$$\frac{\partial}{\partial t} [f(x) g(t)] = D \frac{\partial^2}{\partial x^2} [f(x) g(t)] \quad \Rightarrow \quad f(x) \frac{\partial}{\partial t} g(t) = D g(t) \frac{\partial^2}{\partial x^2} f(x) \quad (17)$$

After dividing this equation by $f(x) g(t)$ and also by D , we get:

$$\frac{1}{D g(t)} \frac{\partial}{\partial t} g(t) = \frac{1}{f(x)} \frac{\partial^2}{\partial x^2} f(x) \quad (18)$$

The left side of this equation is a function of one independent variable (time) and the right side is the function of the other independent variable (coordinate). The only way this equation can possibly remain true for all values of x and t is if both sides are independently equal to a constant:

$$\begin{cases} \frac{1}{D g(t)} \frac{\partial}{\partial t} g(t) = const \\ \frac{1}{f(x)} \frac{\partial^2}{\partial x^2} f(x) = const \end{cases} \quad (19)$$

Since the solutions must decay with time, and a second derivative is present, it is convenient to use $-\lambda^2$ as the constant. This reduces the partial differential equation to a system of two independent ordinary differential equations that we know how to solve:

$$\begin{cases} \frac{\partial}{\partial t} g(t) = -\lambda^2 D g(t) \\ \frac{\partial^2}{\partial x^2} f(x) = -\lambda^2 f(x) \end{cases} \quad \Rightarrow \quad \begin{cases} g(t) = A \exp(-\lambda^2 D t) \\ f(x) = B_1 \cos(\lambda x) + B_2 \sin(\lambda x) \end{cases} \quad (20)$$

Both the equation and the initial / boundary conditions are symmetric around the origin, and so the anti-symmetric sine terms must vanish. This leaves us with:

$$\begin{cases} g(t) = A \exp(-\lambda^2 Dt) \\ f(x) = B \cos(\lambda x) \end{cases} \quad (21)$$

The glass wall boundary conditions now come into play. $g(t)$ is never zero, and so we must have:

$$\begin{cases} f'(x)|_{x=+1} = 0 \\ f'(x)|_{x=-1} = 0 \end{cases} \Rightarrow \lambda \sin(\lambda) = 0 \Rightarrow \lambda = \pi n, \quad n \in \mathbb{Z} \quad (22)$$

where \mathbb{Z} is the set of all integers. Because multiple solutions are obtained for λ , we have multiple sets of solutions to Equations (20):

$$\begin{cases} g_n(t) = A_n \exp[-\pi^2 n^2 Dt] \\ f_n(x) = B_n \cos[\pi n x] \end{cases} \quad n \in \mathbb{Z} \quad (23)$$

Any of the products $f_n(x)g_n(t)$ is a solution of the original PDE, and therefore any of their linear combinations must also be a solution. The general solution is therefore the sum of products of $f_n(x)$ and $g_n(t)$ with arbitrary coefficients. Pairs of constants multiply and become single constants:

$$c(x, t) = \sum_{n=0}^{\infty} c_n \cos(\pi n x) \exp(-\pi^2 n^2 Dt) \quad (24)$$

This is the general solution. The coefficients may be determined by inspecting the initial condition:

$$c(x, 0) = \cos^2(\pi x/2) = \frac{1}{2} + \frac{1}{2} \cos(\pi x) \Rightarrow c_0 = \frac{1}{2}, \quad c_1 = \frac{1}{2}, \quad c_{>1} = 0 \quad (25)$$

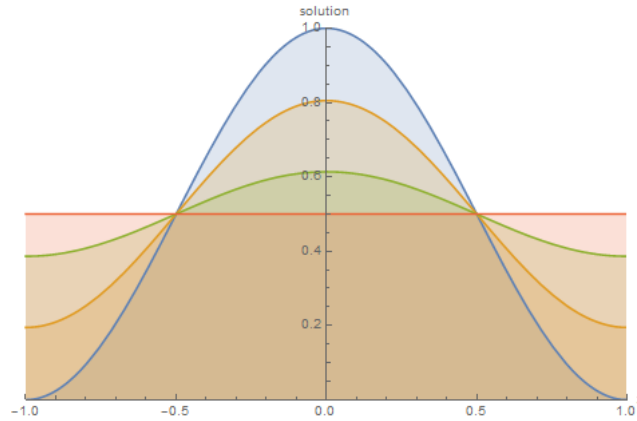


Figure 1. Equation (26), plotted as a function of coordinate for different values of time. The concentration distribution becomes uniform and fills the container.

The particular solution can now be written:

$$c(x, t) = \frac{1}{2} + \frac{1}{2} \cos(\pi x) \exp(-\pi^2 Dt) \quad (26)$$

Plotting this solution as a function of time (Figure 1) produces the physically intuitive picture of the concentration profile filling the available vessel and becoming uniform.