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The dispersion of a buoyant solute in laminar flow in a straight horizontal pipe. Part 1. Predictions from Erdogan & Chatwin's (1967) paper

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This work is concerned with the dispersion of a buoyant solute in a straight horizontal pipe of circular cross-section where dispersion is affected by molecular diffusion, the laminar flow along the pipe and density currents. Erdogan & Chatwin (1967) have derived an equation for the mean concentration $\bar{C}$ of a buoyant solute using a relatively simple asymptotic model, and have predicted that the dispersion induced by buoyancy effects depends on the Péclet number of the flow. In this part of this study an approximate expression is derived for $\bar{C}$ from Erdogan & Chatwin's equation, and an asymptotic form is obtained for the second moment of distributions of buoyant solutes. The examination of the second moment leads to a simple, but important, result: the dispersion induced by density currents at large times is small compared with the dispersion induced by density currents at times when transient effects are significant.

1. Introduction

This work is concerned with the effects on dispersion of a buoyant solute in a straight horizontal pipe of circular cross-section of molecular diffusion, advection by laminar flow along the pipe and density currents. The aim of this paper is to make a useful prediction from the earlier work on this subject by Erdogan & Chatwin (1967). In part 2, the problem will be considered using a more general theory.

It was first shown by Taylor (1953) that the combined effects of cross-sectional diffusion and longitudinal advection make a cloud of solute spread out symmetrically about a point moving with the mean flow speed W. Taylor showed that, for large times, the cross-sectional mean concentration of a passive marker satisfies a diffusion equation with respect to axes moving at speed W. For smaller times when Taylor's asymptotic theory is not valid, numerical solutions for the dispersion of a passive marker have been given by Ananthakrishnan, Gill & Barduhn (1965); and Aris (1956) and Chatwin (1970) have improved Taylor's asymptotic theory by describing the approach to the asymptotic state. These studies have shown that, for a passive solute, the mean concentration ultimately becomes a Gaussian function of distance along the pipe axis.

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Although this theoretical work has been verified experimentally by Taylor (1953) and others, Reejhsinghani, Gill & Barduhn (1966) have shown that the relevant experiments are quite sensitive to buoyancy effects. Reejhsinghani *et al.* then described experiments in which the solute was deliberately chosen to have a density very close to that of the solvent. In this way, it was established that there is a marked variation in the dispersion of a buoyant marker as the Péclet number of the flow changes (the Péclet number P is defined by $P = Wa/\kappa$, where W is the discharge (mean) speed, a is the pipe radius and κ is the molecular diffusivity). Reejhsinghani *et al.* finally affirmed the significance of buoyancy forces by suggesting them as the cause of the anomalous experimental results obtained by Bournia, Coull & Houghton (1961).

The first analytical model to investigate the effect of density currents on the dispersion of contaminants in Poiseuille flow was proposed by Erdogan & Chatwin (1967, hereafter called E & C). E & C described the following two particular dynamical effects that are introduced by a buoyant, as opposed to a passive, marker.

(i) The solute causes axial density gradients, which induce mean longitudinal density currents away from the centre of mass of the dispersing cloud. This effect increases the dispersion of the solute.

(ii) A buoyant solute also causes increased cross-sectional mixing; that is, secondary flows in a vertical plane caused by radial and azimuthal variations in density. This effect acts to decrease the dispersion.

E & C investigated these competing effects in a time-independent model which incorporated a uniform axial gradient for the mean concentration. Their model, which is the buoyancy-affected analogue of Taylor's (1953) study, is described in §2. E & C suggested, in partial support of the observations of Reejhsinghani *et al.*, that the Péclet number of the flow is the significant factor in determining whether dispersion is enhanced or decreased with dynamically active markers. They predicted that the dispersion would be increased for flows at low Péclet numbers and decreased for flows with large values of this parameter. In flows with values of P near a critical number P_c (depending on other parameters of the flow), they suggested that buoyant and passive markers would disperse similarly.

In the present paper, the analysis of E & C is extended to make several predictions. First, an approximate expression is derived for the mean concentration profile. To form this approximation, an equation is derived, but not solved, for the first term affected by buoyancy forces. The approximation is then used to obtain the asymptotic form of the first two moments of a distribution of buoyant solute.

The properties of the moments derived give an interesting conclusion concerning the amount of dispersion induced by buoyancy effects. (The nth moment $\nu_n(t)$ is defined to be

$$\nu_n(t) = \iiint_{\text{whole pipe}} (z-z_g)^n \, C r \, dr \, d\theta \, dz \Big/ \iiint_{\text{whole pipe}} C r \, dr \, d\theta \, dz, \quad n \geqslant 0, \tag{1.1}$$

where C is the concentration and z_g is the z co-ordinate of the centre of mass of the contaminant cloud in a frame of reference moving at speed W. In particular, the second moment (the variance) describes the extent to which the cloud has been spread: for example, for the Gaussian profile found by Taylor (1953) for a passive solute, the second moment has the asymptotic behaviour $\nu_2(t) \sim \text{constant} \times t$ as $t \to \infty$.) To summarize the results obtained for a buoyant solute, the second moment is found to have the asymptotic behaviour

$$\nu_2(t) \sim \text{constant} \times t + \text{constant} + O(t^{-1}), \quad t \to \infty. \tag{1.2}$$

In this expression, the term proportional to t is the same as for a passive solute, the constant term results from buoyancy-affected dispersion at short and medium times, and only the $O(t^{-1})$ terms are modified by buoyancy effects at asymptotically large times. E & C's model thus predicts that the greatest contributions of buoyancy forces to the dispersion process occur at times when transient effects are significant. It is believed that this conclusion will be of value to workers in dispersion research.

In the adjacent paper (part 2), the problem of dispersing buoyant contaminants is re-examined using a more general time-dependent model. Part 2 describes the approach to the asymptotic state and generalizes the work of Chatwin (1970) on dispersing passive markers. The results obtained in part 2 show that E & C's relatively simple model gives an excellent description of the dispersion induced at large times by buoyancy effects provided that the Schmidt number of the flow is large. (This number is defined in equation (2.14) below and is, in fact, large for commonly encountered conditions.)

2. Equations of motion and the model used by E & C

The following equations may be used to describe the dispersion of a buoyant solute in an incompressible solvent in Poiseuille flow (the moving co-ordinate system (r, θ, z) is explained in figure 1):

$$\frac{\partial u}{\partial t} + w\frac{\partial u}{\partial z} + u\frac{\partial u}{\partial r} + \frac{v}{r}\frac{\partial u}{\partial \theta} - \frac{v^2}{r} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left\{\frac{\partial^2 u}{\partial z^2} + \nabla^2 u - \frac{u}{r^2} - \frac{2}{r^2}\frac{\partial v}{\partial \theta}\right\} - g\cos\theta, \tag{2.1}$$

$$\frac{\partial v}{\partial t} + w\frac{\partial v}{\partial z} + u\frac{\partial v}{\partial r} + \frac{v}{r}\frac{\partial v}{\partial \theta} + \frac{uv}{r} = -\frac{1}{r\rho}\frac{\partial p}{\partial \theta} + \nu\left\{\frac{\partial^2 v}{\partial z^2} + \nabla^2 v + \frac{2}{r^2}\frac{\partial u}{\partial \theta} - \frac{v}{r^2}\right\} + g\sin\theta, \tag{2.2}$$

$$\frac{\partial w}{\partial t} + w\frac{\partial w}{\partial z} + u\frac{\partial w}{\partial r} + \frac{v}{r}\frac{\partial w}{\partial \theta} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left\{\frac{\partial^2 w}{\partial z^2} + \nabla^2 w\right\}, \tag{2.3}$$

$$\frac{\partial C}{\partial t} + w\frac{\partial C}{\partial z} + u\frac{\partial C}{\partial r} + \frac{v}{r}\frac{\partial C}{\partial \theta} = \frac{\partial}{\partial z}\left(\kappa\frac{\partial C}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa\frac{\partial C}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\kappa\frac{\partial C}{\partial \theta}\right), \tag{2.4}$$

$$\frac{\partial w}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{1}{r}\frac{\partial v}{\partial \theta} = 0, \tag{2.5}$$

$$\rho = \rho(C). \tag{2.6}$$

In these equations and all the subsequent work, u, v and w denote respectively radial, azimuthal and axial velocities in a frame of reference moving at speed W and ∇^2 is the two-dimensional Laplacian

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}.$$

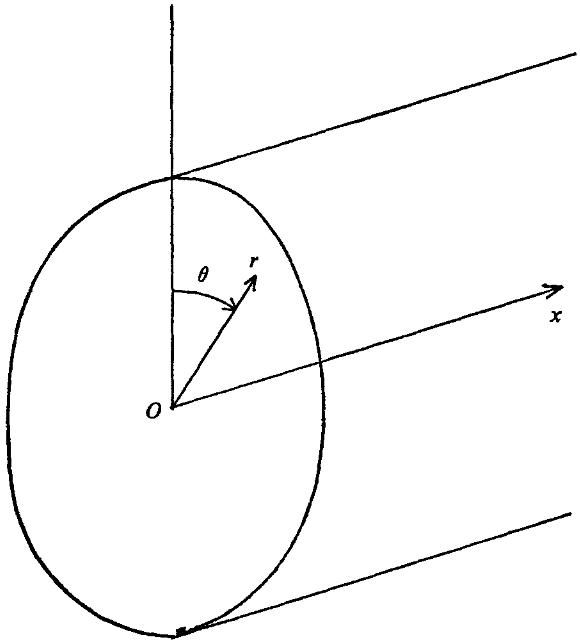

FIGURE 1. The co-ordinate system: (r, θ, x) and (r, θ, z) are, respectively, cylindrical polars in a stationary frame and in a frame moving at the discharge speed W (i.e. $z = \text{constant} + x - Wt$); $\theta = 0$ is the upward vertical and Ox is the (horizontal) axis of the pipe.

Since the velocity components u, v and w should be interpreted as barycentric velocities (in the manner described by Green & Naghdi 1969), (2.5) is only an approximation to the exact form of the continuity equation for incompressible solvents.

In their model, E & C assumed that u, v, w and $\partial C/\partial z$ were independent of t and z, which could be valid only if the mean concentration profile had an axially uniform gradient. This assumption, leading to a concentration profile of the form

$$C = z\frac{\partial \bar{C}}{\partial z} + a\frac{\partial \bar{C}}{\partial z}F(r,\theta), \tag{2.7}$$

is the same as that used by Taylor (1953) to discuss the passive-contaminant case. E & C assumed that the density of the fluid was given by

$$\rho = \rho_0(1+\alpha C), \tag{2.8}$$

where ρ_0 and α are constants, independent of concentration; and further, they neglected the change in density caused by concentration except in the body-force term. That is, they used the Boussinesq approximation. With slightly different notation, E & C's equations were

$$\sigma\left(u\frac{\partial u}{\partial r}+\frac{v}{r}\frac{\partial u}{\partial \theta}-\frac{v^2}{r}\right) = -\frac{P^2}{\sigma}\frac{\partial p}{\partial r}+\sigma\left(\nabla^2 u-\frac{u}{r^2}-\frac{2}{r^2}\frac{\partial v}{\partial \theta}\right)-R\cos\theta(1+\alpha C), \tag{2.9}$$

$$\sigma\left(u\frac{\partial v}{\partial r}+\frac{v}{r}\frac{\partial v}{\partial \theta}+\frac{uv}{r}\right) = -\frac{P^2}{\sigma r}\frac{\partial p}{\partial \theta}+\sigma\left(\nabla^2 v-\frac{v}{r^2}+\frac{2}{r^2}\frac{\partial u}{\partial \theta}\right)+R\sin\theta(1+\alpha C), \tag{2.10}$$

$$\sigma\left(u\frac{\partial w}{\partial r}+\frac{v}{r}\frac{\partial w}{\partial \theta}\right) = -aP\frac{\partial p}{\partial z}+\sigma\nabla^2 w, \tag{2.11}$$

$$\sigma\left(u\frac{\partial C}{\partial r}+\frac{v}{r}\frac{\partial C}{\partial \theta}\right)+Paw\frac{\partial C}{\partial z} = \nabla^2 C, \tag{2.12}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(ru)+\frac{1}{r}\frac{\partial v}{\partial \theta} = 0. \tag{2.13}$$

(In these equations, E & C's pressure p', axial co-ordinate X and axial velocity $w-1$ have been replaced by $\rho_0 W^2 p$, z and w respectively. The velocity components (u, v, w) have been non-dimensionalized, so that the actual velocity components are $(\nu u/a,\ \nu v/a,\ Ww)$.) The numbers P, σ and R are the parameters on which the flow depends, being respectively the Péclet, Schmidt and Rayleigh numbers:

$$P = Wa/\kappa, \quad \sigma = \nu/\kappa, \quad R = ga^3/(\nu\kappa). \tag{2.14}$$

E & C considered only the case where ν and κ were constants, independent of concentration.

The set of nonlinear equations (2.9)–(2.13) was solved by E & C using a perturbation analysis based on the small parameter

$$G = a\alpha\frac{\partial \overline{C}}{\partial z}R/\sigma. \tag{2.15}$$

They found that the flux of solute across cross-sectional planes moving at speed W was

$$Q = \pi a^2\left(\frac{a^2W^2}{48\kappa}\right)\frac{\partial \overline{C}}{\partial z}(-1+G^2Q_2), \tag{2.16}$$

in which Q_2 was given by

$$Q_2 = -\left(\frac{1}{2880}\right)^2\left[-\frac{2569}{8448}P^2\sigma^2+\frac{19797}{197120}P^2+\frac{10425}{56}\sigma+60480\frac{\sigma^2}{P^2}\right]. \tag{2.17}$$

E & C then assumed that the flux was unchanged even when $\partial\overline{C}/\partial Z$ was not constant, and substituted for Q in the equation of conservation of concentration

$$\pi a^2\,\partial\overline{C}/\partial t = -\partial Q/\partial z$$

to derive an equation for $\overline{C}$. (This assumption had previously been used by Taylor (1953) for passive solutes ($\alpha = 0$), and later proved by Aris (1956) to give correctly the leading term in an expansion for $\overline{C}$.) The equation for $\overline{C}$ obtained by E & C was

$$\frac{\partial \overline{C}}{\partial t} = \frac{a^2W^2}{48\kappa}\frac{\partial}{\partial z}\left[\frac{\partial \overline{C}}{\partial z}-\left\{\frac{\alpha g a^4}{\nu^2}\right\}^2 Q_2\left(\frac{\partial \overline{C}}{\partial z}\right)^3\right], \tag{2.18}$$

and this equation replaces the diffusion equation which is known to hold for passive markers. E & C deduced the relative increase or decrease in dispersion owing to buoyancy effects by considering the quantity Q_2 in (2.16) as a function of P.

3. An approximate distribution for $\bar{C}$

An approximate expression for $\bar{C}$ when buoyancy forces are significant can now be derived from (2.18). For convenience, suppose that (2.18) is written as

$$\frac{\partial \bar{C}}{\partial t} = \frac{\partial}{\partial z}\left[A\frac{\partial \bar{C}}{\partial z} + B\left(\frac{\partial \bar{C}}{\partial z}\right)^3\right], \tag{3.1}$$

where A and B are given by

$$A = a^2W^2/48\kappa = \tfrac{1}{2}P^2M^*\kappa \quad (\tfrac{1}{2}M^* = \tfrac{1}{48}) \tag{3.2}$$

and

$$B = -A\{a\alpha R/\sigma\}^2 Q_2. \tag{3.3}$$

The constant M^* in (3.2) is introduced to facilitate comparison with later work. Now it is expected that, at large times, (3.1) will admit a solution consisting of the Gaussian profile found for passive markers plus other terms, of which some result from buoyancy effects at large times. Guided by the work of Taylor (1953) and Chatwin (1970), a suitable representation for $\bar{C}$ would be

$$\bar{C} \sim T^{-1}\overline{C^{(1)}(X)} + \ldots + T^{-n}\overline{C^{(n)}(X)} + \ldots + \phi_B(X, T), \tag{3.4}$$

where X and T are convenient asymptotic co-ordinates

$$X = z/(2At)^{\frac{1}{2}}, \quad T = (2At)^{\frac{1}{2}}/Pa \tag{3.5}$$

and $\phi_B(X, T)$ is the first term representing buoyancy effects.

If it is assumed that, in (3.1),

$$B(\partial\bar{C}/\partial z)^3 \ll A\partial\bar{C}/\partial z \quad \text{as} \quad t\to\infty, \tag{3.6}$$

the term ϕ_B in (3.4) should be small compared with $T^{-1}\,\overline{C^{(1)}(X)}$ for large t, so $\overline{C^{(1)}}$ will satisfy the equation

$$\frac{d^2\overline{C^{(1)}}}{dX^2} + X\frac{d\overline{C^{(1)}}}{dX} + \overline{C^{(1)}} = 0.$$

This equation has the simple solution

$$\overline{C^{(1)}} = \beta\exp(-\tfrac{1}{2}X^2),$$

implying that the first term in (3.4),

$$T^{-1}\overline{C^{(1)}} = \beta T^{-1}\exp(-\tfrac{1}{2}X^2), \tag{3.7}$$

is the Gaussian term originally found by Taylor (1953) for passive markers. (It may now be confirmed that (3.6) and (3.7) are consistent for t sufficiently large since

$$B\left(\frac{\partial\bar{C}}{\partial z}\right)^3\Big/A\frac{\partial\bar{C}}{\partial z} = \frac{B}{A}\left(\frac{\beta}{Pa}\right)^2 T^{-4}X^2\exp(-X^2)$$
$$\ll 1 \quad \text{as} \quad t\to\infty$$

since $X^2\exp(-X^2)$ is bounded.) The term ϕ_B in (3.4) should therefore satisfy the equation

$$\frac{\partial\phi_B}{\partial t} - \frac{\partial}{\partial z}\left(A\frac{\partial\phi_B}{\partial z}\right) = \frac{\partial}{\partial z}\left(B\left[\frac{\partial}{\partial z}[\beta T^{-1}\exp(-\tfrac{1}{2}X^2)]\right]^3\right),$$

which may be re-written using X and T throughout:

$$\left\{\frac{1}{T}\frac{\partial}{\partial T}-\frac{X}{T^2}\frac{\partial}{\partial X}-\frac{1}{T^2}\frac{\partial^2}{\partial X^2}\right\}\phi_B = -\frac{B}{A}\beta^3(Pa)^{-2}T^{-7}\frac{d}{dX}[X^3\exp(-\tfrac{3}{2}X^2)]. \quad (3.8)$$

An expression of the form

$$\phi_B = T^{-\lambda}h(X) \quad (3.9)$$

is consistent with (3.8) only if $\lambda = 5$, whence, using (3.2) and (3.3), $h(X)$ satisfies the equation

$$h_{XX}+Xh_X+5h = -\beta^3\left\{\frac{\alpha R}{P\sigma}\right\}^2 Q_2\frac{d}{dX}[X^3\exp(-\tfrac{3}{2}X^2)]. \quad (3.10)$$

An asymptotic expression for $\bar{C}$ when buoyancy effects are important therefore should include the terms

$$\bar{C} = \beta T^{-1}\exp(-\tfrac{1}{2}X^2)+T^{-5}h(X)+\dots, \quad (3.11)$$

where $h(X)$ is given by (3.10). Clearly this expression is not complete since passive markers alone would produce other terms $O(T^{-2})$ to $O(T^{-5})$ in (3.11). The term $T^{-5}h(X)$ should, however, describe the first contribution to the profile $\bar{C}$ from buoyancy effects at large times.

4. Asymptotic form of the first two moments

In this section, (3.1) is used to deduce the asymptotic form of the first two integral moments of $\bar{C}$ as defined by (1.1). First, the following expressions are obtained from (3.1) by some straightforward calculations:

$$\frac{d}{dt}\int_{-\infty}^{\infty}\bar{C}\,dz = 0, \quad (4.1)$$

$$\frac{d}{dt}\int_{-\infty}^{\infty}z\bar{C}\,dz = -B\int_{-\infty}^{\infty}\left(\frac{\partial\bar{C}}{\partial z}\right)^3 dz, \quad (4.2)$$

$$\frac{d}{dt}\int_{-\infty}^{\infty}z^2\bar{C}\,dz = 2A\int_{-\infty}^{\infty}\bar{C}\,dz-2B\int_{-\infty}^{\infty}z\left(\frac{\partial\bar{C}}{\partial z}\right)^3 dz. \quad (4.3)$$

Now, for large t, (3.11) gives an approximate form for $\bar{C}$, and (4.1) may be used to show that

$$\int_{-\infty}^{\infty}\bar{C}\,dz = \text{constant} = \beta Pa(2\pi)^{\frac{1}{2}}. \quad (4.4)$$

(It is easy to prove from (3.10) that

$$\int_{-\infty}^{\infty}h(X)\,dX$$

is zero.) Then, since $\partial\bar{C}/\partial z$ is an odd function of z (to leading order), (4.2) yields

$$\frac{d}{dt}(z_g) = \frac{d}{dt}\left\{\int_{-\infty}^{\infty}z\bar{C}\,dz\bigg/\int_{-\infty}^{\infty}\bar{C}\,dz\right\} = 0,$$

whence z_g is a constant which can be made zero by a suitable choice for the origin of the moving co-ordinate frame.

Finally, by substituting for $z(\partial\bar{C}/\partial z)^3$ in the second integral in (4.3), it follows that

$$\frac{d}{dt}\nu_2(t) = \frac{d}{dt}\left\{\int_{-\infty}^{\infty}(z-z_g)^2\bar{C}\,dz \bigg/ \int_{-\infty}^{\infty}\bar{C}\,dz\right\}$$
$$= 2A + [\beta Pa(2\pi)^{\frac{1}{2}}]^{-1}\,2B\beta^3(Pa)^{-1}T^{-4}\int_{-\infty}^{\infty}X^4\exp\left(-\tfrac{3}{2}X^2\right)dX. \quad (4.5)$$

Evaluating the integral in this expression, substituting for A and B from (3.2) and (3.3), and integrating with respect to time therefore gives

$$\nu_2(t) \sim \frac{a^2W^2}{24\kappa}t + \text{constant} + \frac{a^2}{M^*t\kappa}\frac{\beta^2}{(27)^{\frac{1}{2}}}\left(\frac{a\alpha R}{\sigma}\right)^2 Q_2 \quad \text{as} \quad t\to\infty. \quad (4.6)$$

In this expression, the first two terms have the same form as the corresponding terms found by Chatwin (1970) for a passive marker, although the constant clearly depends on buoyancy effects at times when transient effects are significant. The constant in (4.6) could be determined by matching $\nu_2(t)$ with its representation for shorter times. The $O(t^{-1})$ term in (4.6) is caused by buoyancy effects at asymptotically large times, and the examination of Q_2 as a function of P [equation (2.17)] shows how this term can increase or decrease the dispersion for particular flow conditions. The important conclusion mentioned in §1 follows immediately from (4.6), that is, *the dispersion induced by buoyancy effects at short and intermediate times* (this quantity is represented by the constant) *is of greater order than the dispersion which is induced at asymptotically large times.*

In conclusion, it is appropriate to make some critical comments. The above analysis is of value only if E & C's work can be justified independently, since the derivation of the crucial equation (2.18) rests on an unproved assertion. In the simpler, or prototype, case where passive markers are considered, the intuitive mathematics used by Taylor (1953) to derive an equation for $\bar{C}$ was validated later by Aris (1956) and in more detail by Chatwin (1970). Thus, in the present consideration of buoyant solutes, it is desirable that an independent description of the approach to the asymptotic state be obtained to justify (2.18) and the conclusions reached from it. The approach to the asymptotic state has, in fact, been considered by the author in the adjacent paper (Barton 1976) and the reader is referred to comments contained therein on the accuracy of E & C's asymptotic model.

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REFERENCES

ANANTHAKRISHNAN, V., GILL, W. N. & BARDUHN, A. J. 1965 *A.I.Ch.E. J.* **11**, 1063.

ARIS, R. 1956 *Proc. Roy. Soc.* A **235**, 67.

BARTON, N. G. 1976 *J. Fluid Mech.* **74**, 91.

BOURNIA, A., COULL, J. & HOUGHTON, G. 1961 *Proc. Roy. Soc.* A **261**, 227.

CHATWIN, P. C. 1970 *J. Fluid Mech.* **43**, 321.

ERDOGAN, M. E. & CHATWIN, P. C. 1967 *J. Fluid Mech.* **29**, 465.

GREEN, A. E. & NAGHDI, P. M. 1969 *University of California, Berkeley, Appl. Mech. Rep.* AM-69-4.

REEJHSINGHANI, N. S., GILL, W. N. & BARDUHN, A. J. 1966 *A.I.Ch.E. J.* **12**, 916.

TAYLOR, G. I. 1953 *Proc. Roy. Soc.* A **219**, 186.