Experiment 2.5: The Diffusion Equation

Introduction

Many physical processes fall into the category of diffusion. Diffusion is a very broad concept, and occurs in a wide variety of situations. It is the progressive drift of some quantity in space away from a region of higher concentration, to a lower. It is due to a tendency of particles to move away from the region of high density inhibited by collisions either with some background fluid or gas, or indeed between the particles themselves. The phenomenon is characterised by a high collision rate, such that the mean free path is much smaller than the characteristic distance associated with the concentration gradient. The particles therefore undergo rapid collisions and execute a random walk. The diffusion of the particles is governed by a diffusion coefficient which may depend on the concentration of the particles. Under these circumstances the diffusion equation governing the time evolution of the concentration becomes non-linear. In this experiment you will develop a finite difference solution to the normal (linear) diffusion equation and test this by comparison with the equilibrium ($t = \infty$) solution.

Objectives

- To construct the diffusion equation and obtain a form for the equilibrium solution.
- Develop a scaled form for the diffusion equation convenient for numerical calculations.
- To develop code for the simulation of diffusion in a potential.
- To test the results of the code against the equilibrium solution.
- To use the code to study the time dependence of the concentration in a colloidal dispersion.

Diffusion in a potential

Consider an ensemble of particles of mass m suspended in a fluid of viscosity ξ. Initially there is a uniform distribution of the particles throughout the height h of the column. Due to the gravitational force the particles will drift downwards with a drift velocity v. This will give rise to a concentration gradient and a net diffusion from the higher to the lower concentration regions. Thus we have 2 opposite currents or fluxes of particles. In equilibrium these currents will be equal and the concentration at a given point will become static. Consider first the flux due to diffusion. This is given by Fick's law

$$\vec{\Gamma_{diff}} = -D\nabla n \tag{1}$$

where n is the concentration and D is the diffusion coefficient. $\vec{\Gamma}$ is the flux, which is the number of particles per second crossing unit area. Fick's law just represents the

process of a transfer of particles away from regions of high concentration (-ve sign), by a diffusional process resulting from the random walk.
In the presence of a potential, there is also a force on the particles, which gives rise to a 'drift' current. In the case of the gravitational field the force is mg. If the particle is travelling at a velocity v in a medium of viscosity ξ, then the force is

$$F = mg - \xi v. \tag{2}$$

Here, ξ is the viscous drag on the particle, given by

$$\xi = 3\pi\eta d, \tag{3}$$

where d is the particle diameter and η is the viscosity of the fluid.
The velocity will increase until the particle reaches its terminal or drift velocity, at which point the force vanishes and thus the drift velocity can be taken as

$$v = mg/\xi \tag{4}$$

It is straightforward to show that the flux arising from the drift velocity is

$$\Gamma_{drift} = nv \tag{5}$$

It is easy to show that, since the quantity n is conserved (the net flux from a closed volume is balanced by a change of n),

$$\frac{\partial}{\partial t}\int_v n dV = -\int_S \vec{\Gamma} d\vec{S}, \tag{6}$$

and using Gauss' law ($\int_S \vec{A} d\vec{S} = \int_V \nabla.\vec{A} dV$) on the RHS we get that

$$\frac{\partial n}{\partial t} = -\nabla\vec{\Gamma} = \nabla.(D\nabla n) \tag{7}$$

Exercise

1. **Construction of the Diffusion equation**. For a column of particles settling under gravity derive an expression for the rate of change of concentration at a given height z, assuming that D is constant. We do this by constructing the expression for the flux and using equ 7. For the 1-D case we are considering, the diffusive flux is $-D\partial n/\partial z$ and the flux due to the downward drift in the gravitational field is $-nv$. Therefore the total flux is

$$\Gamma = -D\frac{\partial n}{\partial z} - nv, \tag{8}$$

so we have

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial z^2} + v\frac{\partial n}{\partial z}. \tag{9}$$

2. **Equilibrium solution**. In equilibrium (as the time $t \to \infty$), $\partial n/\partial t \to 0$. Under these circumstances use the fact that the flux at any height must be zero to show that the variation of n with z is identical to the expression derived from the Boltzmann energy distribution, which states that the probability of a level with energy E being occupied is $p(E) \propto exp(-E/kT)$. By comparison derive an expression for the Diffusion Coefficient D for particles moving in a fluid of viscosity ξ.

3. **Scaled form of the PDE**. It is often very convenient for computational and analytical purposes to cast a PDE in scaled or dimensionless form. In this case the scaling can be carried out based on parameters arising from the equlibrium solution. In this case show that the diffusion equation can be written in the following scaled form

$$\frac{\partial \tilde{n}}{\partial \tau} = \frac{\partial^2 \tilde{n}}{\partial \tilde{z}^2} + \frac{\partial \tilde{n}}{\partial \tilde{z}}, \tag{10}$$

   where the parameters $\tilde{n} = n/n_0$ with n_0 the average concentration, $\tilde{z} = \gamma z$ with $\gamma = mg/kT$ with m the effective mass of the particle (taking into account the density of the background fluid), and $\tau = t/t_0$ with $t_0 = 1/(\gamma^2 D) = kT/mgv$. Note that this analysis has produced a characteristic lengthscale $z_0 = 1/\gamma$ and timescale t_0.

4. **Coding**. Write code to solve the diffusion equation you have developed, using a finite difference representation. To do this you can use the Finite difference expressions for the gradient and second derivative given in Appendix 1. This allows calculation of the RHS of Eq. 10, and the value of $\tilde{n}$ is updated using a simple Euler scheme (Also given in Appendix 1). Calculate the variation of concentration with height and time and show that in the limit of $t \to \infty$ the numerical variation of n with z obeys the analytical expression. **NB Code developments in computational physics will normally involve studying simple cases for which analytical solutions exist so that numerical schemes can be tested.**

5. **Initial and boundary conditions**. You should simulate the gravitational settling of a colloid consisting of nanoscale particles dispersed in some background fluid. Often these are produced by chemical deposition techniques, giving particles of some solid phase in a solvent. The particles are initially uniformly distributed throughout the height of the vessel, so the relevant initial condition is $\tilde{n}(\tau = 0) = 1.0$. The colloid is constrained by the walls of the vessel, and we can consider 1-D diffusion since the particles are settling under gravity. We also assume that the particles are not allowed to escape from the top of the fluid column. This means that if the column is of height h, there can be no flux through the planes at $z = 0, h$. Show that this requirement leads to a condition for the value of $\frac{\partial \tilde{n}}{\partial \tilde{z}}$ at $z = 0, h$. How to introduce this into the code? These are referred to as Neumann boundary conditions (constant gradient) and the computational technique is described in the year II continuum mechanics course, reproduced in appendix 1.

Show that this gives rise to $\tilde{n}(0) = \tilde{n}(1)\frac{1}{1-\Delta z}$ at the lower boundary and derive the equivalent boundary condition for the upper boundary.

The boundary conditions can alternatively be implemented by appending an extra site to each end of the system. The evaluation of the density proceeds identically for each site in the system, including the two end sites. Any diffusion that occurs across the system boundaries is necessarily into the two additional simulation sites. At the end of each time-step, the fluid density at these extra sites is set to zero, and an equivalent density is added to the adjacent site within the system.

That is after having done the time evolution for that time step we correct the system by carrying out $\tilde{n}(1) = \tilde{n}(1) + \tilde{n}(0)$ and reset $\tilde{n}(0) = 0$, with equivalent behaviour required for the top.

6. **Experiments**. Use the code to study the time evolution of the concentration profile,ie $\tilde{n}(\tilde{z}, \tau)$. This should be done as a function of the height h. Show that the expected equilibrium profile is achieved as $\tau \to \infty$, What are the corresponding times involved? Calculate the scaling parameters for the settling of a dispersion of Cobalt particles in a fluid of density $1kgm^{-3}$ and a viscosity of $0.001kgm^{-1}$, and a column height of 10cm. Use your model to predict the equilibrium profile and the timescale for the settling for particle sizes of 5nm and 10nm. NB, an important test of your code arises from the fact that the imposed boundary conditions should conserve the number of particles, ie your solution should obey the condition

$$(\gamma h)^{-1} \int_0^{h\gamma} \tilde{n}(\tau) d\tilde{z} = \tilde{n}(0). \tag{11}$$

You should use this as a test of the accuracy of your integration scheme.

Appendix 1: Finite difference representation

In terms of the finite difference representation the first derivative can be written as

$$\frac{\partial y}{\partial x} = (y_{i+1} - y_{i-1})/(2\Delta x) \tag{12}$$

and the second derivative as

$$\frac{\partial^2 y}{\partial x^2} = (y_{i+1} - 2 * y_i + y_{i-1})/(\Delta x^2) \tag{13}$$

where Δx is the finite interval in the independent variable.

Euler integration scheme.

This is the simplest way to integrate a differential equation. If we expand a function $y(t)$ about $t = t_0$, this gives

$$y(t) = y(t_0) + y'(t_0)(t - t_0) + O((t - t_0)^2), \tag{14}$$

where y' is the first derivative. To first order,

$$y(t_0 + \Delta t) = y(t_0) + y'(t_0)\Delta t, \tag{15}$$

in other words the function is updated based on the value at the previous timestep and the gradient of the function. In the case of the solution of Eq 10,

$$\tilde{n}(\tau_0 + \Delta\tau) = \tilde{n}(\tau_0) + \frac{\partial \tilde{n}}{\partial \tau}\Delta\tau, \tag{16}$$

with $\frac{\partial \tilde{n}}{\partial \tau}$ calculated from Eq. 10.

Boundary conditions.

The nature of the boundary conditions influences our choice of mesh, i.e. where we place the physical boundary with respect to the mesh.

Gradient (Neumann) conditions: Since the finite difference value of the gradient is formed by the difference at two adjacent mesh points, say 0 and 1, the boundary will lie at the midpoint 1/2.
The gradient at the left boundary is equated to $(N_1 - N_0)/\Delta x$. Given that the gradient and N_1 are known, this fixes the value for N_0 to be used in the finite difference calculation. Similarly, if the number of mesh points is I, the right boundary is placed at $(I + 1/2)$ and the value of the gradient there used to obtain N_{I+1}.