J. Fluid Mech. (1983), *vol.* 126, *pp.* 379–397
Printed in Great Britain

Double-diffusive convection caused by coupled molecular diffusion

By TREVOR J. McDOUGALL

Research School of Earth Sciences, Australian National University,
P.O. Box 4, Canberra, A.C.T. 2600

(Received 26 April 1982)

Double-diffusive convection is studied for the case where a large coupled diffusion (or cross-diffusion) effect is present. The Soret effect is a familiar example of this cross-diffusion where the flux of the solute depends not only on its own spatial gradient but also on the *in situ* temperature gradient. The linear stability analysis of double-diffusive convection has been extended to include the two cross-diffusion flux terms and it has been shown that, with a sufficiently large coupled diffusion effect, fingers can form even when the concentrations of *both* components make the fluid's density gradient statically stable. The conditions under which the diffusive instability can occur are compared with those for the formation of fingers and it is shown that these two types of double-diffusive convection cannot occur together in any particular set of linear property gradients. We then consider finite-amplitude, steady, infinitely long fingers and show that a sufficiently large cross-diffusion effect can again allow fingers to exist when the concentrations of both solutes increase with depth. It is also shown that the diffusion of properties from an initially sharp interface may set up vertical gradients that are favourable for the formation of fingers.

1. Introduction

Salt fingers occur in the ocean when hot saline water overlies cooler fresher water and they are now believed to play an important role in the mixing of properties in several regions of the ocean (Williams 1981; Schmitt & Georgi 1982). The fingers form a pattern where each upward-moving finger is surrounded by downward-moving fingers and *vice versa*. The downgoing fingers lose heat to the upgoing fingers, making the downgoing fingers more dense and the upgoing fingers less dense. It is this density difference that maintains the motions against the retarding viscous forces. Because the molecular diffusivity of salt is much less than that of heat, very little salt is transferred between the fingers; this is indicated in figure 1 by the small vertical salinity gradient in both the up and downgoing fingers. The density profiles sketched in figure 1 show that the downgoing fingers are more dense than the upgoing fingers and that the mean density gradient through the fingers is hydrostatically stable.

The extra effect we consider here is that of the coupled fluxes of the two properties due to irreversible thermodynamic effects. The Soret effect is an example of this cross-diffusion where a flux of salt is caused by a spatial gradient of temperature. The corresponding flux of heat caused by a salinity gradient is called the Dufour effect and in liquids is a very small effect indeed, so that we can treat the heat–solute property pair as possessing only one cross-diffusion term, namely that due to the Soret effect. When considering the isothermal coupled diffusion between a solvent and two solutes (called ternary diffusion) we need to include two cross-diffusion effects because each property gradient has a significant influence on the flux of the other property.

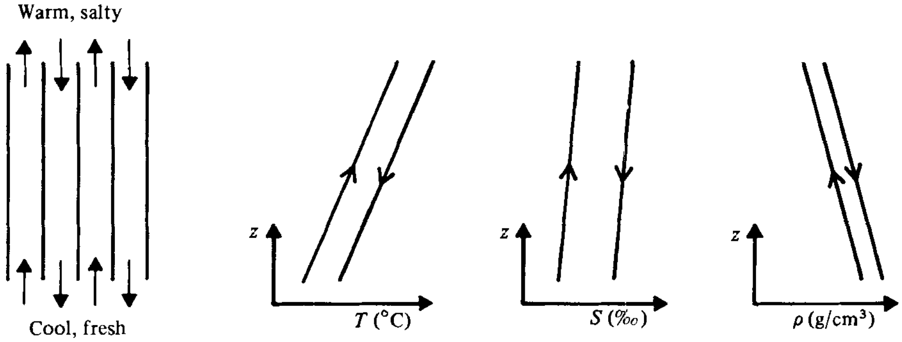


FIGURE 1. Sketch of up- and downgoing salt fingers and their temperatures, salinities and densities. The arrows on the individual profiles distinguish the up- from the downgoing fingers. Note that, in contrast with figure 3, the temperature is plotted here, as opposed to its effect on density.

Hurle & Jakeman (1971) demonstrated the influence of the Soret effect in the classical Rayleigh–Jeffreys problem of heating from below a fluid layer confined between two horizontal conducting plates. They used water–methanol mixtures, for which the Soret coefficient changes sign at 26·5 wt % methanol and they conducted the following experiments. They heated a thin layer of a water–methanol mixture from below and recorded temperature changes to detect the onset of instability. At low methanol concentrations they observed that the instability was oscillatory, indicating the presence of the 'diffusive' double-diffusive instability. Conditions favourable to this instability were formed by the methanol molecules being driven away from the bottom of the layer by the temperature gradient, leaving a water-rich more-dense solution there. At higher methanol concentrations the convective breakdown was direct because the reversal of the Soret effect produced less dense, methanol-rich solution near the lower boundary which reinforced the effect of the temperature gradient.

Convective instabilities have been reported in the diffusion literature for some years, but until recently these were interpreted as implying that the vertical density gradient must be hydrostatically unstable. Miller (1966) observed instability at the diffusing horizontal interface between a solution of 60 % *n*-heptane and 40 % tri-isobutyl phosphate (TiBP) placed above pure cetyl chloride. From his description of the motion and his photographs (particularly his figure 2) it seems clear that what he saw was an example of the fingering mechanism, although there is no reason to suspect that cross-diffusion was significant. These and other experiments (e.g. Miller, Spurling & Mason 1967; Vitagliano *et al.* 1972) where convection was present have been described as cases where the vertical density gradient becomes reversed by ternary diffusion. It is important to realize that double-diffusive convection occurs when the density gradient is hydrostatically stable. A common experimental situation in the diffusion literature is the differential heating and cooling of fluid between two horizontal flat plates. Schechter, Prigogine & Hamm (1972) and Velarde & Schechter (1972) have carried out the linear stability analysis for this situation, making special allowance for the boundary conditions of zero flux at the flat plates. Antoranz & Velarde (1979) review other recent papers that demonstrate the occurrence of double-diffusive convection caused by the Soret effect in this Rayleigh–Jeffreys geometry with the same boundary conditions.

In the present paper we first extend the linear stability analysis of double-diffusive convection to include both cross-diffusion terms of ternary diffusion and we discuss the impact of the cross-diffusion terms on the stability boundaries. We then take the model of Huppert & Manins (1973) of very long fingers and extend it to include the two cross-diffusion terms. This leads to the conditions under which fingers can not only form initially, but can continue indefinitely in particular property gradients. Finally we consider the gradients of properties that occur during diffusion from an initially sharp interface between two fluids and we discuss the conditions under which fingers can form in this situation. Our initial motivation for this work was the striking photographs of fingers in Preston *et al.* (1980), where the diffusion of a solution of macromolecules was studied. The distribution of the polymers was not obviously conducive to ordinary double-diffusive finger convection and so we advance an explanation in terms of the cross-diffusion fluxes.

2. Linear stability analysis of double-diffusive convection with cross-diffusion terms

We consider fluid confined between two horizontal porous plates which maintain a contrast in fluid properties between the plates of ΔT and ΔS. For the purposes of this paper we consider both T and S to be solute concentrations (weight of solute per unit weight of solution) and that positive ΔT and ΔS imply that the concentrations are greater at the lower plate. We consider only two-dimensional instabilities from a rest state that has uniform T and S gradients between the plates. The equations for the conservation of T and S are

$$\frac{\partial T}{\partial t}+\mathbf{U}\,.\,\nabla T = D_{11}\nabla^2 T+D_{12}\nabla^2 S, \tag{1}$$

$$\frac{\partial S}{\partial t}+\mathbf{U}\,.\,\nabla S = D_{22}\nabla^2 S+D_{21}\nabla^2 T, \tag{2}$$

where D_{12} and D_{21} are the two cross-diffusion terms and $\mathbf{U}$ is the two-dimensional velocity vector. The property T is assumed to have a larger diffusivity than S, that is $D_{11} > D_{22}$. The Navier–Stokes equation for the momentum conservation is

$$\frac{\partial \mathbf{U}}{\partial t}+\mathbf{U}\,.\,\nabla\mathbf{U} = -\frac{1}{\rho_0}\nabla p+\mathbf{g}\frac{\rho}{\rho_0}+\nu\nabla^2\mathbf{U}. \tag{3}$$

Here $\mathbf{g}$ is the gravitational acceleration, directed vertically downwards, ρ_0 is the reference density and ρ is the fluid density, given by

$$\rho = \rho_0(1+\alpha T+\beta S). \tag{4}$$

Taking x as the horizontal spatial coordinate and z as the vertical coordinate (defined positive upwards), we define a stream function ψ by

$$\mathbf{U} = (U_x, U_z) = \left(\frac{\partial\psi}{\partial z}, -\frac{\partial\psi}{\partial x}\right). \tag{5}$$

By taking the curl of (3) we obtain (after dropping small second-order quantities)

$$\frac{\partial}{\partial t}(\nabla^2\psi) = \nu\nabla^2(\nabla^2\psi)+g\alpha\frac{\partial T}{\partial x}+g\beta\frac{\partial S}{\partial x}. \tag{6}$$

We now introduce non-dimensional variables in the usual way so that the deviations of T and S from linear vertical gradients $-\Delta T/d$ and $-\Delta S/d$ (where d is the separation of the plates) are normalized by ΔT and ΔS respectively and the timescale is $d^2D_{11}^{-1}$. Equations (1), (2) and (6) are now expressed in terms of the dimensionless variables (the dashed variables are dimensionless)

$$\frac{T'}{\partial t'}-\nabla^2T'-\frac{D_{12}}{D_{11}}\frac{\Delta S}{\Delta T}\nabla^2S' = -\frac{\partial\psi'}{\partial x'}, \tag{7}$$

$$\frac{\partial S'}{\partial t'}-\frac{D_{22}}{D_{11}}\nabla^2S'-\frac{D_{21}}{D_{11}}\frac{\Delta T}{\Delta S}\nabla^2T' = -\frac{\partial\psi'}{\partial x'}, \tag{8}$$

$$\left(\frac{\partial}{\partial t'}-\sigma\nabla^2\right)\nabla^2\psi' = R\frac{\partial T'}{\partial x'}+R_{\mathrm{s}}\frac{\partial S'}{\partial x'}, \tag{9}$$

where the Prandtl number $\sigma \equiv \nu/D_{11}$, the Rayleigh number $R \equiv g\alpha\Delta Td^3/D_{11}\nu$ and the solutal Rayleigh number $R_{\mathrm{s}} \equiv g\beta\Delta Sd^3/D_{11}\nu$ in terms of ΔT, ΔS and d.

We seek solutions to (7)–(9) of the form

$$\psi' = \psi_0 \sin(\pi ax')\sin(\pi nz')\, e^{pt'}, \tag{10a}$$

$$\begin{Bmatrix} T' \\ S' \end{Bmatrix} = \begin{Bmatrix} T_0 \\ S_0 \end{Bmatrix} \cos(\pi ax')\sin(\pi nz')\, e^{pt'}, \tag{10b}$$

which has the correct form to satisfy the equations, and when n is an integer (10) represents a free-slip boundary condition at the two plates. We substitute (10) into (7)–(9) and eliminate ψ_0, T_0 and S_0 to obtain a cubic equation for the growth rate p:

$$p^3+p^2k^2(\sigma+1+\tau)+p\left[k^4(\sigma+\tau\sigma+\tau)+\frac{\sigma(\pi a)^2}{k^2}\left\{R+R_{\mathrm{s}}-\frac{k^6}{(\pi a)^2}\frac{D_{12}D_{21}}{\sigma D_{11}^2}\right\}\right]$$
$$+\sigma\left[\tau k^6+(\pi a)^2\left\{\tau R+R_{\mathrm{s}}-\frac{k^6}{(\pi a)^2}\frac{D_{12}D_{21}}{D_{11}^2}-\frac{D_{12}}{D_{11}}\frac{\Delta S}{\Delta T}R-\frac{D_{21}}{D_{11}}\frac{\Delta T}{\Delta S}R_{\mathrm{s}}\right\}\right] = 0, \tag{11}$$

where $k^2 = \pi^2(a^2+n^2)$ and $\tau \equiv D_{22}/D_{11} < 1$. We form an equivalent Rayleigh number R^{e} and an equivalent solutal Rayleigh number $R_{\mathrm{s}}^{\mathrm{e}}$ such that the curly brackets in the cubic equation are equal to their normal (i.e. if $D_{12} = D_{21} = 0$) expressions in terms of R^{e} and $R_{\mathrm{s}}^{\mathrm{e}}$. That is

$$R^{\mathrm{e}}+R_{\mathrm{s}}^{\mathrm{e}} = R+R_{\mathrm{s}}-\frac{k^6}{(\pi a)^2}\frac{D_{12}D_{21}}{\sigma D_{11}^2} \equiv R+R_{\mathrm{s}}-A, \tag{12}$$

$$\begin{aligned}\tau R^{\mathrm{e}}+R_{\mathrm{s}}^{\mathrm{e}} &= \tau R+R_{\mathrm{s}}-\frac{k^6}{(\pi a)^2}\frac{D_{12}D_{21}}{D_{11}^2}-\frac{D_{12}}{D_{11}}\frac{\Delta S}{\Delta T}R-\frac{D_{21}}{D_{11}}\frac{\Delta T}{\Delta S}R_{\mathrm{s}} \\ &\equiv \tau R+R_{\mathrm{s}}-B,\end{aligned} \tag{13}$$

where we have defined the two shorthand symbols A and B. The equivalent Rayleigh numbers are then

$$R^{\mathrm{e}} = R+\frac{B-A}{1-\tau}, \tag{14}$$

$$R_{\mathrm{s}}^{\mathrm{e}} = R_{\mathrm{s}}+\frac{\tau A-B}{1-\tau}. \tag{15}$$

By setting the growth rate p to be purely imaginary the conditions required for double-diffusive convection are obtained. These conditions are well known for the normal situation where $D_{12} = D_{21} = 0$ and the stability boundaries are lines in the (R, R_{s})-plane. With coupled diffusion, these same stability boundaries apply when drawn in the $(R^{\mathrm{e}}, R_{\mathrm{s}}^{\mathrm{e}})$-plane.

2.1. *Conditions for the onset of the 'finger' instability*

For the formation of fingers in our geometry, the normal requirements of double-diffusive convection are

$$R_s^e < 0, \quad R^e > 0, \quad -R_s^e > \tau R^e + \tfrac{27}{4}\pi^4\tau, \tag{16}$$

where the factor $\frac{27}{4}\pi^4$ is equal to $k^6/(\pi a)^2$ at the most-unstable values of $n = 1$, $a = 2^{-\frac{1}{2}}$. In terms of the physical Rayleigh numbers, the third inequality in (16) becomes

$$-R_s > \tau(R + \tfrac{27}{4}\pi^4) - B.$$

Now for $R > 0$, that is for the density gradient due to the faster-diffusing component αT_z negative and therefore statically stabilizing, this expression becomes

$$\left(\frac{\beta}{\alpha}\frac{D_{21}}{D_{22}} - 1\right) + \frac{1}{\tau}\frac{\beta S_z}{\alpha T_z}\left(\frac{\alpha}{\beta}\frac{D_{12}}{D_{11}} - 1\right) > \frac{27}{4}\frac{\pi^4}{R}\left(1 - \frac{D_{12}D_{21}}{D_{11}D_{22}}\right), \tag{17}$$

where $\beta S_z/\alpha T_z$ is simply R_s/R. For $R < 0$, that is $\alpha T_z > 0$, the above inequality is reversed. Hydrostatic stability is assured by $R_s + R > 0$, that is $\alpha T_z + \beta S_z < 0$, and with this constraint it can be shown that the inequality (17) for the formation of fingers is more restrictive than the two other conditions of (16), namely $R_s^e < 0$ and $R^e > 0$. In most situations $\frac{27}{4}\pi^4$ is small in comparison with a typical Rayleigh number and so the right-hand side of (17) is approximately zero.

The normal condition for fingers to form without cross diffusion is readily recovered from (17). In this case $\beta S_z > 0$, $\alpha T_z < 0$ and the well-known condition is $|\beta S_z/\alpha T_z| > \tau$. The presence of the cross-diffusion terms changes this criterion to

$$\left|\frac{\beta S_z}{\alpha T_z}\right|\left(1 - \frac{\alpha}{\beta}\frac{D_{12}}{D_{11}}\right) > \tau\left(1 - \frac{\beta}{\alpha}\frac{D_{21}}{D_{22}}\right), \quad \beta S_z > 0, \quad \alpha T_z < 0. \tag{18}$$

This shows that a positive D_{21} (that is, where the flux of the more slowly diffusing component S is augmented by the T-gradient) encourages the appearance of fingers, whereas a positive D_{12} discourages their occurrence.

We now briefly turn our attention to the specialized initial conditions created in a Rayleigh–Bénard-type experiment that has two horizontal boundaries that are impervious to the S-property, but between which a constant difference of the T-property is maintained. We investigate the stability when the vertical flux of S is zero at all depths and so R and R_s are directly related (from (2)) by $R_s/R = -\beta D_{21}/\alpha D_{22}$. Substituting this relation between R_s and R into (17) we obtain

$$\frac{\beta D_{21}}{\alpha D_{22}} > \frac{\tau}{1+\tau} + \frac{1}{(1+\tau)}\frac{D_{12}D_{21}}{D_{11}D_{22}} + \frac{27}{4}\frac{\pi^4\tau}{R(1+\tau)}\left(1 - \frac{D_{12}D_{21}}{D_{11}D_{22}}\right) \tag{19}$$

as the condition for a particular type of finger perturbation to grow in this geometry. This is an extension of the corresponding conditions of Hurle & Jakeman (1971, equation (19)) and Antoranz & Velarde (1979, equation (14)) to include both of the cross-diffusion terms, and is the relevant condition for perturbations which see perfectly conducting and permeable boundaries where the imposed values of T and S are maintained. For large R (in relation to $\frac{27}{4}\pi^4 = 657$), (19) reduces to

$$\frac{\beta D_{21}}{\alpha D_{22}} \gtrsim \tau\left[1 + \tau - \frac{\alpha}{\beta}\frac{D_{12}}{D_{11}}\right]^{-1}. \tag{20}$$

Since impervious boundary conditions are assumed to give rise to the S-gradient but

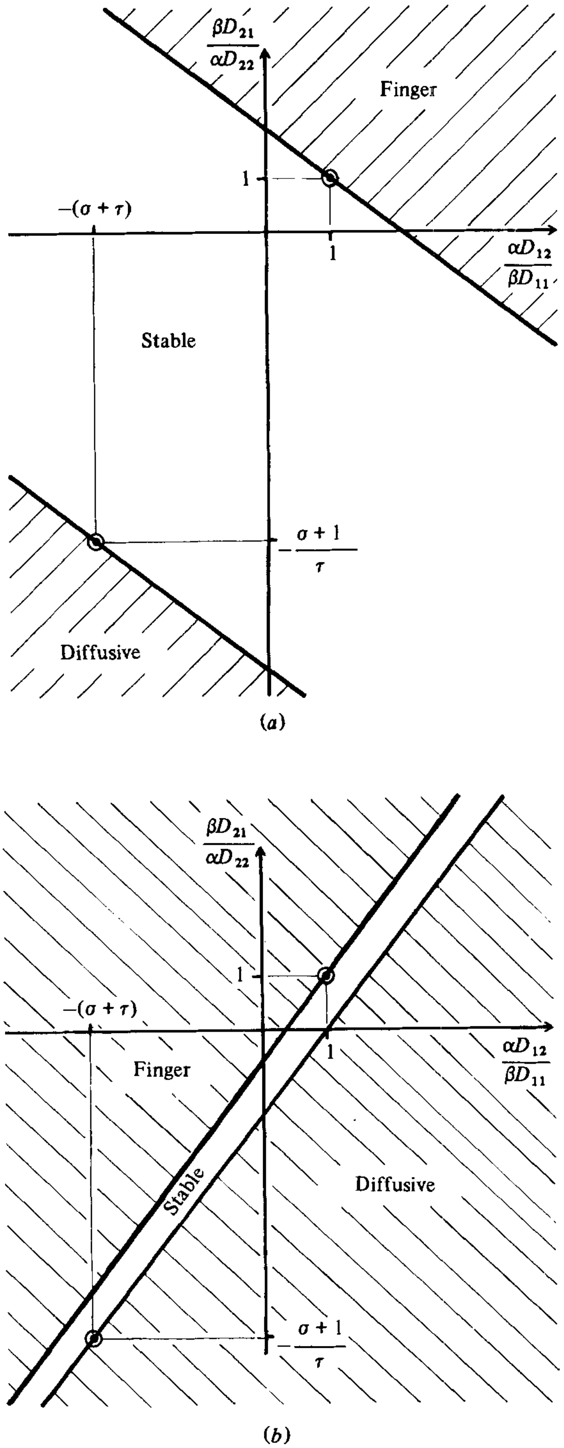
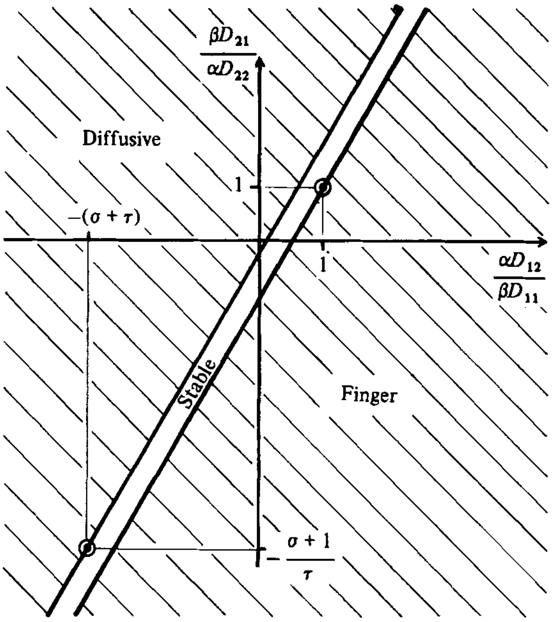


FIGURE 2 (*a*, *b*). For caption see facing page.



(*c*)

FIGURE 2. Sketch of the stability boundaries as a function of $\beta D_{21}/\alpha D_{22}$ and $\alpha D_{12}/\beta D_{11}$ for the three different ranges of αT_z and βS_z. (*a*) has $\alpha T_z < 0$ and $\beta S_z < 0$ (i.e. both components stably distributed); (*b*) has $\alpha T_z < 0$ and $\beta S_z > 0$ (i.e. an apparently 'finger' property distribution); (*c*) has $\alpha T_z > 0$ and $\beta S_z < 0$ (i.e. an apparently 'diffusive' property distribution).

perfectly permeable boundary conditions are assumed for the instability, (19) and (20) are not the accurate conditions for instability. An accurate treatment would include both cross-diffusion terms in a normal-mode analysis like that of Antoranz & Velarde (1979). Note that usually the Rayleigh number in these 'Soret' experiments is defined in terms of a temperature difference and has the opposite sign to R considered in this paper.

If both T and S are stably stratified ($\alpha T_z < 0$ and $\beta S_z < 0$) then we see from (17) that, as a minimum condition for the formation of fingers, either $\beta D_{21}/\alpha D_{22} > 1$ or $\alpha D_{12}/\beta D_{11} > 1$. We defer a more complete discussion of the constraint (17) until after we have considered the model of finite-amplitude steady fingers in §3.

2.2. *Conditions for the onset of the 'diffusive' instability*

We return now to the cubic equation (11) for the growth rate p of infinitesimally small disturbances and consider the conditions under which the 'diffusive' type of double-diffusive convection will occur. The well-known conditions for the diffusive instability to form in normal double-diffusive convection are

$$R_s^e > 0, \quad R^e < 0, \quad -R^e > R_s^e \frac{(\sigma+\tau)}{(\sigma+1)} + \frac{27\pi^4}{4} \frac{(1+\tau)(\sigma+\tau)}{\sigma}, \tag{21}$$

when both the T- and the S-properties are fixed at the free-slip horizontal boundaries. In terms of the physical Rayleigh numbers this last inequality is

$$-R > R_s \frac{\sigma+\tau}{\sigma+1} + \frac{B - A(\sigma+1+\tau)}{\sigma+1} + \frac{27\pi^4}{4} \frac{(1+\tau)(\sigma+\tau)}{\sigma}, \tag{22}$$

and if the cross-diffusion terms B and A are both zero then we recover the condition for the diffusive instability for ordinary double-diffusive convection. In the special initial conditions of a Rayleigh–Bénard experiment with both cross-diffusion fluxes, (22) becomes (with $R_s/R = -\beta D_{21}/\alpha D_{22}$ and $R < 0$)

$$\frac{\beta D_{21}}{\alpha D_{22}} < 1+\frac{1}{\sigma}-\frac{1}{\sigma}\frac{D_{12}D_{21}}{D_{11}D_{22}}+\frac{27}{4}\frac{\pi^4(1+\tau)}{R\sigma^2}\left\{(\sigma+\tau)(\sigma+1)-\frac{D_{12}D_{21}}{D_{11}D_{22}}\tau\right\}, \tag{23}$$

which is the extension of Hurle & Jakeman's condition for this geometry (their equation (21)) when both cross-diffusion terms are important.

In the more general situation where αT_z and βS_z are set independently, we can obtain the criterion for the onset of the diffusive instability as (ignoring terms in (22) of order $\frac{27}{4}\pi^4$)

$$\tau\alpha T_z\left(\frac{\beta D_{21}}{\alpha D_{22}}+\frac{\sigma+1}{\tau}\right)+\beta S_z\left(\frac{\alpha D_{12}}{\beta D_{11}}+\sigma+\tau\right) > 0. \tag{24}$$

It can readily be shown that (24), together with the static stability restriction $\sigma T_z+\beta S_z < 0$, implies that $R_s^e > 0$, $R^e < 0$, as (21) requires. In aqueous solutions $\sigma \approx 7$, and in the case where both T and S are stably distributed (24) shows that either $\alpha D_{12}/\beta D_{11}$ or $\beta D_{21}/\alpha D_{22}$ have to be less than -7 (or even more negative) for diffusive convection to occur.

2.3. *A comparison of the cross-diffusion coefficients conducive to the finger and the diffusive instabilities*

With cross-diffusion coefficients of the appropriate sign and magnitude it is possible to have finger or diffusive convection when both T and S are stably stratified, to have fingers when the properties are distributed in the apparently diffusive fashion and to have diffusive instabilities when the gradients are set up in an apparently finger distribution. In this subsection we answer the important question of whether the conditions for the occurrence of finger and diffusive instabilities can ever be fulfilled simultaneously.

The general condition for the onset of fingers, analogous to (24) for the diffusive instability, is

$$\tau\alpha T_z\left(\frac{\beta D_{21}}{\alpha D_{22}}-1\right)+\beta S_z\left(\frac{\alpha D_{12}}{\beta D_{11}}-1\right) < 0. \tag{25}$$

We now treat αT_z and βS_z as externally imposed and plot the two inequalities (24) and (25) on the axes $\beta D_{21}/\alpha D_{22}$ and $\alpha D_{12}/\beta D_{11}$, subject to the static stability constraint $\alpha T_z+\beta S_z < 0$. Figure 2 shows the regions on these diagrams where finger and diffusive instabilities occur for the three possible distributions of αT_z and βS_z. The straight lines through the points $(1, 1)$ and $(-(\sigma+\tau), -(\sigma+1)/\tau)$ have the same slope for the diffusive and finger criteria in each of figures 2 (*a*–*c*). Figure 2 (*a*) has stable distributions of both T and S, and the slope of the stability boundaries is negative. Figure 2 (*b*) has $\alpha T_z < 0$ and $\beta S_z > 0$, the distribution of properties that is normally conducive to fingers, and the slope of the stability boundaries is between 0 and τ^{-1}. Figure 2 (*c*) has $\alpha T_z > 0$ and $\beta S_z < 0$, the distribution of properties that is normally conducive to the diffusive instability, and the slope of the stability boundaries is greater than τ^{-1}.

These stability boundaries show that the two types of double-diffusive instabilities never occur together, even though both types of instability can occur in property gradients that are normally conducive to the other type of instability.

3. Finite-amplitude finger analysis with the cross-diffusion terms

Huppert & Manins (1973) present a linear model of finite-amplitude, steady, very long salt fingers. The nonlinear advective terms in the Navier–Stokes equation are equal to zero because the motion is assumed to be vertical. We extend this model to include the two cross-diffusion flux terms.

The vertical momentum equation is

$$0 = -\frac{1}{\rho_0}\frac{dp}{dz} - g(1+\alpha T+\beta S)+\nu\nabla^2 w \tag{26}$$

and the T- and S-conservation equations are

$$wT_z = D_{11}\nabla^2 T + D_{12}\nabla^2 S, \tag{27}$$

$$wS_z = D_{22}\nabla^2 S + D_{21}\nabla^2 T. \tag{28}$$

Since the horizontal velocities are zero, $\partial w/\partial z$ must be zero, and so $\nabla^2 w$ in (26) is simply $\nabla_2^2 w = \partial^2 w/\partial x^2 + \partial^2 w/\partial y^2$. The horizontal momentum equations show that p is a function of z only, and so from (26) we see that $\alpha T+\beta S$ must be the sum of a function of z only and a function of x and y only. Assuming that this functional form applies to αT and βS separately, we write

$$\alpha T(x,y,z) = \alpha \bar{T}(z) + \alpha T'(x,y), \tag{29}$$

$$\beta S(x,y,z) = \beta \bar{S}(z) + \beta S'(x,y), \tag{30}$$

where the overbar means an average in the horizontal plane and T' and S' have a zero horizontal average. Substituting these forms for αT and βS into (27) and (28) and taking the horizontal average shows that either $D_{11}D_{22}-D_{12}D_{21} = 0$ (which we discount) or

$$\frac{d^2\bar{T}}{dz^2} = 0 = \frac{d^2\bar{S}}{dz^2}. \tag{31}$$

Subtracting (26) from its horizontal average gives

$$\alpha T' + \beta S' = \frac{\nu}{g}\nabla_2^2 w, \tag{32}$$

and (27) and (28) become

$$w\bar{T}_z = D_{11}\nabla_2^2 T' + D_{12}\nabla_2^2 S', \tag{33}$$

$$w\bar{S}_z = D_{22}\nabla_2^2 S' + D_{21}\nabla_2^2 T'. \tag{34}$$

We seek solutions of these three equations of the form

$$(W, T', S') = (W_0, T_0, S_0)\cos mx \cos ny \tag{35}$$

and find upon substitution that

$$-\alpha\bar{T}_z\left(\frac{\beta}{\alpha}D_{21}-D_{22}\right)-\beta\bar{S}_z\left(\frac{\alpha}{\beta}D_{12}-D_{11}\right) = \frac{\nu k^4}{g}(D_{11}D_{22}-D_{12}D_{21}), \tag{36}$$

where $k^2 = m^2+n^2$. In order for fingers to form, k^4 must be positive, and, taking $D_{11}D_{22}-D_{12}D_{21} > 0$, the left-hand side of (36) must be positive. We consider first the case where T is stably stratified ($\alpha\bar{T}_z < 0$), then fingers will form if

$$\left(\frac{\beta}{\alpha}\frac{D_{21}}{D_{22}}-1\right)+\frac{1}{\tau}\frac{\beta\bar{S}_z}{\alpha\bar{T}_z}\left(\frac{\alpha D_{12}}{\beta D_{11}}-1\right) > 0, \tag{37}$$

and the inequality is reversed if $\alpha\overline{T}_z > 0$. This is the same criterion as (17) except for the small term there proportional to $27\pi^4/4R$. The gradients $\overline{T}_z$ and $\overline{S}_z$ in (37) are the vertical gradients of the horizontally averaged T- and S-fields through an array of finite-amplitude steady fingers, whereas the gradients T_z and S_z in (17) are uniform in the horizontal direction and are the gradients that exist before any fingering sets in. Subject to this different interpretation of the vertical gradients, the conditions required for the *maintenance* of steady fingers is the same as that for the *formation* of fingers as determined by the linear stability analysis. This same similarity was found by Huppert & Manins (1973) for ordinary salt fingers without cross-diffusion effects.

We have deferred until now an extensive discussion of the linear stability analysis criterion for finger formation (17) because of its similarity to the finite-amplitude finger criterion (37). We have already considered the two cases where the solutes are distributed in the 'normal' fingering fashion ($\alpha T_z < 0$, $\beta S_z > 0$) (see (18)) and when the S-gradient is set up so as to maintain zero vertical flux of S, such as in a Rayleigh–Bénard convection experiment (see (19)). Both of these criteria also apply to the maintenance of finite-amplitude fingers, although, in the second case, the salinity gradient is set up on a slow diffusion timescale involving D_{22} and so the presence of fingers will quickly destroy this gradient. More realistic vertical structures of the properties T, S and ψ in this case have been investigated by Velarde & Schechter (1972) using a linear normal-mode analysis when there is only one non-zero cross-diffusion coefficient.

A few comments are in order here about the cross-diffusion coefficients D_{12} and D_{21}. First, the Onsager reciprocal relationship is often not of practical use in relating D_{12} and D_{21} as this requires knowledge of the dependence of the chemical potential of each species on concentration, and this data is often not available (Miller 1960). For the ternary systems that have been studied experimentally, D_{12} and D_{21} are often quite different. Secondly, the framework of linear irreversible thermodynamics applies only for small concentration gradients (or small concentration differences) and so it is conventional to write equations such as (1) and (2) as though D_{12} and D_{21} are universal constants, whereas in reality they should be interpreted as the values applicable to the mean concentrations $\overline{T}$ and $\overline{S}$ of a particular experiment. Leaist & Lyons (1980) have shown theoretically that for small concentrations $D_{12} \propto \overline{T}$ and $D_{21} \propto \overline{S}$ (their equations (60) and (61)), and experimental data (Leaist & Lyons 1980; Wendt & Shamim 1970) have shown agreement with this concentration dependence of the cross-diffusion coefficients.

We return to the situation where both $\overline{T}$ and $\overline{S}$ are stably stratified ($\alpha\overline{T}_z < 0$, $\beta\overline{S}_z < 0$). It is useful to focus attention on the cases where one of D_{12} or D_{21} is zero. If say $D_{12} = 0$, so that cross-diffusion affects the flux of S alone, then (37) can be written as

$$\frac{\beta D_{21}}{\alpha D_{22}} > 1 + \frac{1}{\tau}\frac{\beta\overline{S}_z}{\alpha\overline{T}_z}, \quad D_{12} = 0, \tag{38}$$

and, if $D_{21} = 0$ so that cross-diffusion affects the flux of T alone, we have

$$\frac{\alpha D_{12}}{\beta D_{11}} > 1 + \tau\frac{\alpha\overline{T}_z}{\beta\overline{S}_z}, \quad D_{21} = 0. \tag{39}$$

For $D_{12} = 0$, fingers can form more readily for small $\beta\overline{S}_z$ and large $\alpha\overline{T}_z$, while, for $D_{21} = 0$, they are favoured by small $\alpha\overline{T}_z$ and large $\beta\overline{S}_z$. As an extreme example, fingers

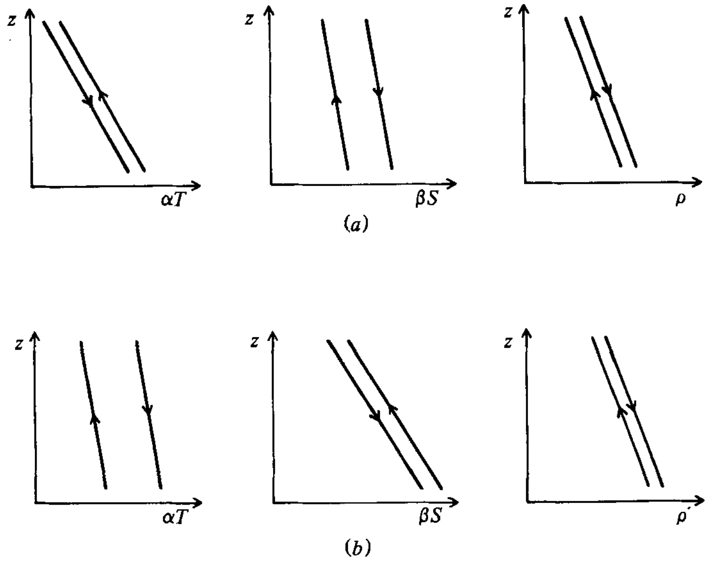


FIGURE 3. Sketch of the vertical profiles of αT, βS and ρ in the centres of up- and downgoing (indicated by the arrows) fingers for $\alpha \overline{T}_z < 0$, $\beta \overline{S}_z < 0$; that is with both T and S stably stratified. (*a*) has $D_{12} = 0$, and D_{21} (> 0) satisfies (38); (*b*) has $D_{21} = 0$, and D_{12} (> 0) satisfies (39).

will form with $D_{12} = 0$ with a zero vertical gradient of $\overline{S}$ if $\beta D_{21}/\alpha D_{22} > 1$, while, for $D_{21} = 0$, fingers will appear in a zero vertical gradient of $\overline{T}$ if $\alpha D_{12}/\beta D_{11} > 1$. In the more general case where both D_{12} and D_{21} are non-zero, we see from (37) and from figure 2(*a*) that the occurrence of fingers is assisted by large positive values of both D_{12} and D_{21}, and that at least one of $\beta D_{21}/\alpha D_{22}$ and $\alpha D_{12}/\beta D_{11}$ must exceed unity.

The driving energy for normal fingering motion comes from the unstably stratified component S, and this potential energy is released by the rapid diffusion of T between the fingers. In the fingering motion that we have just described we have shown that even if both of the components T and S are distributed in a hydrostatically stable fashion, finger convection can still occur if the cross-diffusion terms are large enough to satisfy (37). The total gravitational potential energy of the fluid decreases owing to the fingering, but in this case it is the *cross-diffusion* between the fingers that allows the release of the gravitational potential energy even though no separate solute is unstably stratified. The T-, S- and ρ-profiles in upgoing and downgoing fingers are sketched in figure 3 for the two cases when one of the cross-diffusion coefficients is zero. In figure 3(*a*) with $D_{12} = 0$ the T-concentration of the downgoing fingers increases owing to the conduction of T from the upgoing into the downgoing fingers in the normal fashion because the T-flux is unaffected by coupled diffusion. The S-concentration of the downgoing fingers is also increasing in this case, even though at each depth the downgoing fingers are more concentrated in S than the upgoing fingers. This is caused by the cross-diffusion horizontal flux of S due to the horizontal gradients of T and the large value of D_{21} which satisfies (38). A similar explanation applies to the profiles in figure 3(*b*) when $D_{21} = 0$ and D_{12} satisfies (39). Here the S-profiles are unaffected by cross-diffusion and the T-concentrations of the fingers are significantly influenced by the cross-diffusive flux of T. Note that, in both figures 3(*a*, *b*), the horizontally averaged density gradient is statically stable ($\overline{\rho}_z < 0$) and that the downgoing fingers are more dense than the upgoing fingers.

The relative magnitudes of the concentration differences between the upgoing and downgoing fingers are obtained from (33) and (34) with the substitution (35). In this way we have

$$\frac{\alpha T_0}{\beta S_0} = \frac{1 - \dfrac{1}{\tau}\dfrac{\alpha D_{12}}{\beta D_{11}}\dfrac{\beta \overline{S}_z}{\alpha \overline{T}_z}}{\dfrac{1}{\tau}\dfrac{\beta \overline{S}_z}{\alpha \overline{T}_z} - \dfrac{\beta D_{21}}{\alpha D_{22}}}.$$

The sign of the vertical velocity W_0 is given in terms of T_0 and S_0 by (from (32))

$$\beta S_0\left(1+\frac{\alpha T_0}{\beta S_0}\right) = -\frac{\nu}{g}k^2 W_0.$$

This equation shows that downgoing fingers (i.e. $W_0 < 0$) have a positive density anomaly ($\alpha T_0 + \beta S_0 > 0$), as we expect. For given values of τ, D_{12}, D_{21} and the vertical property gradients $\alpha\overline{T}_z$ and $\beta\overline{S}_z$ we can evaluate the ratio $\alpha T_0/\beta S_0$, and, using this and the above equation, the signs of βS_0 and αT_0 can be determined. The fluxes of T and S are proportional to $W_0 T_0$ and $W_0 S_0$ respectively, and so once we have found the signs of T_0 and S_0 (in relation to the sign of W_0) we can immediately deduce whether the fluxes of T and S are down their respective concentration gradients or whether they are against these gradients. It is well known in double-diffusive convection that the flux of density is always against the density gradient. This general result also applies to all the types of fingering motions we describe in this paper because the downgoing fingers are always denser than the upgoing fingers. In normal double-diffusive convection the fluxes of the individual properties T and S are down their respective gradients, but with the cross-diffusion terms this is often not the case. For example in figure 3(*a*) the flux of S is against its gradient and in figure 3(*b*) the flux of T is countergradient.

Another unlikely distribution of property gradients can also lead to fingers. If *both* the T- and the S-gradients are the reverse of those normally required for fingers, that is if $\alpha\overline{T}_z > 0$ and $\beta\overline{S}_z < 0$ (i.e. the distribution of T and S required for the normal diffusive instability), the criterion for fingers to exist is now just the reverse of the inequality (37), and we can write this in the form

$$\frac{\beta D_{21}}{\alpha D_{22}} < 1 + \frac{1}{\tau}\frac{\beta\overline{S}_z}{\alpha\overline{T}_z}\left(1-\frac{\alpha D_{12}}{\beta D_{11}}\right). \tag{40}$$

Here $\beta\overline{S}_z/\alpha\overline{T}_z$ must be less than -1 for static stability and this is the case depicted in figure 2(*c*). For small τ this condition requires $\beta D_{21}/\alpha D_{22}$ to be negative and large in magnitude, while, for $\tau \approx 1$, it is not so severe. Rearranging (40) to put D_{12} on the left-hand side, we see that

$$\frac{\alpha D_{12}}{\beta D_{11}} > 1 + \tau\frac{\alpha\overline{T}_z}{\beta\overline{S}_z}\left(1-\frac{\beta D_{21}}{\alpha D_{22}}\right). \tag{41}$$

For small values of D_{21}, $\alpha D_{12}/\beta D_{11}$ is required to be greater than some positive number which is less than 1. Figure 4 shows the gradients of αT and βS for the two cases where $D_{12} = 0$ with D_{21} satisfying (40) and $D_{21} = 0$ and D_{12} satisfying (41). With a very large value of $-D_{21}$, the difference in S-concentration between the up- and downgoing fingers in figure 4(*a*) can be the reverse of that shown. When both D_{12} and D_{21} are non-zero, the occurrence of fingers is assisted by negative values of D_{21} and positive values of D_{12}, as can be seen in figure 2(*c*). Note that the flux of S in the case of figure 4(*a*) is downgradient as drawn, but can be countergradient for larger

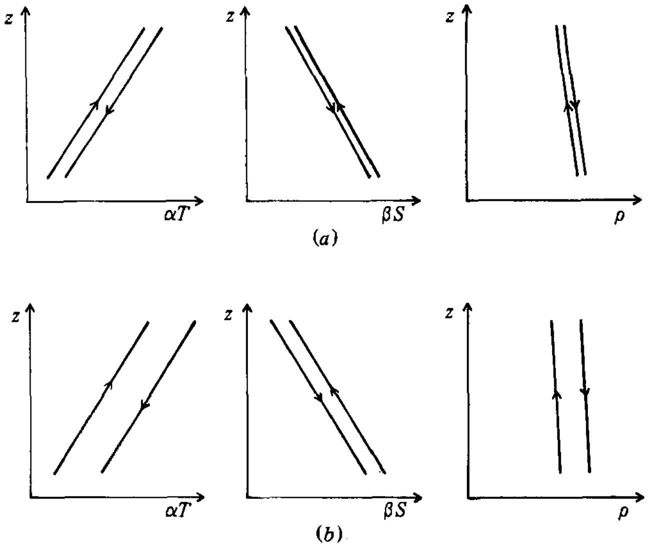


FIGURE 4. Sketch of the vertical profiles of αT, βS and ρ in the centres of up- and downgoing (indicated by the arrows) fingers for $\alpha \overline{T}_z > 0$ and $\beta \overline{S}_z < 0$; that is with property distributions apparently conducive to the diffusive instability. (*a*) has $D_{12} = 0$, and D_{21} (< 0) satisfies (40); (*b*) has $D_{21} = 0$, and D_{12} (> 0) satisfies (41). With a stronger cross-diffusion effect the difference in S-concentration between the up- and downgoing fingers in (*a*) can be the reverse of that shown.

values of $-D_{21}$. The flux of T in the case of figure 4(*b*) is downgradient just as it is in normal double-diffusive convection, even though the fingers are now caused by the cross-diffusion coefficient D_{12}.

Perhaps the most questionable assumption in this model of finite-amplitude fingers is the sinusoidal variation of both T and S in the horizontal directions x and y. In their numerical model of salt fingers, Piacsek & Toomre (1980) have shown that while the vertical velocity and T-profiles may be well described by a simple sinusoid, the S-profiles through the fingers have sharper gradients between the fingers than does a simple sinusoid. From a consideration of the magnitude of the fluxes between the fingers, these sharper gradients of S would make the cross-diffusion term D_{21} less effective at driving fingers, but it would make the term D_{12} more effective. We do not, however, imagine this complication to be too important because of the experimental work of Huppert & Manins (1973). They studied the onset of fingers at a diffusing interface between two solutions of different salts and found that fingers first appeared and then remained present when the instability theory indicated that they should. If the extra sharpness of the horizontal gradients of S was to have a large influence on the fingers then we should expect that their formation would not agree so well with the model.

4. Diffusion of an initially sharp fluid interface

Some methods of measuring diffusion coefficients (e.g. the Gouy diffusiometer) involve the diffusion of two solutions into each other across an initially sharp interface. Some instabilities observed at such diffusing interfaces may be due to double-diffusive convection. For example Vitagliano, Sartorio & Constantino (1974) used aqueous solutions of the salts NaCl and NH_4Cl which were set up in the 'diffusive' sense, that is, with the faster-diffusing component more concentrated in the upper solution and with the slower-diffusing component more concentrated in the lower solution.

Huppert & Manins (1973) have analysed the diffusion of two properties from an initially sharp interface when the layer properties are distributed in the finger sense and they obtained the conditions for the formation of fingers. We are most interested in this section to examine cases where fingers may occur even though the overall distribution of properties is not favourable to them. The extra factor we consider is the cross-diffusion process which can significantly affect the gradients of properties at a diffusing interface.

The solution for the diffusion of two species T and S from an initially sharp boundary with both cross-diffusion terms has been derived by Fujita & Gosting (1956), but unfortunately it is analytically very messy to write down, and for this reason we prefer to discuss the simpler cases where only one of the cross-diffusion coefficients is non-zero.

We consider first the case where $D_{12} = 0$. The initial T- and S-concentrations are greater in the lower layer than in the upper layer by the amounts ΔT and ΔS respectively. The diffusion equations are

$$\frac{\partial T}{\partial t} = D_{11}\frac{\partial^2 T}{\partial z^2}, \tag{42}$$

$$\frac{\partial S}{\partial t} = D_{22}\frac{\partial^2 S}{\partial z^2} + D_{21}\frac{\partial^2 T}{\partial z^2}. \tag{43}$$

The solution to (42) is

$$T(v = z/2(D_{11}t)^{\frac{1}{2}}) = -\frac{\Delta T}{2}\frac{2}{\sqrt{\pi}}\int_0^v e^{-r^2}dr = -\tfrac{1}{2}\Delta T\,\mathrm{erf}\,(v), \tag{44}$$

and by using the transformation of the variables z and t in (43) to $zt^{-\frac{1}{2}}$ we can readily find the solution for S as

$$S(w = z/2(D_{22}t)^{\frac{1}{2}}) = \frac{D_{21}}{D_{22}}\frac{\Delta T}{2}\frac{\tau}{1-\tau}\{\mathrm{erf}\,(w) - \mathrm{erf}\,(\tau^{\frac{1}{2}}w)\} - \tfrac{1}{2}\Delta S\,\mathrm{erf}\,(w). \tag{45}$$

From these expressions we obtain the ratio of the vertical gradients of S and T at $z = 0$ as

$$\frac{\beta S_z}{\alpha T_z} = \tau^{-\frac{1}{2}}\frac{\beta\Delta S}{\alpha\Delta T} - \frac{\beta D_{21}}{\alpha D_{22}}\tau\frac{\tau^{-\frac{1}{2}}-1}{1-\tau}. \tag{46}$$

It is readily shown that for $\Delta T > 0$, $\Delta S > 0$ the most favourable depth z for the occurrence of fingers is at $z = 0$. Notice from (46) that the vertical gradient of S will be reversed at $z = 0$ (i.e. $S_z > 0$) if

$$\frac{\beta\Delta S}{\alpha\Delta T} < \frac{\beta D_{21}}{\alpha D_{22}}\frac{\tau}{1-\tau}(1-\tau^{\frac{1}{2}}).$$

Figure 5(*a*) shows the vertical profile of S as a function of $w = z/2(D_{22}t)^{\frac{1}{2}}$ for $\Delta S = 0$ (i.e. no initial difference between the S-concentrations of the two layers) for two different values of τ, namely $\tau = \frac{1}{80}$ and $\frac{1}{3}$. Figure 5(*b*) shows the vertical profiles when ΔS is just large enough to make S_z zero at $z = 0$.

To obtain a criterion for the onset of fingers at a diffusing interface we use the expression (46) for the magnitude of the S-gradient in the inequality (38), giving

$$\frac{\beta D_{21}}{\alpha D_{22}} > \tau^{\frac{1}{2}}\frac{1-\tau}{1-\tau^{\frac{3}{2}}}\left\{1 + \tau^{-\frac{3}{2}}\frac{\beta\Delta S}{\alpha\Delta T}\right\}, \quad D_{12} = 0. \tag{47}$$

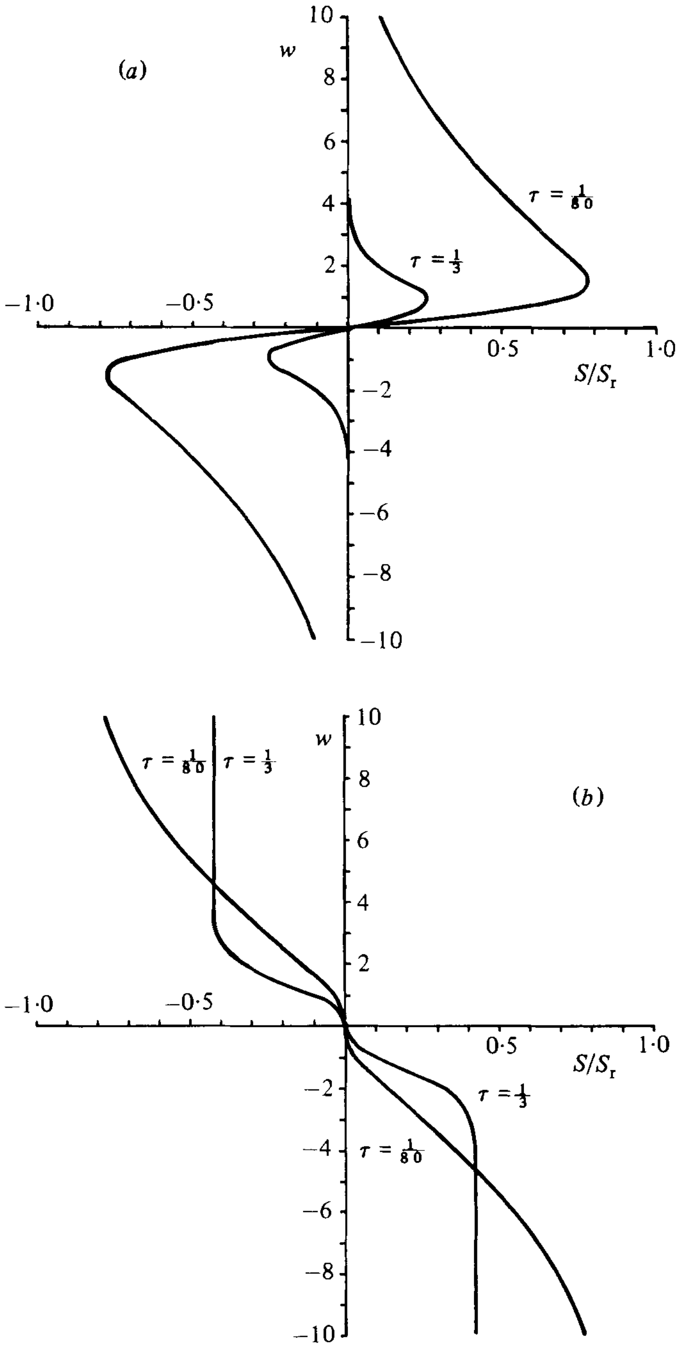


FIGURE 5. Profiles of the S-concentration at a diffusing interface with $D_{12} = 0$. The vertical coordinate w is equal to $z/2(D_{22}t)^{\frac{1}{2}}$, and the reference S value S_r is $\frac{1}{2}\Delta T(D_{21}/D_{22})\tau/(1-\tau)$. ($a$) has the initial contrast ΔS in S-concentrations between the two layers equal to zero; (b) has a positive ΔS just large enough to give a zero vertical S-gradient at $z = 0$.

Now if $S_z = 0$ at $z = 0$ (as in figure 5(*b*), fingers will occur if $\beta D_{21}/\alpha D_{22} > 1$, whereas if $\Delta S = 0$ (as in figure 5*a*) then the criterion is $\beta D_{21}/\alpha D_{22} > \tau^{\frac{1}{2}}(1-\tau)/(1-\tau^{\frac{3}{2}})$. This condition is much easier to fulfil as $\tau^{\frac{1}{2}}(1-\tau)/(1-\tau^{\frac{3}{2}})$ is approximately 0·5 for $\tau = \frac{1}{3}$ and is approximately 0·1 for $\tau = \frac{1}{80}$. It is the reversal of the S-gradient in the centre of the interface, caused by the cross-diffusion coefficient D_{21}, which makes the occurrence of fingers more likely by the above factor.

It is interesting to calculate the density gradient in a diffusing interface. Hydrodynamic static stability requires ρ_z to be negative. From (44) and (45) we obtain

$$\frac{\rho_z}{\dfrac{\alpha\Delta T}{\pi^{\frac{1}{2}}}\dfrac{1}{2(D_{11}t)^{\frac{1}{2}}}} = -\left\{1-\frac{\beta}{\alpha}\frac{D_{21}}{D_{22}}\tau^{\frac{1}{2}}\frac{(1-\tau^{\frac{1}{2}})}{(1-\tau)}\right\}-\tau^{-\frac{1}{2}}\frac{\beta\Delta S}{\alpha\Delta T}, \tag{48}$$

and so a statically unstable density gradient is obtained if

$$\frac{\beta D_{21}}{\alpha D_{22}} > \frac{1-\tau}{\tau^{\frac{1}{2}}(1-\tau^{\frac{1}{2}})}\left(1+\tau^{-\frac{1}{2}}\frac{\beta\Delta S}{\alpha\Delta T}\right). \tag{49}$$

It is more difficult to satisfy this inequality than to get fingers (see (47)). For example, if ΔS is zero there is a ratio of approximately τ between the right-hand sides of (47) and (49). The above inequality can also be used to determine when an unstable density gradient can occur in the absence of any cross-diffusion effects in the 'normal' salt-fingering situation where $\Delta T > 0$, $\Delta S < 0$. The condition for a density reversal is

$$R_\rho \equiv \left|\frac{\alpha\Delta T}{\beta\Delta S}\right| < \tau^{-\frac{1}{2}}, \quad D_{12} = 0, \quad D_{21} = 0, \tag{50}$$

whereas fingers can form at such an interface if (from (47))

$$R_\rho \equiv \left|\frac{\alpha\Delta T}{\beta\Delta S}\right| < \tau^{-\frac{3}{2}}, \quad D_{12} = 0, \quad D_{21} = 0. \tag{51}$$

This last result was first derived by Huppert & Manins (1973). These two inequalities show for example that if $\tau = \frac{1}{80}$ fingers can form at the diffusing interface if $R_\rho < 715$, and a density reversal can occur at the centre of the interface if $R_\rho < 9$. Here again the condition for a statically unstable density gradient to develop is more restrictive than the condition for fingers to form. Huppert & Manins (1973) found good agreement between (51) and the observed formation of fingers at diffusing interfaces, and experience with double-diffusive convection suggests that the lower the value of R_ρ the more active is the convection. Hence we dismiss the formation of a statically unstable density gradient as physically irrelevant both with and without cross-diffusion effects, since fingers will form instead and so modify the purely vertical diffusion process we have considered in arriving at (49) and (50).

So far in this section we have considered the cross-diffusion case with $D_{12} = 0$. We now outline the results when D_{12} is non-zero and $D_{21} = 0$. The ratio of the T- and S-gradients in the centre of the diffusing gradients is given by

$$\frac{\alpha T_z}{\beta S_z} = \tau^{\frac{1}{2}}\frac{\alpha\Delta T}{\beta\Delta S}-\frac{\alpha D_{12}}{\beta D_{11}}\frac{1-\tau^{\frac{1}{2}}}{1-\tau}, \tag{52}$$

and fingers can form if (from 39)

$$\frac{\alpha D_{12}}{\beta D_{11}} > \frac{1-\tau}{1-\tau^{\frac{3}{2}}}\left(1+\tau^{\frac{3}{2}}\frac{\alpha\Delta T}{\beta\Delta S}\right), \quad D_{21} = 0. \tag{53}$$

For small values of $\alpha\Delta T/\beta\Delta S$ the T-gradient can be reversed (i.e. $T_z > 0$, see (52)) and this facilitates the formation of fingers at such an interface. This result is quite surprising in that the gradients of both T and S are just the reverse of those required for normal finger convection, that is, they are in the sense normally associated with the 'diffusive' instability. So long as D_{12} is large enough to satisfy the inequality (53), we have demonstrated (mathematically) the possibility of fingers with $S_z < 0$ and T_z either positive or negative. The physical mechanism behind this fingering motion in apparently inhospitable property gradients is explained in §3 of this paper in connection with figure 4(*b*).

Owing to the unfortunate complexity of the unwieldy expressions for T_z and S_z in the case with two cross-diffusion terms we cannot come to any general quantitative conclusions regarding the formation of fingers at a diffusing interface in this situation. By manipulating the algebra a little for the case $\Delta S = 0$ we were able to show that positive values of D_{12} and D_{21} lead to $S_z > 0$ at $z = 0$, and this will assist in the formation of fingers at the interface with $T_z < 0$ (see (17)).

In the special cases where either D_{12} or D_{21} is zero, similar analyses to the above can be used to obtain the conditions under which fingers can occur at a diffusing interface when $\Delta T < 0$ and $\Delta S > 0$, that is, when the overall property differences between the layers is in the ostensibly diffusive stratification. For the sake of brevity we will not go into this case here.

5. Discussion and conclusions

Our initial interest in the influence of coupled diffusion on double-diffusive convection was sparked by the paper of Preston *et al.* (1980), where fingering motion was observed in solutions of macromolecules in which the distributions of the polymers were not obviously conducive to double-diffusive convection. In some of these experiments, fingers were observed to grow between an upper aqueous solution of dextran and a lower more concentrated aqueous solution of dextran to which sorbitol had been added. We suggest that the mechanism of formation of fingers in this situation may rely on the cross-diffusion fluxes of dextran and sorbitol in the presence of gradients of both properties. In the absence of any values for the cross-diffusion coefficients D_{12} and D_{21} in this case it is not possible to assert unequivocally that this process is the cause of the fingering and it is hoped that this work may serve as a catalyst to encourage the measurements of such coefficients.

The fluxes of properties across a normal double-diffusive interface are expected to vary as the one-third power of g, the gravitational acceleration. Stern (1975) (§11.4) derives this power law as a result of his collective instability process acting on fingers resulting from the fastest-growing linear instability. The same power law is usually derived by a variation of the scaling argument used for the Rayleigh–Bénard convection geometry that for high Rayleigh numbers the heat flux should be independent of the vertical length scale of the convecting region. Turner (1973, equation (8.3.2)) expresses this result in non-dimensional form. This dependence on g has never before been tested and some experiments performed in a centrifuge by Preston *et al.* (1980) have shown that the fluxes vary as $g^{0\cdot 2}$. It remains to be proven of course whether their experiments with macromolecules were double-diffusive in character, but it is encouraging to note that a rather small power ($\frac{1}{3}$) is also expected with double-diffusive convection.

As an alternative to finding the size of the cross-diffusion coefficients in the water–dextran–sorbitol system, we have endeavoured to find simpler substances (salts and small-molecular-weight organic compounds) that exhibit large cross-diffusion fluxes. Some aqueous solutions of salts at low temperatures come close to the condition $\beta D_{21}/\alpha D_{22} \approx 1$ (e.g. NaCl (Caldwell 1974), where D_{21}/D_{22} is actually the Soret coefficient multiplied by $S(1-S)$, where S is the concentration of the salt). In conducting experiments with NaCl at temperatures close to 0 °C we encountered two problems which could not easily be overcome. The heat conduction through the sidewalls of the experimental tank, though kept small with polystyrene sheeting, was large enough to cause mixing at the interface between the lower and upper fluid layers. The other problem was that when we saw fingers develop at the interface we could not determine whether they were caused by the cross-diffusion effect or by small amounts of evaporation of water from the upper layer causing its salinity to increase sufficiently (an increase of 3×10^{-4}‰ would suffice) to cause fingers in the normal manner. Cussler (1976) provides a list of references of measurements of all four ternary diffusion coefficients. On looking these up we found that one of the few substances to exhibit large cross-diffusion fluxes was another polymer, polystyrene, which had a molecular weight of 190000. Cussler & Lightfoot (1965) used the polystyrene–toluene–cyclohexane combination and found values of $D_{12}/D_{11} < -1$. They also give a simple argument which purports to explain the large cross-diffusion effect in terms of the chemical potential as a function of temperature for the two binary mixtures, polystyrene–toluene and polystyrene–cyclohexane.

In order to understand the mechanism of finger formation in situations such as those discussed by Preston *et al.* (1980) we suggest that the next logical step is to endeavour to measure the cross-diffusion fluxes for some of these long-chain polymers in the presence of each other.

In summary, we have concentrated in this paper on the formation of fingers due to cross-diffusion fluxes when the vertical distributions of the two solutes T and S are apparently unfavourable for double-diffusive convection. In particular we have considered the case where both T and S are stably stratified and have shown that fingers can form with sufficiently large and positive values of the cross-diffusion coefficients D_{12} and D_{21}. The finite-amplitude finger model and figures 3 and 4 show the physical mechanism involved in the maintenance of steady fingering motions in these apparently unfavourable mean vertical property gradients. We have also shown that the mutual diffusion of properties at a horizontal interface can cause property gradients that favour the formation of fingers.

Sincere thanks are due to Professor J. Stewart Turner who provided continual enthusiasm and advice. Enlightening conversations with Drs B. A. Pailthorpe, R. Mills and L. A. Woolf are also gratefully acknowledged.

REFERENCES

ANTORANZ, J. C. & VELARDE, M. G. 1979 Thermal diffusion and convective stability: The role of uniform rotation of the container. *Phys. Fluids* **22**, 1038–1043.

CALDWELL, D. R. 1974 Experimental studies on the onset of thermohaline convection. *J. Fluid Mech.* **64**, 347–367.

CUSSLER, E. L. 1976 *Multicomponent Diffusion*. Elsevier.

CUSSLER, E. L. & LIGHTFOOT, E. N. 1965 Multicomponent diffusion involving high polymers. I. Diffusion of monodisperse polystyrene in mixed solvents. *J. Phys. Chem.* **69**, 1135–1144.

FUJITA, H. & GOSTING, L. J. 1956 An exact solution of the equations of free diffusion in three-component systems with interacting flows, and its use in evaluation of the diffusion coefficients. *J. Chem. Soc. Am.* **78**, 1099–1107.

GIGLIO, M. & VENDRAMINI, A. 1977 Buoyancy-driven instability in a dilute solution of macromolecules. *Phys. Rev. Lett.* **39**, 1014–1017.

HUPPERT, H. E. & MANINS, P. C. 1973 Limiting conditions for salt-fingering at an interface. *Deep-Sea Res.* **20**, 315–323.

HURLE, D. T. J. & JAKEMAN, E. 1971 Soret-driven thermosolutal convection. *J. Fluid Mech.* **47**, 667–687.

LEAIST, D. G. & LYONS, P. A. 1980 Multicomponent diffusion in dilute solutions of mixed electrolytes. *Aust. J. Chem.* **33**, 1869–1887.

MILLER, D. G. 1960 Thermodynamics of irreversible processes. *Chem. Rev.* **60**, 15–36.

MILLER, L. 1966 Instabilities in multicomponent liquid diffusion. *J. South African Chem. Inst.* **19**, 125–129.

MILLER, L., SPURLING, T. H. & MASON, E. A. 1967 Instabilities in ternary diffusion. *Phys. Fluids* **10**, 1809–1813.

PIACSEK, S. A. & TOOMRE, J. 1980 Nonlinear evolution and structure of salt fingers. In *Marine Turbulence* (ed. J. C. J. Nihoul), pp. 193–219. Elsevier.

PRESTON, B. N., LAURENT, T. C., COMPER, W. D. & CHECKLEY, G. J. 1980 Rapid polymer transport in concentrated solutions through the formation of ordered structures. *Nature* **287**, 499–503.

SCHECHTER, R. S., PRIGOGINE, I. & HAMM, J. R. 1972 Thermal diffusion and convective stability. *Phys. Fluids* **15**, 379–386.

SCHMITT, R. W. & GEORGI, D. T. 1982 Fine structure and microstructure in the North Atlantic current. Submitted for publication.

STERN, M. E. 1975 *Ocean Circulation Physics.* Academic.

TURNER, J. S. 1973 *Buoyancy Effects in Fluids.* Cambridge University Press.

VELARDE, M. G. & SCHECHTER, R. S. 1972 Thermal diffusion and convective stability. II. An analysis of the convected fluxes. *Phys. Fluids* **15**, 1707–1714.

VITAGLIANO, V., SARTORIO, R. & COSTANTINO, L. 1974 Cation exchange diffusion experiments. *J. Phys. Chem.* **22**, 2292–2296.

VITAGLIANO, V., ZAGARI, A., SARTORIO, R. & CORCIONE, M. 1972 Dissipative structures and diffusion in ternary systems. *J. Phys. Chem.* **76**, 2050–2055.

WENDT, R. P. & SHAMIM, M. 1970 Isothermal diffusion in the system water–magnesium chloride–sodium chloride as studied with the rotating diaphram cell. *J. Phys. Chem.* **74**, 2770–2783.

WILLIAMS, A. J. 1981 The role of double-diffusion in a Gulf Stream frontal intrusion. *J. Geophys. Res.* **86**, 1917–1928.