In this case, such complexing will be enhanced by the ready electron availability at the sulphur atoms.

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References

Barnard, D. 1956 *J. Chem. Soc.* p. 489. (part V).
Barnard, D. & Hargrave, K. R. 1952 *Analyt. chim. acta*, **6**, 23.
Barnard, D., Hargrave, K. R. & Higgins, G. 1956 *J. Chem. Soc.* (in the Press).
Bateman, L. & Cunneen, J. 1955 *J. Chem. Soc.*, p. 1596 (part III).
Bateman, L. & Hargrave, K. R. 1954*a* *Proc. Roy. Soc.* A, **224**, 389 (part I).
Bateman, L. & Hargrave, K. R. 1954*b* *Proc. Roy. Soc.* A, **224**, 399 (part II).
Bateman, L. & Shipley, F. W. 1955 *J. Chem. Soc.* p. 1996 (part IV).
Boozer, C. E. & Hammond, G. S. 1954 *J. Amer. Chem. Soc.* **76**, 3861.

On the dispersion of a solute in a fluid flowing through a tube

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Sir Geoffrey Taylor has recently discussed the dispersion of a solute under the simultaneous action of molecular diffusion and variation of the velocity of the solvent. A new basis for his analysis is presented here which removes the restrictions imposed on some of the parameters at the expense of describing the distribution of solute in terms of its moments in the direction of flow. It is shown that the rate of growth of the variance is proportional to the sum of the molecular diffusion coefficient, D, and the Taylor diffusion coefficient $\kappa a^2 U^2/D$, where U is the mean velocity and a is a dimension characteristic of the cross-section of the tube. An expression for κ is given in the most general case, and it is shown that a finite distribution of solute tends to become normally distributed.

1. Introduction

In three recent papers, Sir Geoffrey Taylor has discussed the dispersion of soluble matter in a fluid flowing in a straight tube (Taylor 1953, 1954*a*, *b*). In the first of these, viscous flow through a tube of circular cross-section was considered, and it was found that the solute was dispersed about a point moving with the mean velocity of flow, U, with an apparent diffusion coefficient $a^2U^2/48D$. Here D is the molecular diffusion coefficient and a the radius of the tube. In the last of these papers, Taylor showed that the conditions under which this analysis was valid could be expressed as $4L/A \gg Ua/D \gg 6{\cdot}9$, where L is the length over which appreciable changes in concentration occur.

It might be hoped that so elegant a result should have some meaning when these restrictions are removed, and it is possible to obtain this by fixing attention on the movement of the centre of gravity of the distribution of solute and the growth of its higher moments. These may be studied in some detail and give a useful picture of the dispersion under the most general conditions.

2. The general equations of diffusion and flow in a straight tube

Consider an infinite tube whose axis is parallel to the axis Ox of a rectangular co-ordinate system $Oxyz$. Let S denote the domain occupied by the interior of the tube in the plane Oyz, and let s be its area and the curve Γ its perimeter. In steady uniform flow the velocity u is everywhere in the direction Ox and is a function of y and z given by

$$u(y,z) = U\{1+\chi(y,z)\}, \tag{1}$$

where U is the mean velocity and χ defines the velocity relative to the mean. If there is no slip at the wall of the tube $\chi = -1$ on Γ.

Let $C(x,y,z,t)$ denote the concentration of solute at the point x, y, z and time t, and let $D\psi(y,z)$ be its diffusion coefficient. The function ψ defines the variation of the diffusion coefficient and D is its mean value over the cross-section of the tube. The equation governing C is thus

$$\frac{1}{D}\frac{\partial C}{\partial t} = \nabla(\psi\nabla C) - \frac{U}{D}(1+\chi)\frac{\partial C}{\partial x}. \tag{2}$$

It is convenient to take an origin moving with the mean speed of the stream and to reduce the variables to dimensionless form. Let a be a dimension characteristic of the cross-section S and let

$$\left.\begin{aligned} \xi &= (x-Ut)/a, \\ \eta &= y/a, \\ \zeta &= z/a, \\ \tau &= Dt/a^2, \\ \mu &= Ua/D, \end{aligned}\right\} \tag{3}$$

then the equation for C becomes

$$\frac{\partial C}{\partial \tau} = \psi\frac{\partial^2 C}{\partial \xi^2} - \mu\chi\frac{\partial C}{\partial \xi} + \frac{\partial}{\partial \eta}\left(\psi\frac{\partial C}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\psi\frac{\partial C}{\partial \zeta}\right). \tag{4}$$

The conditions to be applied to the solution are

$$C(\xi,\eta,\zeta,0) = C_0(\xi,\eta,\zeta), \tag{5}$$

$$\psi\frac{\partial C}{\partial \nu} = 0 \quad \text{on} \quad \Gamma, \tag{6}$$

where $\partial/\partial\nu$ denotes differentiation along the normal to Γ, and sufficient conditions on the behaviour of C as $\xi \to \pm\infty$. Let

$$c_p(\eta,\zeta,\tau) = \int_{-\infty}^{+\infty} \xi^p C(\xi,\eta,\zeta,\tau)\,\mathrm{d}\xi \tag{7}$$

and

$$m_p(\tau) = \overline{c_p} = \frac{1}{s}\iint_S c_p\,\mathrm{d}\eta\,\mathrm{d}\zeta \tag{8}$$

be the pth moment of the distribution of solute in the filament through η, ζ at time t and the pth moment of the distribution of solute in the tube. The condition to be imposed on C as $\xi \to \pm\infty$ is thus that these moments should exist and be finite, a condition fulfilled if the solute is originally contained in a finite length of the tube. Multiplying equation (4) by ξ^p and integrating with respect to ξ from $-\infty$ to $+\infty$, we have

$$\frac{\partial c_p}{\partial \tau} = \frac{\partial}{\partial \eta}\left(\psi \frac{\partial c_p}{\partial \eta}\right) + \frac{\partial}{\partial \zeta}\left(\psi \frac{\partial c_p}{\partial \zeta}\right) + p(p-1)\,\psi c_{p-2} + p\mu\chi c_{p-1}, \tag{9}$$

and the conditions (5) and (6) become

$$c_p(\eta, \zeta, 0) = c_{p0}(\eta, \zeta), \tag{10}$$

$$\psi \frac{\partial c_p}{\partial \nu} = 0 \quad \text{on} \quad \Gamma. \tag{11}$$

If equation (9) is averaged over the cross-section, the use of Green's theorem and the condition (11) reduces it to

$$\frac{\mathrm{d}m_p}{\mathrm{d}\tau} = p(p-1)\,\overline{\psi c_{p-2}} + p\mu\,\overline{\chi c_{p-1}} \tag{12}$$

(where, as in equation (8), a bar denotes the average over S) and the condition (10) becomes

$$m_p(0) = m_{p0}. \tag{13}$$

The equations (9) subject to conditions (10) and (11) for $p = 0, 1, 2, \ldots$ now form a sequence of inhomogeneous equations which can be solved for the moments c_p. In principle these might be solved to a sufficiently high value of p for the distribution to be constructed to any degree of accuracy, but a very useful picture of the progress of the dispersion can be obtained from the first three or four moments. Since it will be shown that the distribution ultimately tends to normality the first two moments are ultimately sufficient to describe the distribution.

3. The tube of circular cross-section

Before proceeding with the discussion of the general case, it is interesting to consider the case of a tube of circular cross-section and to note how the present treatment agrees with Taylor's. In this case we take Ox to be the axis and a to be the radius of the tube and transform to polar co-ordinates

$$\eta = \rho\cos\theta, \quad \zeta = \rho\sin\theta.$$

In the case of viscous flow $\chi = (1-2\rho^2)$, $\psi = 1$ and D is the molecular diffusion coefficient.

Then
$$\frac{\partial c_p}{\partial \tau} = \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial c_p}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2 c_p}{\partial \theta^2} + p(p-1)\,c_{p-2} + \mu p(1-2\rho^2)\,c_{p-1}, \tag{14}$$

and of this equation we seek solutions of period 2π in θ and satisfying

$$c_p(\rho, \theta, 0) = c_{p0}(\rho, \theta), \tag{15}$$

$$\frac{\partial c_p}{\partial \rho} = 0, \quad \rho = 1. \tag{16}$$

Equation (12) becomes

$$\frac{\mathrm{d}m_p}{\mathrm{d}\tau} = p(p-1)\,m_{p-2} + (p\mu/\pi)\int_0^{2\pi}\mathrm{d}\theta\int_0^1 \rho(1-2\rho^2)\,c_{p-1}\,\mathrm{d}\rho. \tag{17}$$

In particular, $\mathrm{d}m_0/\mathrm{d}\tau = 0$ so that m_0 is a constant which we may take as unity. This of course merely states that the total quantity of solute is constant.

For $p = 0$, equations (14) and (16) give

$$c_0(\rho,\theta,\tau) = 1 + \sum_{m=0}^{\infty}\sum_{n=1}^{\infty}\{A_{mn}^0\cos m\theta + B_{mn}^0\sin m\theta\}\,J_m(\alpha_{mn}\rho)\exp(-\alpha_{mn}^2\tau), \tag{18}$$

where α_{mn} is the nth zero of $\mathrm{d}J_m(\rho)/\mathrm{d}\rho$. The constants A and B are chosen to satisfy equation (15), i.e.

$$\frac{\pi}{2}\left(1-\frac{m^2}{\alpha^2}\right)\{J_m(\alpha)\}^2\frac{A_{mn}^0}{B_{mn}^0} = \int_0^{2\pi}\mathrm{d}\theta\int_0^1 \frac{\cos m\theta}{\sin m\theta}\,\rho J_m(\alpha\rho)\,c_{00}(\rho,\theta)\,\mathrm{d}\rho, \tag{19}$$

the suffixes m and n to α being understood. (It will generally cause no confusion to suppress the suffixes mn on α, A^p and B^p.)

For $p = 1$ equation (17) gives

$$\frac{\mathrm{d}m_1}{\mathrm{d}\tau} = \frac{\mu}{\pi}\int_0^{2\pi}\mathrm{d}\theta\int_0^1 \rho(1-2\rho^2)\,c_0\,\mathrm{d}\rho.$$

In this integral the constant term vanishes since the mean value of $(1-2\rho^2)$ is zero and the terms with $m>0$ vanish by integration round the circle. Hence

$$\begin{aligned}\frac{\mathrm{d}m_1}{\mathrm{d}\tau} &= \mu\Sigma A_{0n}^0\,\mathrm{e}^{-\alpha^2\tau}\int_0^1 2\rho(1-2\rho^2)\,J_0(\alpha\rho)\,\mathrm{d}\rho \\ &= -8\mu\Sigma A_{0n}^0\,\alpha_{0n}^{-2}\,\mathrm{e}^{-\alpha^2\tau}\,J_0(\alpha_{0n}).\end{aligned}$$

Thus as $\tau\to\infty$, $\mathrm{d}m_1/\mathrm{d}\tau\to 0$ and the centre of gravity ultimately moves with the mean speed of the stream. Choosing the origin in the original plane of the centre of gravity, $m_{10} = 0$ and

$$m_1 = -8\mu\sum_{n=1}^{\infty} A_{0n}^0\,\alpha_{0n}^{-4}\,J_0(\alpha_{0n})\{1-\exp(-\alpha_{0n}^2\tau)\}. \tag{20}$$

Thus the centre of gravity ultimately moves to a position

$$m_{1\infty} = -8\mu\Sigma A_{0n}^0\,\alpha_{0n}^{-4}\,J_0(\alpha_{0n}) \tag{21}$$

relative to its original position. The actual distance moved is proportional to a^2U/D, the constant of proportionality depending on the initial distribution of solute. If the mean speed of the stream is being measured by the time taken for the centre of gravity of the distribution to move between two points there will be a slight error, though in practice it will usually be negligible.

For a more detailed picture of the variation in position of centre of gravity across the tube, equation (14) must be solved. For $p = 1$ this becomes

$$\frac{\partial c_1}{\partial\tau} - \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial c_1}{\partial\rho}\right) - \frac{1}{\rho^2}\frac{\partial^2 c_1}{\partial\theta^2} = \mu(1-2\rho^2)\,c_0, \tag{22}$$

of which the complete solution consists of three parts: (i) the term in the particular integral arising from the constant part of c_0; (ii) the rest of the particular integral which may be written

$$\mu\Sigma(A^0\cos m\theta + B^0\sin m\theta)\,\phi(\rho)\exp(-\alpha^2\tau),$$

with ϕ_{mn} satisfying the equation

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\phi}{\partial\rho}\right)+\left(\alpha^2-\frac{m^2}{\rho^2}\right)\phi = -J_m(\alpha\rho)\,(1-2\rho^2);$$

and (iii) the complementary function

$$\Sigma(A^1\cos m\theta + B^1\sin m\theta)\,J_m(\alpha\rho)\exp(-\alpha^2\tau),$$

with A^1 and B^1 chosen to fit the initial value $c_{10}(\rho,\theta)$.

The first part is independent of τ and θ, being $-\frac{1}{4}\mu\rho^2(1-\frac{1}{2}\rho^2)$, and choosing A_0^1 so that $m_{10}=0$, the expression for c_1 is

$$\begin{aligned} c_1 = {} & \tfrac{1}{4}\mu(\tfrac{1}{3}-\rho^2+\tfrac{1}{2}\rho^4)+\mu\Sigma(A^0\cos m\theta+B^0\sin m\theta)\,\phi(\rho)\exp(-\alpha^2\tau) \\ & -\mu\Sigma A^0_{0n}\overline{\phi}_{0n}+\Sigma(A^1\cos m\theta+B^1\sin m\theta)\,J_m(\alpha\rho)\exp(-\alpha^2\tau). \end{aligned} \tag{23}$$

Thus ultimately the centre of gravity is distributed across the tube according to the formula

$$c_1 \sim m_{1\infty}+\tfrac{1}{4}\mu(\tfrac{1}{3}-\rho^2+\tfrac{1}{2}\rho^4). \tag{24}$$

It may readily be seen by averaging the equation for ϕ_{0n} that the form given for $m_{1\infty}$ in equation (23) agrees with that previously derived in equation (21). It is interesting that the ultimate distribution of c_1 is independent of θ; physically this is because circumferential diffusion brings a molecule into a stream of precisely the same speed and so contributes nothing to the movement of the centre of gravity.

In Taylor's analysis (1953, 1954*b*) an expression is derived for the variation of C with ρ when $\partial C_m/\partial x$ is constant. Equation (6) of Taylor (1954*b*) may be written in the notation of this paper

$$(C_m - C)\bigg/\frac{\partial C_m}{\partial\xi} = \tfrac{1}{4}\mu(\tfrac{1}{3}-\rho^2+\tfrac{1}{2}\rho^4), \tag{25}$$

which with $\partial C_m/\partial\xi$ constant means that the distance from any plane to the point at which the concentration $C=C_m$, the mean concentration in the plane, is given by the expression on the right-hand side of (25), i.e. this is the shape of the surfaces of constant concentration. It follows that the centres of gravity would then be distributed on the same surface. Equation (24) shows that this last statement is true even though $\partial C_m/\partial\xi$ is not constant.

Substituting the value of c_1 in equation (17) with $p=2$ and neglecting terms which tend to zero we have

$$\begin{aligned}\frac{\mathrm{d}m_2}{\mathrm{d}\tau} &= 2+\mu^2\int_0^1\rho(1-2\rho^2)\,(\tfrac{1}{3}-\rho^2+\tfrac{1}{2}\rho^4)\,\mathrm{d}\rho+O\{\exp(-\alpha^2\tau)\} \\ &\sim 2(1+\mu^2/48).\end{aligned}$$

Thus the rate of growth of the variance rapidly becomes constant and

$$m_2 \sim 2(1+\mu^2/48)\,\tau + \text{a constant}$$

which becomes negligible by comparison.

If V is the variance of the distribution of solute about the moving origin, i.e.

$$V = \frac{1}{s}\iint_S \mathrm{d}y\,\mathrm{d}z \int_{-\infty}^{+\infty} (x-Ut)^2\, C(x,y,z,t)\,\mathrm{d}x,$$

then

$$\lim_{t\to\infty} \frac{1}{2}\frac{\mathrm{d}V}{\mathrm{d}t} = D + \frac{a^2U^2}{48D} = K. \tag{26}$$

It is not unreasonable to use the left-hand side of this equation as the definition of the effective diffusion constant K, the more so as it will be shown that any distribution tends to normality. With this definition K is the sum of the molecular diffusion coefficient, D, and the apparent diffusion coefficient $k = a^2U^2/48D$, which was discovered by Taylor in his first paper (Taylor 1953, equation (25)). Equation (26), however, is true without any restriction on the value of μ, or on the distribution of solute. The constant $1/48$ is a function of the profile of flow, and for so-called piston flow with $\chi \equiv 0$ this constant is zero and $K = D$ as it should.

In the full expression for c_2 the terms which do not vanish as $\tau \to \infty$ are $m_2(\tau)$, a constant function of ρ and a constant depending on the initial value of c_2. The constant function of ρ must satisfy the equation

$$\frac{1}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\rho\frac{\mathrm{d}f}{\mathrm{d}\rho}\right) = \tfrac{1}{4}\mu^2(-\tfrac{1}{3}+\tfrac{5}{3}\rho^2-\tfrac{5}{2}\rho^4+\rho^6)+\tfrac{1}{48}\mu^2+2\mu m_{1\infty}(1-2\rho^2),$$

i.e.

$$f = g(\rho)+\tfrac{1}{2}\mu m_{1\infty}(-\tfrac{1}{3}+\rho^2-\tfrac{1}{2}\rho^4),$$

where

$$g(\rho) = \frac{\mu^2}{16}\left\{\tfrac{1}{16}\rho^8-\tfrac{5}{18}\rho^6+\tfrac{5}{12}\rho^4-\tfrac{1}{4}\rho^2+\frac{31}{5\times 9\times 16}\right\}.$$

This is precisely the polynomial obtained by Taylor under the assumption that $\partial C_m/\partial\xi$ is not quite constant but that the second derivative $\partial^2 C_m/\partial\xi^2$ is (Taylor 1954*b*, equation (24)).

Thus, apart from a constant, c_2 is ultimately given by

$$c_2 \sim 2(1+\mu^2/48)\,\tau+\tfrac{1}{2}\mu m_{1\infty}(-\tfrac{1}{3}+\rho^2-\tfrac{1}{2}\rho^4)+g(\rho)$$

and

$$\frac{\mathrm{d}m_3}{\mathrm{d}\tau} \sim 6m_{1\infty}+3\mu\int_0^1 2\rho(1-2\rho^2)\,c_2\,\mathrm{d}\rho$$
$$= 6m_{1\infty}(1+\mu^2/48)+7\mu^3/2^{10}.$$

Neglecting constant terms which become negligible in comparison to the dominant term proportional to τ, this equation gives

$$m_3-3m_{1\infty}m_2 \sim 7\mu^3\tau/2^{10}. \tag{27}$$

Apart from a term m_1^3, which is a constant, the expression on the left-hand side of (27) is the third moment about the mean m_1 so that the absolute skewness $\beta_1 = m_3^2/m_2^3$ is

$$\beta_1 = 49\mu^6/2^{20}(1+\mu^2/48)^3\,\tau,$$

which tends to zero as $\tau\to\infty$. Thus any distribution of solute tends to become more symmetrical.

An examination of the equation for c_3 shows that the dominant terms will be proportional to τ and will be $m_3(\tau)$ and the product of τ and a function of ρ. In general,

$$m_{2n} = M_{2n}\tau^n, \quad m_{2n+1} = M_{2n+1}\tau^n, \tag{28}$$

where M_{2n} and M_{2n+1} are even and odd polynomials in μ of degree $2n$ and $2n+1$ respectively, and

$$c_{2n} = M_{2n}\tau^n + G_{2n}(\rho)\,\tau^{n-1}, \quad c_{2n+1} = M_{2n+1}\tau^n + G_{2n+1}(\rho)\,\tau^n, \tag{29}$$

where the mean values of the functions $G_{2n}(\rho)$ and $G_{2n+1}(\rho)$ are zero. This remark may be used to show that the distribution tends to normality but the proof of this will be left for the general case.

4. Some special initial distributions of solute

The case of a distribution of solute initially constant over any cross-section of the tube is particularly simple for $A^0 = B^0 = 0$, and so by (21) $m_{1\infty} = 0$. When $\tau = 0$, c_1 is independent of ρ and so $A^1 = B^1 = 0$ for all $m > 0$ and

$$\Sigma A^1_{0n} J_0(\alpha_{0n}\rho) = -\tfrac{1}{4}\mu(\tfrac{1}{3} - \rho^2 + \tfrac{1}{2}\rho^4),$$

i.e.

$$A^1_{0n} = -8\mu/\alpha^4_{0n} J_0(\alpha_{0n}) \quad (n \geqslant 1)$$

and

$$c_1 = \frac{\mu}{4}(\tfrac{1}{3} - \rho^2 + \tfrac{1}{2}\rho^4) - 8\mu \sum_{n=1}^{\infty} \alpha_{0n}^{-4} \frac{J_0(\alpha_{0n}\rho)}{J(\alpha_{0n})} \exp(-\alpha^2_{0n}\tau). \tag{30}$$

Inserting this value in the equation for m_2 and integrating

$$\begin{aligned} m_2 &= m_{20} + 2(1 + \mu^2/48)\,\tau + 128\mu^2 \Sigma\alpha_{0n}^{-8}\{1 - \exp(-\alpha^2_{0n}\tau)\} \\ &\sim m_{20} + 2(1+\mu^2/48)\,\tau + \mu^2/360. \end{aligned}$$

The smallness of the last term may be judged by considering the case $\mu^2 \gg 48$. Then $m_2 - m_{20} = (\mu^2/24)(\tau + 1/15)$, so that this last term is equivalent to an additional time of $a^2/15D$.

The case of an instantaneous point source at $\rho = \rho_0$, $\theta = 0$ is of interest. All the moments are initially zero and $c_{00} = 0$ for $\rho \neq \rho_0$, $\theta \neq 0$ and $m_0 = 1$. Then

$$c_0 = 1 + 2\Sigma\left(1 - \frac{m^2}{\alpha^2}\right)^{-1} \mathrm{e}^{-\alpha^2\tau} \cos m\theta J_m(\alpha\rho)\, J_m(\alpha\rho_0)/\{J_m(\alpha)\}^2, \tag{31}$$

and

$$m_{1\infty} = -16\mu\Sigma\alpha^{-4} J_0(\alpha\rho_0)/J_0(\alpha) = \mu(\tfrac{1}{6} - \tfrac{1}{2}\rho_0^2 + \tfrac{1}{4}\rho_0^4). \tag{32}$$

The dependence of $m_{1\infty}$ on the distance of the point source from the axis is the same as the dependence of the centre of gravity of the solute in any filament on its distance from the axis.

5. The general case

The general case of a tube of arbitrary cross-section, flow profile and variation of diffusion coefficient, for which the equations were set up in § 1, may be considered in a similar way. Again, m_0 must be a constant, which may be taken as unity, and for c_0 we have the equations

$$\left.\begin{aligned} \nabla(\psi\nabla c_0) &= \frac{\partial c_0}{\partial \tau}, \\ c_0(\eta, \zeta, 0) &= c_{00}(\eta, \zeta), \\ \psi\frac{\partial c_0}{\partial \nu} &= 0 \quad (\text{on } \Gamma). \end{aligned}\right\} \tag{33}$$

Under very general conditions on Γ and ψ there will exist a positive increasing sequence of eigenvalues λ_n and a complete set of ortho-normal eigenfunctions v_n satisfying the equation

$$\nabla(\psi \nabla v_n) + \lambda_n v_n = 0 \tag{34}$$

in S and the boundary conditions

$$\psi \frac{\partial v_n}{\partial \nu} = 0 \tag{35}$$

on Γ. Any function satisfying the boundary conditions and with continuous derivatives up to the second order can be expanded in a series of these functions (see, for example, Courant & Hilbert 1937). If the constants A_n are such that

$$c_{00}(\eta, \zeta) = 1 + \sum_{n=1}^{\infty} A_n v_n(\eta, \zeta), \tag{36}$$

then the solution of the equations (33) is

$$c_0(\eta, \zeta, \tau) = 1 + \sum_{n=1}^{\infty} A_n v_n(\eta, \zeta) \exp(-\lambda_n \tau). \tag{37}$$

As before, the density of solute in any streamline rapidly becomes uniform across the tube, the relaxation time being of the order of λ_1^{-1}, where λ_1 is the smallest of the eigenvalues.

Inserting this value of c_0 in equation (12) with $p = 1$, it is again evident that the centre of gravity ultimately moves with the mean speed of the stream. Its final position relative to a moving origin originally at the centre of gravity is

$$m_{1\infty} = \mu \sum_{n=1}^{\infty} A_n \lambda_n^{-1} \overline{\chi v_n}, \tag{38}$$

where the bar denotes an average over the cross-section of the tube.

Apart from $m_{1\infty}$ and terms which vanish as $\tau \to \infty$, c_1 will contain a constant function of η and ζ whose mean value is zero. This function arises from the constant term 1 in c_0 when this is inserted in equation (9) with $p = 1$ and so must satisfy the equations

$$\left.\begin{aligned} \nabla(\psi \nabla \phi) &= -\chi, \\ \psi \frac{\partial \phi}{\partial \nu} &= 0 \quad (\text{on } \Gamma). \end{aligned}\right\} \tag{39}$$

Then $c_1 \sim m_{1\infty} + \mu\phi(\eta, \zeta)$ for all other terms will vanish at least as rapidly as $\exp(-\lambda_1 \tau)$.

From equation (12) with $p = 2$

$$\frac{1}{2}\frac{\mathrm{d}m_2}{\mathrm{d}\tau} \sim \overline{\psi} + \mu^2 \overline{\chi\phi}, \tag{40}$$

where again the vanishing terms have been neglected. But by definition $\overline{\psi} = 1$ and $\overline{\chi\phi} = \kappa$, a pure number dependent only on the geometry of the cross-section and the functions ψ and χ. Thus again defining the effective diffusion constant K as one-half the rate of growth of the variance

$$K = D + \kappa a^2 U^2 / D, \tag{41}$$

showing how a Taylor diffusion coefficient can be found in the general case. By Green's theorem and equations (39) we have $\kappa = \overline{\phi\chi} = -\overline{\phi\nabla(\psi\nabla\phi)} = \overline{\psi(\nabla\phi)^2}$.

Consideration of the dominant terms in the successive moments again shows that c_{2n} and c_{2n+1} are of the form

$$\left.\begin{aligned} c_{2n} &= M_{2n}\tau^n + G_{2n}(\eta,\zeta)\tau^{n-1}, \\ c_{2n+1} &= M_{2n+1}\tau^n + G_{2n+1}(\eta,\zeta)\tau^n, \end{aligned}\right\} \tag{42}$$

where the mean values of the functions G are zero.

Substituting c_{2n+1} in equation (9) with $p = 2n+1$ and neglecting all except the dominant term

$$\nabla(\psi\nabla G_{2n+1}) + (2n+1)\mu M_{2n}\chi = 0,$$

so that

$$G_{2n+1}(\eta,\zeta) = (2n+1)\mu M_{2n}\phi(\eta,\zeta),$$

where ϕ has already been defined by the equations (39). Substituting this value of G_{2n+1} in equation (12) with $p = (2n+2)$ and again neglecting all save the dominant terms

$$\begin{aligned} \frac{\mathrm{d}m_{2n+2}}{\mathrm{d}\tau} &= (2n+2)(2n+1)M_{2n}\tau^n + (2n+2)(2n+1)\mu^2 M_{2n}\tau^n\overline{\phi\chi} \\ &= (2n+1)M_{2n}2(1+\kappa\mu^2)(n+1)\tau^n, \end{aligned}$$

and the dominant term of m_{2n+2} is

$$m_{2n+2} \sim (2n+1)M_{2n}\tau^n 2(1+\kappa\mu^2)\tau = (2n+1)m_{2n}m_2.$$

It follows that as $\tau\to\infty$

$$(m_{2n+1})^2/(m_2)^{2n+1} \to 0,$$

$$m_{2n}/(m_2)^n \to (2n-1)(2n-3)\dots 3.1.$$

These are the relations which exist between the moments of the normal distribution and in this sense the mean concentration is ultimately distributed about a point moving with the mean speed of the stream according to the normal law of error, the variance being $2(1+\kappa\mu^2)\tau$. It should be noted that the approach to normality is as τ^{-1}, a very much slower process than the vanishing of terms in the expressions for the moments, which is as $\exp(-\lambda_1\tau)$.

6. Turbulent flow in a tube of circular cross-section

The case of turbulent flow and diffusion which was treated in Taylor's second paper (Taylor 1954*a*) clearly comes under the general case. If ψ and χ are functions of $\rho = (\eta^2+\zeta^2)^{\frac{1}{2}}$ only and a is the radius of the tube equation (9) becomes

$$\frac{\partial c_p}{\partial\tau} = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left\{\rho\psi(\rho)\frac{\partial c_p}{\partial\rho}\right\} + p(p-1)\psi(\rho)c_{p-2} + p\mu\chi(\rho)c_{p-1}$$

and the equation for ϕ is

$$\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\rho\psi(\rho)\frac{\mathrm{d}\phi}{\mathrm{d}\rho}\right) + \rho\chi(\rho) = 0,$$

of which the solution is

$$\phi(\rho) = -\int_0^\rho \frac{\mathrm{d}\rho'}{\rho'\psi(\rho')}\int_0^{\rho'}\rho''\chi(\rho'')\,\mathrm{d}\rho''.$$

This is the function tabulated in column (8) of table 1 (Taylor 1954*a*), and the final column (11) of this table is

$$\kappa = \int_0^1 2\rho\chi(\rho)\,\phi(\rho)\,\mathrm{d}\rho.$$

In § 4 of this paper the effect of longitudinal diffusion is estimated and is added to diffusion coefficient $\kappa\mu^2$. Equation (41) of the present paper supplies a rigorous justification for this.

7. Viscous flow in a tube of arbitrary cross-section

It is well known that the velocity $u(\eta, \zeta)$ for viscous flow in a straight pipe satisfies the equations

$$\left.\begin{aligned} \nabla^2 u &= -a^2\frac{\mathrm{d}P}{\mathrm{d}x}\Big/\mu \quad (\text{in } S),\\ u &= 0 \quad (\text{on } \Gamma), \end{aligned}\right\} \tag{43}$$

where in this equation P is the pressure and μ the viscosity, and it follows that χ satisfies the equations

$$\nabla^2\chi = -\alpha \quad (\text{in } S)$$

$$\chi = -1 \quad (\text{on } \Gamma),$$

where $\alpha = a^2\dfrac{\mathrm{d}P}{\mathrm{d}x}\Big/\mu U$ is a constant.

Combining this equation with equation (39), and putting $\psi = 1$, we have the equations for ϕ,

$$\left.\begin{aligned} \nabla^4\phi &= \alpha \qquad (\text{in } S),\\ \left.\begin{aligned}\nabla^2\phi &= 1\\ \frac{\partial\phi}{\partial\nu} &= 0\end{aligned}\right\} & \quad (\text{on } \Gamma), \end{aligned}\right\} \tag{44}$$

which enables ϕ and so κ to be calculated for any cross-section.

As an illustration of this a tube of elliptical cross-section may be considered. If the major and minor semi-axes are a and b respectively

$$\chi(y, z) = 1 - 2(y^2/a^2) - 2(z^2/b^2). \tag{45}$$

Taking a as the characteristic length it may be shown, after a certain amount of algebraic labour, that

$$\kappa = \frac{1}{48}\,\frac{24 - 24e^2 + 5e^4}{24 - 12e^2}, \tag{46}$$

where $e = (1 - b^2/a^2)^{\frac{1}{2}}$ is the eccentricity of the cross-section. For $e = 0$, κ is $1/48$ as it should be for a circle and when $e = 1$, κ is $5/12$ of this value. A very small value of $(1-e)$ represents a very narrow elliptical slit and in such a slit diffusion across the slit renders the concentration very nearly constant in this direction, so there are effectively only two spatial dimensions.*

* I am indebted to Mr C. H. Bosanquet for pointing this out.

Let $O\zeta$ be in the direction of the narrow dimension of the slit, $2a$ be its major dimension, and $\beta(\eta)$ be proportional to the breadth of the slit at any point. Then the equation for C is

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \xi^2} + \frac{1}{\beta}\frac{\partial}{\partial \eta}\left(\beta \frac{\partial C}{\partial \eta}\right) - \mu\chi(\eta)\frac{\partial C}{\partial \xi}.$$

The function $\chi(\eta)$ is here the mean value of $\chi(\eta, \zeta)$ across the slit, so that

$$\int_{-1}^{+1} \beta(\eta)\,\chi(\eta)\,\mathrm{d}\eta = 0.$$

In fact all averages must be taken with $\beta(\eta)$ as a weighting factor. An equation similar to equation (9) obtains for the moment c_p, namely,

$$\frac{\partial c_p}{\partial \tau} = \frac{1}{\beta}\frac{\partial}{\partial \eta}\left(\beta \frac{\partial c_p}{\partial \eta}\right) + p(p-1)\,c_{p-2} + \mu p c_{p-1}$$

and

$$\frac{\mathrm{d}m_p}{\mathrm{d}\tau} = p(p-1)\,m_{p-2} + \mu p \int_{-1}^{+1} \beta\chi c_{p-1}\,\mathrm{d}\eta \Big/ \int_{-1}^{+1} \beta\,\mathrm{d}\eta$$

In precisely the same way as before we derive the value of κ,

$$\kappa = \int_{-1}^{+1} \phi(\eta)\,\chi(\eta)\,\beta(\eta)\,\mathrm{d}\eta \Big/ \int_{-1}^{+1} \beta(\eta)\,\mathrm{d}\eta,$$

where

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\beta(\eta)\frac{\mathrm{d}\phi}{\mathrm{d}\eta}\right) = -\chi(\eta)\,\beta(\eta)$$

and

$$\frac{\mathrm{d}\phi}{\mathrm{d}\eta} = 0 \quad \text{at} \quad \eta = \pm 1.$$

In the case of an elliptical slit

$$\beta(\eta) = (1-\eta^2)^{\frac{1}{2}},$$
$$\chi(\eta) = \tfrac{1}{3}(1-4\eta^2),$$
$$\phi(\eta) = -\tfrac{1}{6}\eta^2(1-\tfrac{1}{2}\eta^2),$$

and $\kappa = 5/12 \times 48$, which confirms the limiting value in equation (46).

It is well known that for a given pressure drop, the flow is greater in a circular tube than in an elliptical one of the same area, and if in the Taylor diffusion coefficient a^2 is replaced by the area of cross-section (πa^2 for the circle and πab for the ellipse) the constant κ is least for $e = 0$. Thus the dispersion in a circular tube is less than in an elliptical tube of the same area.

References

Courant, R. & Hilbert, D. 1937 *Methoden der mathematischen Physik*, **1**. Berlin: Springer.
Taylor, Sir Geoffrey 1953 *Proc. Roy. Soc.* A, **219**, 186.
Taylor, Sir Geoffrey 1954*a* *Proc. Roy. Soc.* A, **223**, 446.
Taylor, Sir Geoffrey 1954*b* *Proc. Roy. Soc.* A, **225**, 473.