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DIFFUSION IN A CLOSED SYSTEM: AN ANALYTICAL TOOL FOR MEASURING DIFFUSIVITY

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ABSTRACT

An analytical solution is presented for the problem of diffusion in a tube with boundary conditions imposed by well-stirred end-bulbs (two-chamber diffusion). Although these boundary conditions make the problem non self-adjoint still an analytical solution can be obtained by the method of separation of variables. This method applies to a wider class of problems, for instance to the one-chamber case in which the two end-bulbs are connected. An analytical solution for this one-chamber case is also presented. As a result of this approach a new technique can be applied to measure gaseous diffusion in porous media.

1 INTRODUCTION

Knowledge of the rate of diffusive transport of liquids or gases through porous media is important, e.g. in agriculture (soil aeration and irrigation on plant growth). Other examples are the movement of liquids or gases in natural reservoirs and the transport of reactants to catalytic surfaces.

There is a long history of measurements of diffusion rates via steady-state experiments starting with Buckingham (1904). In a typical example of such an experiment gas streams of different composition are led over the ends of a porous column. After steady-state is reached these gas streams are analyzed to estimate diffusivity. Penman (1940) and Van Bavel (1952) also employed a steady state technique.

Non steady-state methods are less time consuming and are of interest in their own right because of the important role of transient diffusion in real systems. The experimental technique, applied by Dye and Dallavalle (1958), Weller et al. (1974), Ball et al. (1981), Reible and Shair (1982) and Sallam et al. (1984), uses an apparatus composed of two chambers connected by a tube filled with porous test material, see Figure 1. A tracer gas is injected into one of the chambers and is allowed to diffuse through the tube. The gases within the chambers are kept well-stirred and the concentration of the tracer gas is measured as a function of time in both chambers.

In order to estimate the diffusivity of the tracer gas in the porous material a careful formulation of the related diffusion problem is needed. Barnes (1934) and Bird et al. (1960) derived explicit solutions for specific symmetric two-chamber cases. Reible and Shair (1982) used the analytical solution of Shair and Cohen (1969) for their measurements of effective diffusivities of a gas in dry and moist porous beds. Sallam et al. (1984) solved the diffusion equation for the relevant initial and boundary conditions using a numerical approach.

In order to solve the general two-chamber case for an arbitrary initial condition we extend the standard separation of variables technique. This new technique enables us to solve as well the one-chamber case for an arbitrary initial condition. In this last case the diffusion tube is contained in the (one) chamber, see Figure 2. Such an experimental set up may considerably simplify the measurement of diffusion rates.

2 TWO MATHEMATICAL MODELS

2.1. The two-chamber case.

Consider a cylindrical tube with cross-sectional area S and length L. The x-axis coincides with the axis of this cylinder. At x = 0 there is a chamber A with volume V_A and at x = L there is a second chamber B with volume V_B, see Figure 1.

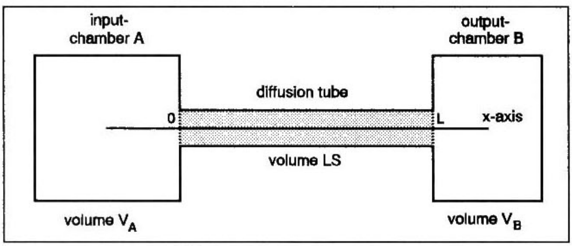

FIGURE 1. Two chamber system.

Both chambers are kept well-mixed, which means that the concentration in chamber A is uniform and equal to the concentration in the tube at $x = 0$. Likewise the concentration in chamber B is uniform and equal to the concentration in the tube at $x = L$. In the tube transport takes place by diffusion. Thus the equation for $C(x,t)$, the concentration of the tracer gas in the tube at place x and time t, is

$$\frac{\partial C}{\partial t}(x,t) = D\frac{\partial^2 C}{\partial x^2}(x,t) \quad \text{for } 0 \le x \le L \text{ and } t > 0 \ , \tag{2.1}$$

where D is the diffusivity of the tracer gas through the porous medium. The boundary conditions are

$$V_1 \frac{\partial C}{\partial t}(0,t) = SD\frac{\partial C}{\partial x}(0,t) \quad \text{for } t > 0 \ , \tag{2.2}$$

$$-V_2 \frac{\partial C}{\partial t}(L,t) = SD\frac{\partial C}{\partial x}(L,t) \quad \text{for } t > 0 \ . \tag{2.3}$$

Boundary condition (2.2) states that a flux of the tracer gas into the tube at $x = 0$ results in a decrease of the concentration of the tracer gas in chamber A. Likewise Eq. (2.3) states that a flux of the tracer gas out of the tube at $x = L$ results in an increase of the concentration of the tracer gas in chamber B.

In Section 3 we solve the boundary value problem stated in Eqs. (2.1), (2.2) and (2.3) for a general initial condition by applying a variation on the usual separation of variables technique. A little care is needed in formulating the initial condition:

$$C(x,0) = \begin{cases} C_A & \text{for } x = 0 \\ \varphi(x) & \text{for } 0 < x < L \\ C_B & \text{for } x = L \end{cases} \ . \tag{2.4}$$

In this way chamber A is represented solely by the point $x = 0$ and in the same way chamber B is represented by the point $x = L$. We expect continuity of $C(x,t)$ at $x = 0$ and $x = L$ for $t > 0$ only. The function $\varphi(x)$ describes the initial concentration in the tube.

A simple mass balance yields

$$C_\infty = \frac{C_A V_A + S\int_0^L \varphi(x)\,dx + C_B V_B}{V_A + LS + V_B} \ , \tag{2.5}$$

where C_∞ is the equilibrium concentration of the system, that is the concentration uniform throughout the system which is reached after infinite time.

2.2. The one-chamber case.

Next we consider the situation in which the two chambers are not only linked by the diffusion tube but also by a connecting pipe. Then there is in effect only one chamber and we can imagine that the diffusion tube is contained in this chamber, see Figure 2.

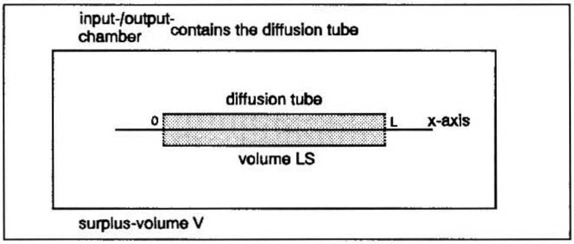

FIGURE 2. One chamber system.

Transport in the tube still occurs by diffusion. The equation for $C_1(x,t)$, the concentration of the tracer gas in the diffusion tube at place x and time t, is again

$$\frac{\partial C_1}{\partial t}(x,t) = D\frac{\partial^2 C_1}{\partial x^2}(x,t) \quad \text{for } 0 \leq x \leq L \text{ and } t > 0 \ . \tag{2.6}$$

Since there is no concentration gradient in the chamber the concentrations at the two endpoints of the diffusion tube are equal

$$C_1(0,t) = C_1(L,t) \quad \text{for } t > 0 \ , \tag{2.7}$$

which is our first boundary condition. This implies

$$\frac{\partial C_1}{\partial t}(0,t) = \frac{\partial C_1}{\partial t}(L,t) \quad \text{for } t > 0 \ . \tag{2.8}$$

The second boundary condition states that the total flux of the tracer gas into the tube at $x = 0$ and $x = L$ results in a decrease of the concentration of the tracer gas in the chamber. This means

$$V\frac{\partial C_1}{\partial t}(0,t) = SD\left[\frac{\partial C_1}{\partial x}(0,t) - \frac{\partial C_1}{\partial x}(L,t)\right] = V\frac{\partial C_1}{\partial t}(L,t) \quad \text{for } t > 0 \ , \tag{2.9}$$

where V is the volume of the chamber (outside the tube).

In Section 4 we solve the boundary value problem stated in Eqs. (2.6), (2.7) and (2.9) for a general initial condition applying the same variation on the usual separation of variables technique as already mentioned before. Again some care is needed in formulating the initial condition:

$$C_1(x,0) = \begin{cases} C_{init} & \text{for } x = 0 \\ \varphi(x) & \text{for } 0 < x < L \\ C_{init} & \text{for } x = L \end{cases} , \qquad (2.10)$$

where C_{init} is the initial concentration in the chamber. The function $\varphi(x)$ describes again the initial concentration of the tracer gas in the diffusion tube. Now the chamber is represented solely by the point $x = 0$ (or solely by the point $x = L$). Again we expect continuity of $C_1(x,t)$ at $x = 0$ and $x = L$ for $t > 0$ only.

A mass balance now yields

$$C_{1,\infty} = \frac{C_{init} V + S \int_0^L \varphi(x)\, dx}{V + LS} , \qquad (2.11)$$

where $C_{1,\infty}$ is again the equilibrium concentration of this system.

3 ANALYSIS OF THE TWO-CHAMBER CASE

In this section we determine the function $C(x,t)$ that solves the boundary value problem stated in Eqs. (2.1), (2.2) and (2.3) subject to initial condition (2.5). Our first step is the introduction of a dimensionless distance η and a dimensionless time τ:

$$\eta = \frac{x}{L} \quad \text{and} \quad \tau = \frac{Dt}{L^2} . \qquad (3.1)$$

Using Eq. (2.5) we define the dimensionless concentration

$$\theta(\eta,\tau) = \frac{C(x,t)}{C_\infty} \qquad (3.2)$$

and the dimensionless volumes

$$\delta = \frac{V_A}{LS} \qquad \text{and} \qquad \varepsilon = \frac{V_B}{LS} \ . \tag{3.3}$$

Then the non-dimensional boundary value problem to be solved is

$$\frac{\partial\theta}{\partial\tau}(\eta,\tau) = \frac{\partial^2\theta}{\partial\eta^2}(\eta,\tau) \quad \text{for } 0 \le \eta \le 1 \text{ and } \tau > 0 \ , \tag{3.4}$$

$$\frac{\partial\theta}{\partial\eta}(0,\tau) = \delta\frac{\partial\theta}{\partial\tau}(0,\tau) \quad \text{for } \tau > 0 \ , \tag{3.5}$$

$$\frac{\partial\theta}{\partial\eta}(1,\tau) = -\varepsilon\frac{\partial\theta}{\partial\tau}(1,\tau) \quad \text{for } \tau > 0 \ . \tag{3.6}$$

Using Eq. (2.5) again we define the dimensionless initial concentrations

$$\alpha = \frac{C_A}{C_\infty}, \qquad \phi(\eta) = \frac{\varphi(x)}{C_\infty}, \qquad \beta = \frac{C_B}{C_\infty} \ . \tag{3.7}$$

Then the non-dimensional initial condition to be fulfilled is

$$\theta(\eta,0) = \begin{cases} \alpha & \text{for } \eta = 0 \\ \phi(\eta) & \text{for } 0 < \eta < 1 \\ \beta & \text{for } \eta = 1 \end{cases} \ . \tag{3.8}$$

From Eq. (3.2) we deduce for the non-dimensional equilibrium concentration θ_∞

$$\theta_\infty = \lim_{\tau\to\infty} \theta(\eta,\tau) = 1 \ . \tag{3.9}$$

We set out to solve the boundary value problem stated in Eqs. (3.4), (3.5) and (3.6) by separation of variables. With

$$\theta(\eta,\tau) = X(\eta)T(\tau) \tag{3.10}$$

we obtain from Eq. (3.4) in the usual way

$$X''(\eta) + \mu^2 X(\eta) = 0 \tag{3.11}$$

$$T'(\tau) + \mu^2 T(\tau) = 0 \ , \tag{3.12}$$

where μ^2 ($\mu \ge 0$) is the common separation constant, which in this case takes only non-negative values. From Eq. (3.11) and from Eqs. (3.5), (3.6) and (3.12) we infer the following eigenvalue problem for $X(\eta)$

$$\begin{cases} X''(\eta) = & -\mu^2 X(\eta) \qquad \text{for } 0 \leq \eta \leq 1\,, \\ X'(0) = & -\delta\mu^2 X(0)\,, \\ X'(1) = & \varepsilon\mu^2 X(1)\,. \end{cases} \tag{3.13}$$

The eigenvalues μ_0, μ_1, μ_2, ... are the non-negative roots of

$$(1 - \delta\varepsilon\,\mu^2)\sin(\mu) + (\delta + \varepsilon)\,\mu\cos(\mu) = 0 \;. \tag{3.14}$$

The associated eigenfunctions are (for $n = 0, 1, 2, \ldots$)

$$X_{1,n}(\eta) = \cos(\mu_n\eta) - \delta\mu_n\sin(\mu_n\eta)\,, \tag{3.15}$$

or also

$$X_{2,n}(\eta) = \cos(\mu_n(1-\eta)) - \varepsilon\mu_n\sin(\mu_n(1-\eta))\,. \tag{3.16}$$

Of course $X_{1,n}$ and $X_{2,n}$ differ merely a multiplicative constant, which depends only on n. If we interchange the role of δ and ε and apply the transformation $\eta \rightarrow 1-\eta$ these two sets of eigenfunctions change into one another. We introduce at this point two equivalent sets of eigenfunctions in order to simplify later results and to regain a certain degree of symmetry, which is absent if δ is unequal to ε.

Next we infer from the superposition principle and from Eq. (3.15) and Eq. (3.12) the following general solutions for Eqs. (3.4), (3.5) and (3.6)

$$\theta(\eta,\tau) = \sum_{n=0}^{\infty} A_n X_{1,n}(\eta)\exp(-\mu_n^2\tau) \;. \tag{3.17}$$

Using Eq. (3.16) instead of Eq. (3.15) we get an analogous result.

From initial condition (3.8) and from Eqs. (3.17) it follows

$$\sum_{n=0}^{\infty} A_n X_{1,n}(\eta) = \theta(\eta,0) = \begin{cases} \alpha & \text{for } \eta = 0 \\ \phi(\eta) & \text{for } 0 < \eta < 1 \;. \\ \beta & \text{for } \eta = 1 \end{cases} \tag{3.18}$$

Usually the coefficients A_n are determined by an orthogonality principle. However the appearance of the separation constant in the boundary conditions makes the problem non-self-adjoint in the 'usual' sense, as already stated by Shair and Cohen (1969). However the following version of Lagrange's identity is easily proved for functions $f(\eta)$, $g(\eta)$ which fulfil the boundary conditions stated in Eq. (3.13):

$$\int_0^1 f'''(\eta)g'(\eta) - f'(\eta)g'''(\eta)\, d\eta = 0. \tag{3.19}$$

From this identity it follows that the eigenvalue problem stated in Eq. (3.13) is self-adjoint with respect to the following inner product:

$$(f,g) = \int_0^1 f'(\eta)\,\overline{g}'(\eta)\, d\eta \ , \tag{3.20}$$

where the functions $f(\eta)$, $g(\eta)$ are of course determined only up to an additive constant.

By this procedure we lose the first eigenvalue $\mu_0 = 0$ and the first eigenfunctions $X_{1,0}(\eta) = X_{2,0}(\eta) = 1$. Since we are studying closed systems this is not a real problem: thanks to our non-dimensionalisation convention the constant part in a final solution, which represents the total mass in the system, will always be equal to one.

The self-adjointness of the problem with respect to the inner product as stated in Eq. (3.20) implies the completeness of the two sets of eigenfunctions and justifies the eigenfunction expansion given in Eq. (3.17). In particular we deduce the following orthogonality relation for eigenfunctions (with i or j equal to 1 or 2):

$$\int_0^1 X_{i,n}'(\eta)X_{j,m}'(\eta)\, d\eta = 0 \qquad \text{for } n \neq m \ . \tag{3.21}$$

Now it is possible to calculate the coefficients A_n in Eq. (3.18) for $n \geq 1$:

$$A_n = \frac{\displaystyle\int_0^1 \frac{\partial \theta}{\partial \eta}(\eta,0)\, X_{2,n}'(\eta)\, d\eta}{\displaystyle\int_0^1 X_{1,n}'(\eta)\, X_{2,n}'(\eta)\, d\eta} \ . \tag{3.22}$$

Of course some care is needed with the right-hand side of Eq. (3.22). At points η with a jump discontinuity for $\theta(\eta,0)$ we have to interpret this right-hand side as a Dirac delta function. We will deal with this aspect in a later section. The value of A_0 follows from Eqs. (3.9) and (3.17)

$$A_0 = \lim_{\tau \to \infty} \theta(\eta,\tau) = \theta_\infty = 1 \ . \tag{3.23}$$

The problem is now completely solved. Using the original coordinates the final solution reads

$$C(x,t) = C_{\infty} + C_{\infty} \sum_{n=1}^{\infty} A_n X_{1,n}(\frac{x}{L}) \exp(-\frac{\mu_n^2 D t}{L^2}) \tag{3.24}$$

with μ_n from Eq. (3.14), $X_{1,n}(\eta)$ from Eqs. (3.15) and the coefficients A_n from Eq. (3.22).

4 Analysis of the One-Chamber Case

The purpose of this section is to determine the function $C_1(x,t)$ that solves the boundary value problem stated in Eqs. (2.6), (2.7) and (2.9) subject to initial condition (2.10). We introduce a dimensionless distance η and dimensionless time τ as in Eq. (3.1). Using this time Eq. (2.11) we define the dimensionless concentration

$$\theta_1(\eta,\tau) = \frac{C_1(x,t)}{C_{1,\infty}} \tag{4.1}$$

and the dimensionless volume

$$\lambda = \frac{V}{LS} \ . \tag{4.2}$$

Now the non-dimensional boundary value problem to be solved is

$$\frac{\partial \theta_1}{\partial \tau}(\eta,\tau) = \frac{\partial^2 \theta_1}{\partial \eta^2}(\eta.\tau) \quad \text{for } 0 \leq \eta \leq 1 \text{ and } \tau > 0 \ , \tag{4.3}$$

$$\theta_1(0,\tau) = \theta_1(1,\tau) \quad \text{for } \tau > 0 \ , \tag{4.4}$$

$$\lambda \frac{\partial \theta_1}{\partial \tau}(0,\tau) = \frac{\partial \theta_1}{\partial \eta}(0,\tau) - \frac{\partial \theta_1}{\partial \eta}(1,\tau) = \lambda \frac{\partial \theta_1}{\partial \tau}(1,\tau) \quad \text{for } \tau > 0 \ . \tag{4.5}$$

Using Eq. (2.11) again we define the dimensionless initial concentrations

$$\gamma = \frac{C_{init}}{C_{1,\infty}} \quad \text{and} \quad \phi_1(\eta) = \frac{\varphi(x)}{C_{1,\infty}} \ . \tag{4.6}$$

Now the non-dimensional initial condition to be fulfilled is

$$\theta_1(\eta,0) = \begin{cases} \gamma & \text{for } \eta = 0 \\ \phi_1(\eta) & \text{for } 0 < \eta < 1 \\ \gamma & \text{for } \eta = 1 \end{cases} \ . \tag{4.7}$$

From Eq. (4.1) we infer again for the non-dimensional equilibrium concentration $\theta_{1,\infty}$

$$\theta_{1,\infty} = \lim_{\tau \to \infty} \theta_1(\eta,\tau) = 1 \ . \tag{4.8}$$

We solve the boundary value problem stated in Eqs. (4.3), (4.4) and (4.5) by separation of variables. With

$$\theta_1(\eta,\tau) = Y(\eta)T(\tau) \tag{4.9}$$

we obtain from Eq. (4.3) as before

$$Y''(\eta) + \mu^2 Y(\eta) = 0 \tag{4.10}$$

$$T'(\tau) + \mu^2 T(\tau) = 0 \ , \tag{4.11}$$

where μ^2 ($\mu \geq 0$) is again the common separation constant, which also in this case takes only non-negative values. From Eq. (4.10) and from Eqs. (4.4), (4.5) and (4.11) we infer the following eigenvalue problem for $Y(\eta)$

$$\begin{cases} Y''(\eta) = -\mu^2 Y(\eta) \qquad \text{for } 0 \leq \eta \leq 1 \ , \\ Y(0) = Y(1) \ , \\ \lambda\mu^2 Y(0) = Y'(1) - Y'(0) = \lambda\mu^2 Y(1). \end{cases} \tag{4.12}$$

The eigenvalues μ_0, μ_1, μ_2, ... are the non-negative roots of

$$\sin(\frac{\mu}{2})[\sin(\frac{\mu}{2}) + \lambda\frac{\mu}{2}\cos(\frac{\mu}{2})] = 0 \ . \tag{4.13}$$

The associated eigenfunctions can be written as (for n = 0, 1, 3, 5, ...)

$$Y_n(\eta) = \cos(\mu_n(\eta - \tfrac{1}{2})) \tag{4.14^a}$$

and (for n = 2, 4, 6, ...)

$$Y_n(\eta) = \sin(n\pi(\eta - \tfrac{1}{2})) \ . \tag{4.14^b}$$

This form of the eigenfunctions reflects the fundamental symmetry of the problem.

The version of Lagrange's identity stated in Eq. (3.19) also holds for functions $f(\eta)$, $g(\eta)$ which fulfil the boundary conditions in Eq. (4.12). Therefore the same reasoning as used before yields the completeness of this set of eigenfunctions and justifies the eigenfunction expansion with respect to this set. In particular we infer the following orthogonality relation:

$$\int_0^1 Y_n'(\eta)\, Y_m'(\eta)\, d\eta = 0 \qquad \text{for } n \neq m \ . \tag{4.15}$$

Thus from Eqs. (4.14) and (4.11) and from the superposition principle we obtain the following general solution for this boundary value problem

$$\theta_1(\eta,\tau) = \sum_{n=0}^{\infty} C_n\, Y_n(\eta) \exp(-\mu_n^2 \tau) \ . \tag{4.16}$$

The initial condition (4.7) and Eq. (4.16) now yield

$$\sum_{n=0}^{\infty} C_n\, Y_n(\eta) = \theta_1(\eta,0) = \begin{cases} \alpha & \text{for } \eta = 0 \\ \phi_1(\eta) & \text{for } 0 < \eta < 1 \\ \alpha & \text{for } \eta = 1 \end{cases} \ . \tag{4.17}$$

The coefficients C_n in the left-hand side of Eq. (4.16) are determined for positive values of n by an application of the orthogonality relation stated in Eq. (4.15):

$$C_n = \frac{\displaystyle\int_0^1 \frac{\partial \theta_1}{\partial \eta}(\eta,0)\, Y_n'(\eta)\, d\eta}{\displaystyle\int_0^1 Y_n'(\eta)^2\, d\eta} \ . \tag{4.18}$$

At points η with a jump discontinuity for $\theta_1(\eta,0)$ we have to interpret the derivative of this initial function in Eq. (4.18) once more as a Dirac delta function. As said before, we deal with this aspect in a later section. The value of C_0 follows from Eqs. (4.8) and (4.16)

$$C_0 = \lim_{\tau \to \infty} \theta_1(\eta,\tau) = \theta_{1,\infty} = 1 \ . \tag{4.19}$$

The problem is now completely solved. For the original coordinates the final solution reads

$$C_1(x,t) = C_{1,\infty} + C_{1,\infty} \sum_{n=1}^{\infty} C_n\, Y_n\left(\frac{x}{L}\right) \exp\left(-\frac{\mu_n^2 D t}{L^2}\right) \tag{4.20}$$

with μ_n from Eqs. (4.13)), $Y_n(\eta)$ from Eq. (4.14) and the coefficients C_n from Eq. (4.18).

5 THE TWO-CHAMBER CASE REVISITED

In this section we exploit the general result obtained in Section 3. In particular we clarify how to handle a jump discontinuity for $\theta(\eta,0)$ in the right-hand side of Eq. (3.20) or for $\theta_1(\eta,0)$ in the right-hand side of Eq. (4.18). Also we discuss a special case, which in a sense connects the one- and two-chamber cases.

5.1 A discontinuous initial condition.

Consider the non-dimensional boundary value problem as stated in Eqs. (3.4), (3.5) and (3.6), subject to the dimensionless initial condition

$$\theta(\eta,0) = \phi(\eta) = \begin{cases} K & \text{for } 0 \le \eta < \kappa \\ 0 & \text{for } \kappa < \eta \le 1 \end{cases}, \tag{5.1}$$

see Figure 3[a]. A value for the initial concentration at the jump point is not needed. By our non-dimensionalisation conventions we are not free to choose K given a value for κ. From a non-dimensional analogue of Eq. (2.5) and from Eq. (3.9) we deduce

$$K = \frac{\delta + 1 + \varepsilon}{\delta + \kappa} \ . \tag{5.2}$$

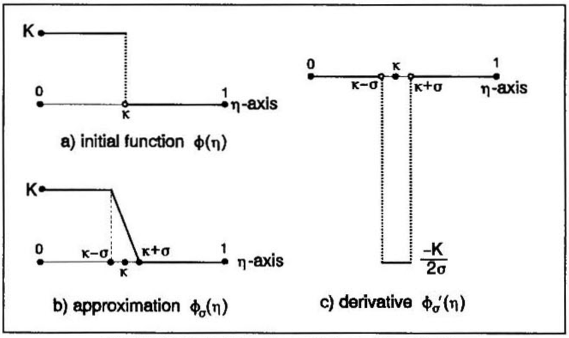

FIGURE 3. Initial function with jump discontinuity.

Next we approximate the discontinuous initial function $\phi(\eta)$ with a continuous one

$$\phi_\sigma(\eta) = \begin{cases} K & \text{for} \quad 0 \le \eta < \kappa - \sigma \\ \dfrac{\kappa + \sigma - \eta}{2\sigma} K & \text{for } \kappa - \sigma \le \eta \le \kappa + \sigma \\ 0 & \text{for } \kappa + \sigma < \eta \le 1 \end{cases}, \tag{5.3}$$

see Figure 3^b.

First we start to solve the boundary value problem stated in Eqs. (3.4), (3.5) and (3.6) subject to the continuous initial condition (5.3). The numerator of the right-hand side of Eq. (3.22) becomes

$$\int_0^1 \phi_\sigma{}'(\eta)\, X_{2,n}{}'(\eta)\, d\eta = -K\left(\frac{X_{2,n}(\kappa+\sigma) - X_{2,n}(\kappa-\sigma)}{2\sigma}\right) , \tag{5.4}$$

where we have used Eq. (5.3). At this point we take the limit for $\sigma \to 0$. Then $\phi_\sigma{}'(\eta)$ changes into $\phi'(\eta)$ and from Eqs. (5.4) it becomes clear that we have to interpret the last derivative as a multiple of the Dirac delta function

$$\phi'(\eta) = \lim_{\sigma\to 0} \phi_\sigma{}'(\eta) \equiv -K\,\delta(\eta - \kappa) . \tag{5.5}$$

Thus we have

$$\int_0^1 \phi'(\eta)\, X_{2,n}{}'(\eta)\, d\eta = \int_0^1 -K\,\delta(\eta - \kappa)\, X_{2,n}{}'(\eta)\, d\eta = -K\, X_{2,n}{}'(\kappa) , \tag{5.6}$$

in accordance with Eq. (5.4).

Next we calculate the denominator in the right-hand side of Eq. (3.22). This yields

$$\int_0^1 X_{1,n}{}'(\eta)\, X_{2,n}{}'(\eta)\, d\eta =$$

$$= \frac{\mu_n}{2}\left[(1 - \delta\varepsilon\mu_n^2)\mu_n\cos(\mu_n) - (1 + \delta\mu_n^2 + \varepsilon\mu_n^2 + \delta\varepsilon\mu_n^2)\sin(\mu_n)\right] , \tag{5.7}$$

where we have used Eqs. (3.15) and (3.16). Adding to the part between brackets in the right-hand side of Eq. (5.7) the left-hand side of the eigenvalue equation (3.14) we obtain

$$\int_0^1 X_{1,n}{}'(\eta)\, X_{2,n}{}'(\eta)\, d\eta =$$

$$= \frac{\mu_n^2}{2}\left[(1 + \delta + \varepsilon - \delta\varepsilon\mu_n^2)\cos(\mu_n) - (\delta + \varepsilon + 2\delta\varepsilon)\mu_n\sin(\mu_n)\right] . \tag{5.8}$$

Now we have at our disposal all we need for the construction of a solution for our original initial value problem. From Eq. (3.17) in conjunction with Eqs. (3.22), (3.23), (5.6), (5.8), (3.15) and (3.16) we obtain

$$\theta(\eta,\tau) = 1 + \tag{5.9}$$

$$- 2K\sum_{n=1}^{\infty} \frac{[\sin(\mu_n(1-\kappa)) + \varepsilon\mu_n\cos(\mu_n(1-\kappa))][\cos(\mu_n\eta) - \delta\mu_n\sin(\mu_n\eta)]\exp(-\mu_n^2\tau)}{\mu_n[(1+\delta+\varepsilon-\delta\varepsilon\mu_n^2)\cos(\mu_n) - (\delta+\varepsilon+2\delta\varepsilon)\mu_n\sin(\mu_n)]}$$

with μ_n from Eq. (3.14) and K from Eq. (5.2). Interchanging the role of $X_{1,n}(\eta)$ and $X_{2,n}(\eta)$ we find in the same way

$$\theta(\eta,\tau) = 1 + \tag{5.10}$$

$$+ 2K\sum_{n=1}^{\infty} \frac{[\sin(\mu_n\kappa) + \delta\mu_n\cos(\mu_n\kappa)][\cos(\mu_n(1-\eta)) - \varepsilon\mu_n\sin(\mu_n(1-\eta))]\exp(-\mu_n^2\tau)}{\mu_n[(1+\delta+\varepsilon-\delta\varepsilon\mu_n^2)\cos(\mu_n) - (\delta+\varepsilon+2\delta\varepsilon)\mu_n\sin(\mu_n)]} .$$

Of course the equality of these solutions (5.9) and (5.10) is easily checked with help of the eigenvalue equation (3.14).

Eq. (5.10) we recognize, but for a typographical error, as the solution Shair and Cohen (1969) obtained for $\kappa \leq \eta \leq 1$. Here we show that this solution holds on the full interval [0,1], which makes it possible to abandon the very complicated solution of Shair and Cohen (1969) for $0 \leq \eta < \kappa$. It is important to note, that the solutions presented in Eqs. (5.9) and (5.10) are also valid if the jump occurs at $\kappa = 0$ or $\kappa = 1$. The technique we used before is still applicable, although we have to modify slightly the definition of our approximate initial function $\phi_\sigma(\eta)$.

The solution technique we employed in this example answers to the question we raised in Section 3 and 4, how to deal with the derivative of the initial function at a point where a jump occurs. Apparently we have to confine ourselves to initial functions which are piece-wise differentiable. For those points where a jump occurs we have to interpret the derivative of the initial function as in Eqs. (3.22) or (4.18) as a multiple of the Dirac delta function. The value of the multiplication factor is of course determined by the direction and magnitude of the jump.

5.2 An example.

Consider the problem formulated in Eqs. (2.1), (2.2) and (2.3) for the following initial condition:

$$C(x,0) = \begin{cases} 0 & \text{for } x = 0 \\ x & \text{for } 0 < x < L \\ 0 & \text{for } x = L \end{cases} . \tag{5.11}$$

Using our non-dimensionalisation conventions we get the transformed problem formulated in Eqs. (3.4), (3.5) and (3.6) for the following transformed initial condition:

$$\theta(\eta,0) = \begin{cases} 0 & \text{for } \eta = 0 \\ K\eta & \text{for } 0 < \eta < 1 \\ 0 & \text{for } \eta = 1 \end{cases} , \tag{5.12}$$

with

$$K = \frac{L}{C_\infty} = 2\delta + 2 + 2\varepsilon . \tag{5.13}$$

There is a jump discontinuity at $\eta = 1$ of magnitude $-K$. Therefore the numerator in the right-hand side of Eq. (3.22) yields

$$\int_0^1 \frac{\partial\theta}{\partial\eta}(\eta,0)\, X_{2,n}'(\eta)\, d\eta = \int_0^1 K\, X_{2,n}'(\eta)\, d\eta - K\, X_{2,n}'(1) . \tag{5.14}$$

Using Eq. (3.16) we get

$$\int_0^1 \frac{\partial\theta}{\partial\eta}(\eta,0)\, X_{2,n}'(\eta)\, d\eta = K - K\cos(\mu_n) + K\varepsilon\mu_n\sin(\mu_n) - K\varepsilon\mu_n^2 . \tag{5.15}$$

The denominator in the right-hand side of Eq. (3.22) is already found in Eq. (5.8). Thus the final solution of the transformed problem is

$$\theta(\eta,\tau) = 1 + \tag{5.16}$$

$$+ 2K\sum_{n=1}^{\infty} \frac{[1 - \cos(\mu_n) + \varepsilon\sin(\mu_n) - \varepsilon\mu_n][\cos(\mu_n\eta) - \delta\mu_n\sin(\mu_n\eta)]\exp(-\mu_n^2\tau)}{\mu_n^2[(1+\delta+\varepsilon-\delta\varepsilon\mu_n^2)\cos(\mu_n) - (\delta+\varepsilon+2\delta\varepsilon)\mu_n\sin(\mu_n)]}$$

In the original coordinates this solution reads

$$C(x,t) = \frac{L}{2\delta + 2 + 2\varepsilon} + \tag{5.17}$$

$$+ 2L\sum_{n=1}^{\infty} \frac{[1 - \cos(\mu_n) + \varepsilon\mu_n\sin(\mu_n) - \varepsilon\mu_n^2][\cos(\mu_n\frac{x}{L}) - \delta\mu_n\sin(\mu_n\frac{x}{L})]\exp(-\frac{\mu_n^2 Dt}{L^2})}{\mu_n^2[(1+\delta+\varepsilon-\delta\varepsilon\mu_n^2)\cos(\mu_n) - (\delta+\varepsilon+2\delta\varepsilon)\mu_n\sin(\mu_n)]} .$$

If we take the limit $\delta \to 0$ and $\varepsilon \to 0$ it follows from Eq. (3.14) that $\mu_n \to n\pi$; C(x,t) then changes into

$$C(x,t) = \frac{L}{2} + 2L\sum_{n=1}^{\infty} \frac{(-1)^n - 1}{n^2\pi^2}\cos(\frac{n\pi x}{L})\exp(-\frac{n^2\pi^2}{L^2}Dt) . \tag{5.18}$$

This is the well-known solution of Eq. (2.1) for non-flux boundary conditions and for the initial condition as stated in Eq. (5.11), which is a problem that is self-adjoint in the normal sense.

5.3 The symmetric case.

If we take in Eqs. (3.4), (3.5) and (3.6) $\delta = {}^1/_2\lambda = \varepsilon$ the resulting boundary value problem is symmetric around $\eta = {}^1/_2$. From Eq. (3.14) we infer that the eigenvalues μ_0, μ_1, μ_2, ... of a symmetric two-chamber problem are the non-negative roots of

$$[\sin(\frac{\mu}{2}) + \lambda\frac{\mu}{2}\cos(\frac{\mu}{2})][\cos(\frac{\mu}{2}) - \lambda\frac{\mu}{2}\sin(\frac{\mu}{2})] = 0 . \tag{5.19}$$

The associated eigenfunctions follow from Eqs. (3.15) or (3.16). The eigenfunctions are (for n = 0, 2, 4, ...)

$$X_n(\eta) = \cos(\frac{\mu_n}{2})X_{1,n}(\eta) = \cos(\mu_n(\eta - \tfrac{1}{2})) \tag{5.20^a}$$

and (for n = 1, 3, 5, ...)

$$X_n(\eta) = -\sin(\frac{\mu_n}{2})X_{1,n}(\eta) = \sin(\mu_n(\eta - \tfrac{1}{2})) . \tag{5.20^b}$$

From Eqs. (4.13) and (4.14) and the results stated in Eqs. (5.19) and (5.20) we see that the symmetrical two-chamber case and the one-chamber case have the same set of symmetrical eigenfunctions, but a different set of anti-symmetric eigenfunctions. It is therefore obvious that these two cases do have the same solution indeed, if the initial condition is symmetric around $\eta = {}^1/_2$. This is of course not true if the initial condition is not symmetric.

For the limiting case $\delta \rightarrow 0$ and $\varepsilon \rightarrow 0$ which represents so called no-flux boundary conditions, the eigenvalue equation (3.14) and both sets of eigenfunctions as represented in Eqs. (3.15) and (3.16) change into the well-known eigenvalue equation and set of eigenfunctions for this no-flux case, which is self-adjoint in the usual sense. Also the solutions as represented in Eqs. (5.9) and (5.10) change into the well-known solution of this no-flux case for the given initial condition.

6 The One-Chamber Case Revisited

In this section we utilize the general result of the one-chamber case we obtained in Section 4. We present an analytical solution for an interesting special type of initial condition. And we will come to understand how Fourier's ring gets its double set of eigenfunctions.

6.1 The initially empty tube.

Suppose at $\tau = 0$ the concentration of the tracer gas throughout the diffusion tube equals zero and therefore the tracer gas is to be found entirely in the well-stirred chamber. Then we have to solve the boundary value problem formulated in Eqs. (4.3), (4.4) and (4.5) subject to the specific initial condition

$$\theta_1(\eta,0) = \begin{cases} K & \text{for } \eta = 0 \\ 0 & \text{for } 0 < \eta < 1 \\ K & \text{for } \eta = 1 \end{cases} . \tag{6.1}$$

By our non-dimensionalisation conventions K cannot be chosen freely. Due to these conventions the non-dimensional equilibrium concentration $\theta_{1,\infty}$ equals 1. From a non-dimensional analogue of Eq. (2.11) and from Eq. (4.8) it follows

$$K = \frac{\lambda + 1}{\lambda} . \tag{6.2}$$

A straightforward application of the results of Section 4 and the technique developed in Section 5.1 yields the solution for the above initial value problem. This solution is already described in Eq. (4.16). The coefficients C_n appearing in the right-hand side of this equation are to be determined from Eq. (4.18). The eigenfunctions $Y_n(\eta)$ are given in Eq. (4.14).

First we determine the numerator of the right-hand side of Eq. (4.18). In this case the derivative of the initial function equals zero for $0 < \eta < 1$. Therefore we only have to take into account the jump discontinuities at $\eta = 0$ and $\eta = 1$. Applying the technique for handling such jump discontinuities (see Section 5.1), we get

$$\int_0^1 \frac{\partial \theta_1}{\partial \eta}(\eta,0)\, Y_n'(\eta) d\eta = \int_0^1 [-K\delta(\eta - 0) + K\delta(\eta - 1)]\, Y_n'(\eta)\, d\eta \ . \qquad (6.3)$$

Using Eq. (4.14ᵃ) we obtain (for $n = 1, 3, 5, \ldots$) for the right-hand side of Eq. (6.3)

$$K\mu_n \sin(-\frac{\mu_n}{2}) - K\mu_n \sin(\frac{\mu_n}{2}) = -2K\mu_n \sin(\frac{\mu_n}{2}) \ . \qquad (6.4)$$

Moreover, using Eq. (4.14ᵇ) we obtain (for $n = 2, 4, 6, \ldots$) for the right-hand side of Eq. (6.3)

$$-K\mu_n \cos(-\frac{\mu_n}{2}) + K\mu_n \cos(\frac{\mu_n}{2}) = 0 \ , \qquad (6.5)$$

which of course also follows from a symmetry argument.

Next we determine the denominator of the right-hand side of Eq. (4.18). Using again Eq. (4.14ᵃ) we obtain (for $n = 0, 1, 3, 5, \ldots$)

$$\int_0^1 Y_n'(\eta)^2 d\eta = \frac{\mu_n^2}{2} - \frac{\mu_n}{2}\sin(\mu_n) \ . \qquad (6.6)$$

It follows

$$C_{2k-1} = \frac{-4K\sin(\frac{\mu_{2k-1}}{2})}{\mu_{2k-1} - \sin(\mu_{2k-1})} \qquad \text{for } k = 1, 2, 3, \ldots \qquad (6.7)$$

and

$$C_{2k} = 0 \qquad \text{for } k = 1, 2, 3, \ldots \ . \qquad (6.8)$$

Eq. (6.7) reduces with help of Eq. (4.13) to

$$C_{2k-1} = \frac{(-1)^k 4K\lambda\sqrt{\lambda^2\mu_{2k-1}^2 + 4}}{\lambda^2\mu_{2k-1}^2 + 4\lambda + 4} \qquad \text{for } k = 1, 2, 3, \ldots \quad (6.9)$$

Again we have collected all the facts needed for the construction of the solution. From Eq. (4.16) in conjunction with Eqs. (4.18), (4.19), (6.8), (6.9) and (4.14ª) we obtain

$$\theta_1(\eta,\tau) = 1 + \sum_{k=1}^{\infty} \frac{(-1)^k 4K\lambda\sqrt{\lambda^2\mu_{2k-1}^2 + 4}}{\lambda^2\mu_{2k-1}^2 + 4\lambda + 4} \cos(\mu_{2k-1}(\eta - \frac{1}{2})) \exp(-\mu_{2k-1}^2\tau) \quad (6.10)$$

with μ_n from Eq. (4.13) and K from Eq. (6.2).

6.2 Fourier's ring.

Probably the oldest problem in Fourier Analysis is the following periodic boundary value problem

$$\frac{\partial\theta_P}{\partial\tau}(\eta,\tau) = \frac{\partial^2\theta_P}{\partial\eta^2}(\eta.\tau) \quad \text{for } 0 \le \eta \le 1 \text{ and } \tau > 0 \ , \quad (6.11)$$

$$\theta_p(0,\tau) = \theta_p(1,\tau) \quad \text{for } \tau > 0 \ , \quad (6.12)$$

$$\frac{\partial\theta_P}{\partial\eta}(0,\tau) = \frac{\partial\theta_P}{\partial\eta}(1,\tau) \quad \text{for } \tau > 0 \ , \quad (6.13)$$

normally designated as Fourier's ring. This boundary value problem is not regular in the sense that there are two independent eigenfunctions for every positive eigenvalue. From Eqs. (4.3), (4.4) and (4.5) it is obvious that Fourier's ring is a limit case of the one-chamber case: in taking the limit $\lambda \to 0$ Eq. (4.5) changes into Eq. (6.13). Taking the limit $\lambda \to 0$ for the symmetrical two-chamber case yields the no-flux boundary condition we already discussed in Section 5.2. It is interesting to note what happens with the eigenvalues and eigenfunctions of the one-chamber problem, if we apply this limit procedure.

From Eq. (4.13) we get the following limit-set of eigenvalues

$$\nu_n = 2n\pi \qquad \text{for } n = 0, 1, 2, \ldots \quad (6.14)$$

A closer inspection shows that in this limit procedure an 'old' eigenvalue μ_{2k-1} changes gradually into the 'old' eigenvalue $\mu_{2n} = 2n\pi$ (for $n = 1, 2, 3, \ldots$), in this way producing one 'new' eigenvalue $\nu_n = 2n\pi$. However, the associated 'old' eigenfunction does not change into the corresponding 'old' eigenfunction. The 'old' symmetric eigenfunction $Y_{2k-1}(\eta)$ changes (for $n = 1, 2, 3, \ldots$) up to a minus sign into a 'new' symmetric eigenfunction

$$Z_{n,1}(\eta) = \cos(2n\pi\eta) \qquad \text{for } n = 1, 2, 3, \ldots\,, \tag{6.15^a}$$

while the 'old' anti-symmetric eigenfunction $Y_{2n}(\eta)$ changes (for $n = 1, 2, 3, \ldots$) again up to a minus sign into the 'new' anti-symmetric eigenfunction

$$Z_{n,2}(\eta) = \sin(2n\pi\eta) \qquad \text{for } n = 1, 2, 3, \ldots\,, \tag{6.15^b}$$

as follows readily from Eq. (4.14). In this way we regain the well-known sets of eigenvalues and eigenfunctions of Fourier's ring. We get two 'new' independent eigenfunctions for each positive 'new' eigenvalue. This special limit case shows us how Fourier's ring gets its double set of eigenfunctions indeed.

7 Measuring The Diffusion Constant

In this section we set out a new path for measuring diffusion by making use of the mathematical results of the previous sections.

In a typical steady-state experiment for the measurement of diffusion rates two gas streams of known composition are led alongside the ends of a tube filled with porous material. The analysis of the composition of the outgoing gas streams after steady-state is reached, enables one to determine the diffusion rate. The mathematical requirements for this method are simple, we only have to solve a steady-state diffusion problem. The large amount of gas that is needed and the long experimental time before steady state is reached are disadvantages of this method.

Barnes (1934) and Bird (1960) solved the transient problem for end-bulbs with equal volumes and for special initial conditions. Dye and Dallavalle (1958) and Weller et al. (1974) utilized these solutions for their measurements of diffusion rates in a two-chamber experimental setting. Special care was needed to ensure that both end-bulbs had the same volume indeed.

Shair and Cohen (1969) solved for special initial conditions the transient problem for end-bulbs with arbitrary volumes. This analytical solution clarifies what happens if the volumes of the two end-bulbs are not exactly the same. It was used by Reible and Shair

(1982) for their measurements of diffusion rates of gases in dry and moist porous beds. Also Glauz and Rolston (1989) used this solution for the optimal design of two-chamber diffusion cells.

One important problem in transient-state gaseous diffusion experiments is a possible discrepancy between real and mathematical initial conditions. The action of connecting two compartments may introduce a perturbation, which results in physical initial conditions different from the intended mathematical initial conditions. The general solution for the two-chamber case as described in Section 3 makes it possible to evaluate the effect of such disturbances. Of course the existence of an analytical solution for any initial condition allows for maximal flexibility in the design of an experiment.

There are certainly disadvantages in using two-chamber gas diffusion cells. One chamber will be used as inlet, the other one as exit. This situation is essentially non-symmetrical, which complicates the corresponding mathematics. Perhaps the most striking disadvantage follows from the need to prevent convective transport of the tracer gas in the diffusion tube. Such a convective transport could stem for instance from a pressure difference between the two chambers. Therefore pressure differentials must be monitored and also the temperature of the two chambers must be held equal and constant. This kind of problems seriously complicates a two-chamber experiment.

The analytical solution for the one-chamber case as presented in Section 4 enables us to consider a one-chamber experimental design. The diffusion tube filled with porous material is placed in a chamber, which acts like a calorimeter in an experiment for measuring thermal conductivity, see also Figure 2. If at the start of the experiment the tracer gas is to be found only in the enveloping chamber and not in the diffusion tube, we have a situation that is highly symmetrical and therefore is intrinsically simple in a physical as well as a mathematical sense. Subsequently we follow the drop of the concentration of the tracer gas within the chamber. From these measurements it is easy to estimate the diffusivity of the tracer gas for the porous material in the diffusion tube. The analytical solution for precisely this problem is presented in Section 6.1.

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