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# A Diffusion Problem With Chemical Reaction

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# A DIFFUSION PROBLEM WITH CHEMICAL REACTION

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**Summary**

A substance is subjected to cylindrical Poiseuille flow, diffusion and a chemical reaction. In this paper the stationary state will be considered. It is assumed that the axial component of the diffusion can be neglected. Then the problem can be reduced to an eigenvalue problem determining an orthogonal set of eigenfunctions. Also a simplified model will be considered where the cylindrical wall is replaced by a flat wall. This problem can be solved by means of Laplace transformation. An explicit solution for the concentration at the wall has been obtained.

§ 1. *Introduction.* A fluid is flowing through a circular tube which is determined by $0 \leqslant r \leqslant R$, $0 \leqslant z \leqslant L$ in cylindrical coordinates. The velocity of the fluid is constant and according to Poiseuille's law it is given by

$$v(r) = V\left(1 - \frac{r^2}{R^2}\right).$$

A substance of concentration $C(r, z)$ moves with the fluid and is subjected to a diffusion process with diffusion constant $D$ and a chemical reaction according to which

$$\frac{\partial C}{\partial t} = -KC,$$

where $t$ is the time and $K$ a known coefficient. The substance enters the tube at $z = 0$ with the concentration $C_0$. One asks the concentration at the end of the tube and in particular the concentration at the wall $r = R$. It can be assumed that the stationary state has been reached.

The problem is obviously governed by the partial differential equation

$$D\left(\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}+\frac{\partial^2 C}{\partial z^2}\right)-V\left(1-\frac{r^2}{R^2}\right)\frac{\partial C}{\partial z}-KC=0 \quad (1.1)$$

with the boundary condition

$$z=0,\ C=C_0, \quad (1.2)$$

$$r=R,\ \partial C/\partial r=0. \quad (1.3)$$

In the following sections two different ways of attack will be discussed. In § 2 the simplifying assumption will be made that the axial component of diffusion can be neglected. Then it is possible to represent the solution in the form

$$C(r,z)=\sum_1^\infty a_n\, e^{-\omega_n z^*}\,\varphi_n(r^*), \quad (1.4)$$

where $r^*$ and $z^*$ are dimensionless variables proportional to $r$ and $z$, and where the $\varphi_n$ form an orthogonal set of eigenfunctions with eigenvalues $\omega_n$.

This representation fails when $z^*$ is so small that a great number of eigenfunctions has to be taken into account. In that case supplementary information can be obtained from the second method which will be discussed in § 4. There the concentration is considered only near the wall of the tube. If a new variable $y$ is introduced by means of

$$r=R-y \quad (1.5)$$

and if $R$ is large, (1.1) may be approximated by

$$D\left(\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right)-\frac{2V}{R}y\frac{\partial C}{\partial z}-KC=0 \quad (1.6)$$

with the boundary conditions

$$z=0,\ C=C_0, \quad (1.7)$$

$$y=0,\ \partial C/\partial y=0. \quad (1.8)$$

If again the axial component of diffusion is neglected, the problem can be solved by means of Laplace transformation. The Laplace transform of $C(y,z)$ is a relatively simple expression involving modified Bessel functions of order $\frac{1}{3}$. The inverse transformation can be performed by means of term by term inversion of a power series expansion. We find eventually for the concentration at the wall.

$$C(r, z) = C_0 \sum_{0}^{\infty} d_j z'^{2j/3}, \tag{1.9}$$

where $z'$ is the dimensionless variable determined by

$$z = z' \frac{3V}{R} D^{1/2} K^{-3/2}. \tag{1.10}$$

The first few coefficients are

$$d_0 = 1, \quad d_1 = -1.869, \quad d_2 = 1.978, \quad d_3 = -1.556.$$

§ 2. *First method.* In order to get a first impression of the solution of (1.1) with (1.2) and (1.3) we shall omit the diffusion. For $D = 0$, (1.1) reduces to

$$V\left(1 - \frac{r^2}{R^2}\right)\frac{\partial C}{\partial z} + KC = 0, \tag{2.1}$$

which can be integrated without difficulty. The solution becomes

$$C = C_0 \exp - \left[KV^{-1}\left(1 - \frac{r^2}{R^2}\right)^{-1} z\right]. \tag{2.2}$$

At $r = R$ we have $C = 0$.

The effect of the diffusion will be to yield a non-vanishing concentration at the wall. This effect will be mainly due to the radial component of the diffusion. Therefore the axial component of diffusion in (1.1) will be omitted so that this equation reduces to

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} - \frac{V}{D}\left(1 - \frac{r^2}{R^2}\right)\frac{\partial C}{\partial z} - \frac{K}{D} C = 0. \tag{2.3}$$

The solution of the full equation (1.1) would present analytic complications which do not occur in the treatment of (2.3).

It will be convenient to introduce the following dimensionless variables:

$$r \to r^* R, \quad z \to z^* \frac{VR^2}{4D}, \quad C \to C^* C_0. \tag{2.4}$$

If further $\alpha$ is defined by

$$\alpha = KR^2/4D, \tag{2.5}$$

(2.3) passes into

$$\frac{\partial^2 C^*}{\partial r^{*2}} + \frac{1}{r^*}\frac{\partial C^*}{\partial r^*} - 4(1 - r^{*2})\frac{\partial C^*}{\partial z^*} - 4\alpha C^* = 0. \qquad (2.6)$$

with the boundary conditions

$$z^* = 0, \ C^* = 1, \qquad (2.7)$$

$$r^* = 1, \ \partial C^*/\partial r^* = 0. \qquad (2.8)$$

For simplicity's sake the asterisks will be omitted from now on.

If in (2.6) the trial solution $e^{-\omega z}\varphi(r)$ is substituted for $C(r)$, the following differential equation is obtained

$$\frac{d^2\varphi}{dr^2} + \frac{1}{r}\frac{d\varphi}{dr} + 4[\omega(1 - r^2) - \alpha]\,\varphi = 0. \qquad (2.9)$$

This equation is of the confluent hypergeometric type. Some details concerning its solutions will be given in the following section. There is a regular solution of the type

$$\varphi(r) = \sum_0^\infty b_k r^{2k} \qquad (2.10)$$

and a singular solution which is infinite at $r = 0$. In view of the physical situation only the regular solution can be used.

Substitution of (2.10) into (2.9) gives with $b_0 = 1$:

$$b_1 = -(\omega - \alpha),$$
$$b_2 = \tfrac{1}{4}[\omega + (\omega - \alpha)^2],$$
$$b_3 = \tfrac{1}{36}[5\omega(\omega - \alpha) + (\omega - \alpha)^3], \text{ etc.}$$

Further coefficients can be calculated from the recurrent relation

$$k^2 b_k + (\omega - \alpha)b_{k-1} - \omega b_{k-2} = 0, \ k \geq 2. \qquad (2.11)$$

The boundary condition (2.8) gives the eigenvalue equation

$$\sum_1^\infty k b_k = 0. \qquad (2.12)$$

From this a set of real and positive eigenvalues $\omega_1, \omega_2, \omega_3 \ldots$ can be derived. The corresponding eigenfunctions $\varphi_1, \varphi_2, \varphi_3 \ldots$ form a complete set with the following orthogonality relation:

$$\int_0^1 r(1 - r^2)\,\varphi_m\varphi_n\,dr = 0, \ m \neq n. \qquad (2.13)$$

The proof of (2.13) is as follows. From (2.9) we obtain for $\varphi_m$ and $\varphi_n$

$$r\varphi_m'' + \varphi_m' + 4r[\omega_m(1 - r^2) - \alpha]\varphi_m = 0,$$

and

$$r\varphi_n'' + \varphi_n' + 4r[\omega_n(1 - r^2) - \alpha]\,\varphi_n = 0.$$

If the first relation is multiplied by $\varphi_n$ and the second relation by $\varphi_m$, we find for the difference

$$\frac{\mathrm{d}}{\mathrm{d}r}\,[r(\varphi_m'\varphi_n - \varphi_m\varphi_n')] + 4r(1 - r^2)(\omega_m - \omega_n)\,\varphi_m\varphi_n = 0.$$

Integration of this relation between $r = 0$ and $r = 1$ leads in view of the boundary condition at $r = 1$ at once to (2.13).

If $\alpha$ is small a power series in $\alpha$ can be obtained for the first eigenvalue. We find

$$\omega_1 = 2\alpha - \frac{\alpha^2}{12} + \frac{\alpha^3}{60} + O(\alpha^4). \tag{2.14}$$

If the solution of (2.6) with (2.7) and (2.8) is written in the form

$$C(r, z) = \sum_1^\infty a_n\varphi_n(r)\,\mathrm{e}^{-\omega_n z}, \tag{2.15}$$

then only the boundary condition at $z = 0$ need to be satisfied. This is possible by a suitable choice of the coefficients $a_n$. Condition (2.7) requires

$$1 = \sum_1^\infty a_n\varphi_n(r). \tag{2.16}$$

The coefficients $a_n$ can now be determined by means of the orthogonality relation (2.13). We find

$$a_n\int_0^1 r(1 - r^2))\,\varphi_n{}^2(r)\,\mathrm{d}r = \int_0^1 r(1 - r^2)\,\varphi_n(r)\,\mathrm{d}r. \tag{2.17}$$

If $z$ is large, the first term of the expansion (2.15) gives a result sufficiently accurate for some purposes. Hence for $z$ large

$$C(r, z) \approx \frac{\int_0^1 x(1 - x^2)\,\varphi_1(x)\,\mathrm{d}x}{\int_0^1 x(1 - x^2)\,\varphi_1{}^2(x)\,\mathrm{d}x}\,\varphi_1(r)\,\mathrm{e}^{-\omega_1 z}. \tag{2.18}$$

If also $\alpha$ is small, we have the first order approximation

$$\varphi_1(r) \approx 1 - \alpha r^2(1 - \tfrac{1}{2}r^2), \tag{2.19}$$

so that

$$C(r, z) \approx (1 + \tfrac{1}{4}\alpha)\,[1 - \alpha r^2(1 - \tfrac{1}{2}r^2)]\,\mathrm{e}^{-2\alpha z}. \tag{2.20}$$

§ 3. *Special properties.* In this section some special properties of the eigenfunctions of the previous section are collected. The regular solution of (2.9) can be represented by

$$\varphi(r) = \mathrm{e}^{-r^2\sqrt{\omega}}\,\phi\left(\tfrac{1}{2} - \frac{\omega - \alpha}{2\sqrt{\omega}}, 1; 2r^2\sqrt{\omega}\right), \tag{3.1}$$

where

$$\phi(a, b, x) \overset{\text{def}}{=} 1 + \frac{a}{b}\,\frac{x}{1!} + \frac{a(a+1)}{b(b+1)}\,\frac{x^2}{2!} + \ldots. \tag{3.2}$$

In the familiar notation of the Whittaker function we may also write

$$\varphi(r) = (2r^2\sqrt{\omega})^{-\frac{1}{2}}\,M_{\frac{\omega-\alpha}{2\sqrt{\omega}},\,0}(2r^2\sqrt{\omega}). \tag{3.3}$$

From the formula [1])

$$M_{k,m}(z) = \frac{2^{2m}}{2\pi i}\,\Gamma(2m+1)z^{-m+\frac{1}{2}}\int_L \mathrm{e}^{\frac{1}{2}uz}\left(\frac{u-1}{u+1}\right)^k \frac{\mathrm{d}u}{(u^2-1)^{m+\frac{1}{2}}}, \tag{3.4}$$

where the path of integration $L$ is a loop encircling $-1$ and $+1$ in the positive direction and avoiding the negative real axis, we may derive

$$\varphi(r) = \frac{1}{2\pi i}\int_L \mathrm{e}^{ur^2\sqrt{\omega}}\left(\frac{u-1}{u+1}\right)^{\frac{\omega-\alpha}{2\sqrt{\omega}}} \frac{\mathrm{d}u}{(u^2-1)^{\frac{1}{2}}}. \tag{3.5}$$

The eigenvalue equation becomes

$$\frac{1}{2\pi i}\int_L \mathrm{e}^{u\sqrt{\omega}}\left(\frac{u-1}{u+1}\right)^{\frac{\omega-\alpha}{2\sqrt{\omega}}} \frac{u\,\mathrm{d}u}{(u^2-1)^{\frac{1}{2}}} = 0. \tag{3.6}$$

The asymptotic solution of this eigenvalue equation is determined by the third order saddlepoint at the origin. Proceeding as described in the paper cited above we find

$$\cos\left(\frac{\sqrt{\omega}}{2}+\frac{1}{6}\right)\pi = 0,$$

so that the higher eigenvalues are approximated by

$$\omega_m \approx 4(m+\tfrac{1}{3})^2. \tag{3.7}$$

This approximation is independent of $\alpha$. The influence of $\alpha$ can be expected to influence the lower eigenvalues in the sense that the lowest eigenvalue is most influenced.

§ 4. *Second method.* In this section we shall consider the problem (1.6) with (1.7) and (1.8). If again the axial component of diffusion is neglected, the problem reduces to

$$\frac{\partial^2 C}{\partial y^2} - \frac{2V}{RD} y \frac{\partial C}{\partial z} - \frac{K}{D} C = 0, \tag{4.1}$$

with

$$z = 0, \quad C = C_0, \tag{4.2}$$

$$y = 0, \quad \partial C/\partial y = 0. \tag{4.3}$$

To this we may add the extra boundary condition

$$y = \infty, C = \text{finite}. \tag{4.4}$$

It will be convenient to introduce the following dimensionless variables

$$y \to y' D^{1/2} K^{-1/2}, \quad z \to z' \frac{3V}{R} D^{1/2} K^{-3/2}, \quad C \to C' C_0. \tag{4.5}$$

Then (4.1) passes into

$$\frac{\partial^2 C'}{\partial y'^2} - \frac{2}{3} y' \frac{\partial C'}{\partial z'} - C' = 0, \tag{4.6}$$

with the boundary conditions

$$z' = 0, \quad C' = 1, \tag{4.7}$$

$$y' = 0, \quad \partial C'/\partial y' = 0, \tag{4.8}$$

$$y' = \infty, C' = \text{finite}. \tag{4.9}$$

The choice of the factor $\frac{2}{3}$, somewhat arbitrary at first sight, will prove convenient later on.

This problem will be solved by means of Laplace transformation. If from now on the dashes are omitted, we put

$$f(y, p) = \int_0^\infty e^{-pz} [1 - C(y, z)]\, dz. \tag{4.10}$$

Then (4.6) is transformed into

$$\frac{d^2 f}{dy^2} - (1 + \tfrac{2}{3} p y) f = -\frac{1}{p}, \tag{4.11}$$

with

$$y = 0, \; df/dy = 0,$$

and

$$y = \infty, \; f = \text{finite}.$$

If next the following substitution is performed:

$$x = p^{-3/2}(1 + \tfrac{2}{3} p y),$$

(4.11) passes into

$$\frac{d^2 f}{dx^2} - \tfrac{9}{4} x f = -\tfrac{9}{4} p^{-5/3}, \tag{4.12}$$

with

$$x = p^{-2/3}, \; df/dx = 0, \tag{4.13}$$

$$x = \infty, \; f = \text{finite}. \tag{4.14}$$

The corresponding homogeneous equation

$$\frac{d^2 f}{dx^2} - \tfrac{9}{4} x f = 0 \tag{4.15}$$

has the following fundamental solution

$$f_1(x) = x^{1/2} I_{1/3}(x^{3/2}), \tag{4.16}$$

$$f_2(x) = x^{1/2} K_{1/3}(x^{3/2}). \tag{4.17}$$

A few properties of these functions are collected in the following section. Here we mention the fact that both solutions are regular, but that $f_1(x)$ becomes infinite as $x \to \infty$, whereas $f_2(x)$ converges to zero. Furthermore we have

$$f_1'(x) f_2(x) - f_1(x) f_2'(x) = \tfrac{3}{2}. \tag{4.18}$$

It can be easily verified that the solution of (4.12) is of the following form:

$$f(x) = \tfrac{3}{2}\, p^{-5/3} \left[f_1(x) \int_x^\infty f_2(\xi)\, \mathrm{d}\xi + f_2(x) \int_{x_0}^x f_1(\xi)\, \mathrm{d}\xi + A f_2(x)\right], \qquad (4.19)$$

where $x_0 = p^{-2/3}$ and where A follows from (4.13). We find

$$A = -\frac{f_1'(x_0)}{f_2'(x_0)} \int_{x_0}^\infty f_2(\xi)\, \mathrm{d}\xi. \qquad (4.20)$$

From the behaviour of $f_1(x)$ and $f_2(x)$ at infinity it can be deduced that (4.19) also satisfies the condition (4.14).

The value of $f(x)$ at $x = x_0$ has an important physical significance and in the further discussion we shall restrict ourselves to that value. We have from (4.19) and (4.20)

$$f(x_0) = \tfrac{3}{2}\, p^{-5/3} \frac{f_2'(x_0) f_1(x_0) - f_1'(x_0) f_2(x_0)}{f_2'(x_0)} \int_{x_0}^\infty f_2(\xi)\, \mathrm{d}\xi,$$

which on applying (4.18) reduces to

$$f(x_0) = -\tfrac{9}{4}\, p^{-5/3} \frac{1}{f_2'(x_0)} \int_{x_0}^\infty f_2(\xi)\, \mathrm{d}\xi. \qquad (4.21)$$

Substitution of the expressions (4.16) and (4.17) gives the alternative expression

$$f(x_0) = \frac{\int_{p^{-1}}^\infty K_{\frac{1}{3}}(t)\, \mathrm{d}t}{p K_{-\frac{2}{3}}(p^{-1})} \qquad (4.22)$$

The inversion of this expression is very complicated. However, in a relatively simple way an expansion in negative powers of $p$ can be obtained which leads to a corresponding expansion of $C$ in positive powers of $z$. By means of the expansions given in the following section we obtain

$$f(p^{-2/3}) = \sum_0^\infty c_j p^{-\frac{2j+5}{3}}, \qquad (4.23)$$

where

$$c_0 = 1.688, \quad c_3 = -4.040,$$
$$c_1 = -2.355, \quad c_4 = 5.189,$$
$$c_2 = 3.113, \quad c_5 = -4.026,$$
etc.

The inverse of (4.23) is

$$1 - C(0, z) = \sum_0^\infty \frac{c_j}{\Gamma\left(\frac{2j+5}{3}\right)} z^{\frac{2j+2}{3}}, \tag{4.24}$$

or

$$C(0, z) = \sum_0^\infty d_j z^{\frac{2j}{3}}, \tag{4.25}$$

with

$$d_0 = 1 \qquad d_4 = 1.007$$
$$d_1 = -1.869 \qquad d_5 = -0.560$$
$$d_2 = 1.978 \qquad d_6 = 0.168$$
$$d_3 = -1.556 \qquad \text{etc.}$$

Reintroduction of the original variables gives the first order approximation

$$C(0, z) \approx C_0\left(1 - 0.899 \frac{KR^{2/3} Z^{2/3}}{D^{1/3} V^{2/3}}\right) \tag{4.26}$$

§ 5. *Special properties.* In this section for reference's sake a few special properties of the functions $f_1(x)$ and $f_2(x)$ of the preceding section are collected. The formulae given here can be derived easily from well-known properties of the Bessel functions.

We quote the following formulae:

$$I_\nu(w) = \sum_0^\infty \frac{1}{k!\, \Gamma(k + \nu + 1)} \left(\frac{w}{2}\right)^{\nu+2k}$$

and

$$K_\nu(w) = \frac{\pi}{2 \sin \nu\pi} [I_{-\nu}(w) - I_\nu(w)].$$

For $w \to \infty$ we have the asymptotic formulae

$$I_\nu(w) \sim \frac{e^w}{\sqrt{2\pi w}}\left(1 - \frac{4\nu^2 - 1}{8w} + \dots\right)$$

and

$$K_\nu(w) \sim \sqrt{\frac{\pi}{2w}}\, e^{-w}\left(1 + \frac{4\nu^2+1}{8w} + ..\right)$$

Hence we have

$$f_1(x) = 2^{-1/3} \sum_0^\infty \frac{1}{k!\,\Gamma(k+\frac{4}{3})}\left(\frac{x^3}{4}\right)^k$$

and

$$f_2(x) = 3^{-\frac{1}{2}}\pi\left[2^{1/3} \sum_0^\infty \frac{1}{k!\,\Gamma(k+\frac{2}{3})}\left(\frac{x^3}{4}\right)^k + \right.$$
$$\left. - 2^{-1/3} \sum_0^\infty \frac{1}{k!\,\Gamma(k+\frac{4}{3})}\left(\frac{x^3}{4}\right)^k\right].$$

For $x \to \infty$

$$f_1(x) \sim (2\pi)^{-1/2}\, x^{-1/4}\, e^{x^{3/2}}\left(1 + \frac{5}{72x} \cdots\right),$$
$$f_2(x) \sim (\pi/2)^{1/2}\, x^{-1/4}\, e^{-x^{3/2}}\left(1 - \frac{5}{72x} \cdots\right).$$

From

$$\int_0^\infty K_\nu(w)\, dw = \frac{\pi}{2\cos(\nu\pi/2)}.$$

it follows that

$$\int_0^\infty f_2(\xi)\, d\xi = \frac{2\pi}{3\sqrt{3}}.$$

Furthermore

$$\int_0^x f_2(\xi)\, d\xi = 3^{-1/2}\left[\frac{2^{1/3}}{\Gamma(\frac{2}{3})}x - \frac{2^{-1/3}}{2\Gamma(\frac{4}{3})}x^2 + \frac{2^{1/3}}{16\,\Gamma(\frac{5}{3})}x^4 + \dots\right],$$

$$f_2'(x) = 3^{-1/2}\pi\left[-\frac{2^{-1/3}}{\Gamma(\frac{4}{3})} + \frac{3.2^{1/3}}{4\Gamma(\frac{5}{3})}x^2 - \frac{2^{-1/3}}{\Gamma(\frac{7}{3})}x^3 + \dots\right].$$

The calculation of the coefficients can be facilitated by giving the following numerical constants

$$\Gamma(\tfrac{1}{3}) = 2.678\,939,$$
$$\Gamma(\tfrac{2}{3}) = 1.354\,118,$$
$$2^{1/3} = 1.259\,921,$$
$$2^{2/3} = 1.587\,401.$$

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REFERENCE

1) Lauwerier, H. A., Appl. Sci. Res. A2 (1950) 184.