in a triply diffusive fluid layer

By ARNE J. PEARLSTEIN, RODNEY M. HARRIS† AND GUILLERMO TERRONES

Department of Aerospace and Mechanical Engineering, University of Arizona, Tucson, AZ 85721, USA

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The onset of instability is investigated in a triply diffusive fluid layer in which the density depends on three stratifying agencies having different diffusivities. It is found that, in some cases, three critical values of the Rayleigh number are required to specify the linear stability criteria. As in the case of another problem requiring three Rayleigh numbers for the specification of linear stability criteria (the rotating doubly diffusive case studied by Pearlstein 1981), the cause is traceable to the existence of disconnected oscillatory neutral curves. The multivalued nature of the stability boundaries is considerably more interesting and complicated than in the previous case, however, owing to the existence of heart-shaped oscillatory neutral curves. An interesting consequence of the heart shape is the possibility of 'quasiperiodic bifurcation' to convection from the motionless state when the twin maxima of the heart-shaped oscillatory neutral curve lie below the minimum of the stationary neutral curve. In this case, there are two distinct disturbances, with (generally) incommensurable values of the frequency and wavenumber, that simultaneously become unstable at the same Rayleigh number. This work complements the earlier efforts of Griffiths (1979a), who found none of the interesting results obtained herein.

1. Introduction

If gradients of two stratifying agencies, such as heat and salt, having different diffusivities are simultaneously present in a fluid layer, a variety of interesting convective phenomena can occur which are not possible in a singly stratified or singly diffusive fluid. The case of two stratifying agencies has been the subject of extensive theoretical and experimental studies, which have been reviewed by Turner (1973, 1974, 1985), Schechter, Velarde & Platten (1974), Huppert & Turner (1981*a*), and Platten & Legros (1984).

It has been recognized previously (Griffiths 1979a-c; Turner 1985) that there are important fluid mechanical systems in which the density depends on three or more stratifying agencies having different diffusivities. Examples of what might be called multiply diffusive convection include the solidification of molten alloys, geothermally heated lakes, magmas and their laboratory models, and seawater.

In the first instance, there are many technologically important alloys that contain significant mass fractions of three or more metallic elements. Among these are a number of nickel-based superalloys (Giamei & Kear 1970) used in turbine blades and other high-strength applications. When ingots of these materials are grown by

† Present address: BDM International, Albuquerque, NM 87106, USA.

directional solidification employing cooling from below, the rejection of solutes at the growing interface leads to the development of concentration gradients. If the solutes have higher partial molar densities than the bulk melt, this configuration may be convectively unstable. Given that the planar interface is typically morphologically unstable (Coriell *et al.* 1987) at solidification rates of practical interest, convection may be important in both the interdendritic 'mushy zone' and in the overlying fluid, as discussed by Chen & Chen (1988) for the binary case. In this light, the potential importance of convection in determining macrosegregation in nickel-based super-alloys and other multicomponent alloy-systems is clear.

Another application stems from advances in instrumentation and data reduction techniques which have led to renewed interest among physical chemists in the measurement of multicomponent diffusion coefficients. This has in turn stimulated recent work on the onset of convective instability in isothermal ternary (i.e. three-component) fluids (McDougall 1983; Miller & Vitagliano 1986; Wells 1986), in which there are four independent diffusion coefficients (including cross-terms). Leaist & Noulty (1985) have suggested that the tools are now available for measurement of the nine diffusion coefficients eharacterizing a quaternary (four-component) fluid, for which the relevant theory was developed earlier by Kim (1966, 1969), and have now measured the nine independent quaternary diffusion coefficients in the system $H_2O-KCl-KH_2PO_4-H_3PO_4$ (Noulty & Leaist 1987). In this case, as well as in the case of a non-isothermal ternary fluid, there are three independently diffusing stratifying agencies. By analogy with the doubly diffusive ease in which the density depends on two independently diffusing stratifying agencies, we refer to the isothermal quaternary and non-isothermal ternary cases as being 'triply diffusive'.

Previous work on the stability of isothermal four-component fluids dates to the analytical work of Kim (1970). Kim developed necessary conditions for the existence at all times of a hydrostatically stable density gradient (i.e. density decreases monotonically upward) in a four-component fluid subject to various initial and boundary conditions. He also developed (different) sufficient conditions for hydrostatic stability. If we are to judge from the title and results of his paper, Kim was apparently unaware of the fact that even in the doubly diffusive case, a fluid layer with hydrostatically stable density stratification can be dynamically unstable. Griffiths (1979a), on the other hand, considered the properly formulated convective stability problem with off-diagonal transport coefficients (i.e. cross-term diffusion coefficients and, in the non-isothermal ternary case, the Dufour and Soret coefficients) equal to zero and performed a linear stability analysis. Since the present paper was submitted for publication, Moroz (1989) has, in the context of a nonlinear stability analysis, considered the linear stability problem originally treated by Griffiths. Related experimental work has also been reported by Griffiths (1979b, c) and Huppert & Turner (1981b) on convection in triply diffusive Newtonian fluids. Rudraiah & Vortmeyer (1982) and Poulikakos (1985) have reported calculations on the onset of convection in a triply duffusive fluid saturating a porous medium.

In this paper, we consider the problem previously studied by Griffiths (1979*a*) and Moroz (1989). Because our primary focus is on the elucidation of the basic linear instability mechanisms, we have restricted the analysis to the simple boundary conditions employed in the previous investigations. Our work differs from Griffiths' in that we show that his conclusion 'that marginal stability of oscillatory modes occurs on a hyperboloid in Rayleigh number space, but the surface is very closely approximated by its planar asymptotes for any diffusivity ratios' is incorrect for a number of diffusivity ratios, including those corresponding to the KCl-NaClsucrose- H_2O system studied by Griffiths. Our work also differs from both previous investigations in that we do not assume that the only critical wavenumber is that which corresponds to the linear onset of motion in singly and doubly diffusive fluids. This leads to a 'Hopf-Hopf' bifurcation and the possibility of the motionless basic state losing its stability through the onset of quasi-periodic motion. Thus, the triply diffusive case is capable of supporting several remarkable departures from what occurs in the singly and doubly diffusive cases. The results overlooked by Griffiths and Moroz are reminiscent of those found by Pearlstein (1981) for the onset of motion in a rotating doubly diffusive fluid layer; both cases illustrate the necessity of systematically investigating the topology of the neutral curves in hydrodynamic stability problems.

2. Linear stability analysis

2.1. Disturbance equations and dispersion relation

We begin with the linear perturbation equations (2.4) and boundary conditions of Griffiths (1979a) for a layer of thickness L and infinite horizontal extent bounded above and below by stress-free boundaries at which the concentrations and temperature are held fixed. We make the Boussinesq approximation and neglect the off-diagonal (Soret, Dufour, and cross-diffusion) contributions to the fluxes of the stratifying agencies. We then have

$$\left(\frac{1}{Pr}\frac{\partial}{\partial t} - \nabla^2\right)\nabla^2 \psi = \sum_{i=1}^3 \frac{\partial \theta_i}{\partial x}$$
(2.1)

$$\left(\frac{\partial}{\partial t} - \tau_i \nabla^2\right) \theta_i = R_i \frac{\partial \psi}{\partial x} \quad (i = 1, 2, 3),$$
(2.2)

where the θ_i are dimensionless concentration or temperature perturbations and ψ is a two-dimensional stream function. The boundary conditions considered by Griffiths are

$$\theta_i = \psi = \frac{\partial^2 \psi}{\partial z^2} = 0$$
 at $z = 0, 1$ $(i = 1, 2, 3).$

The restriction to a two-dimensional analysis is possible on account of the onedimensionality of the basic state and the horizontal isotropy of the problem.

Following Griffiths, we define $\tau_i = \kappa_i/\kappa_1$ (i = 1, 2, 3) as the diffusivity ratios, $Pr = \nu/\kappa_1$ as the Prandtl number, and the Rayleigh numbers $R_i = L^3 g \beta_i \Delta C_i/(\nu \kappa_1)$ for i = 1, 2, 3, where β_i relates the fluid density to the *i*th stratifying agency through the equation of state

$$\rho = \rho_m \bigg[1 + \sum_{i=1}^3 \beta_i C_i \bigg].$$

Here, ρ_m is the density at a reference state m and C_i denotes the departure of the concentration or temperature of the stratifying agency i from its value at state m. Finally, ν is the kinematic viscosity and ΔC_i is the total variation of stratifying agency i between the horizontal boundaries. By operating on (2.1) with

$$\mathbf{L}_{6} = \prod_{j=1}^{3} \left(\frac{\partial}{\partial t} - \boldsymbol{\tau}_{j} \nabla^{2} \right),$$

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and

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using (2.2), and letting $\psi = \exp(\sigma t + ik_x x) \sin n\pi z$, we obtain

$$\left\{ \left(\frac{\sigma}{Pr} + n^2 \pi^2 + k^2 \right) \prod_{j=1}^3 \left[\sigma + \tau_j (n^2 \pi^2 + k^2) \right] \right\} (-n^2 \pi^2 - k^2) \\ = -k^2 \sum_{\substack{i=1 \\ i=1}}^3 R_i \prod_{\substack{j=1 \\ i\neq i}}^3 \left[\sigma + \tau_j (n^2 \pi^2 + k^2) \right], \quad (2.3)$$

where k is the magnitude of the horizontal wavevector $\mathbf{k} = (k_x, 0)$ and n is the vertical wavenumber.

Observing that τ_1 is unity, letting $y_n = n^2 \pi^2 + k^2$, and setting $\sigma = 0 + i\omega$, we rearrange (2.3) to

$$\begin{split} R_{1} &= \frac{y_{n}^{3}Pr - \omega^{2}y_{n}}{k^{2}Pr} - R_{2}\frac{\tau_{2}y_{n}^{2} + \omega^{2}}{\tau_{2}^{2}y_{n}^{2} + \omega^{2}} - R_{3}\frac{\tau_{3}y_{n}^{2} + \omega^{2}}{\tau_{3}^{2}y_{n}^{2} + \omega^{2}} \\ &+ \mathrm{i}\omega y_{n} \bigg[\frac{y_{n}(Pr+1)}{k^{2}Pr} - R_{2}\frac{\tau_{2} - 1}{\tau_{2}^{2}y_{n}^{2} + \omega^{2}} - R_{3}\frac{\tau_{3} - 1}{\tau_{3}^{2}y_{n}^{2} + \omega^{2}} \bigg], \quad (2.4) \end{split}$$
 can be written as

which

$$R_1 = f_1(k, \omega, Pr, \tau_2, \tau_3, R_2, R_3, n) + i\omega y_n f_2(k, \omega, Pr, \tau_2, \tau_3, R_2, R_3, n)$$

where ω is the frequency and f_1 and f_2 are real-valued functions of the indicated arguments. Equation (2.4) is used to find the critical value(s) of R_1 , which must be real, by requiring either $\omega = 0$ or $f_2 = 0$.

The $\omega = 0$ case corresponds to steady onset with one temporal eigenvalue crossing the imaginary axis at $\sigma = 0$. Thus,

$$R_1^{\rm s} = \frac{y_n^{\rm s}}{k^2} - \frac{R_2}{\tau_2} - \frac{R_3}{\tau_3} \tag{2.5}$$

is the Rayleigh number above which the layer is unstable with respect to steady onset. To find the critical wavenumber corresponding to R_1^s , we equate to zero the derivative of (2.5) with respect to k, and find $k = n\pi/\sqrt{2}$. Thus, the critical Rayleigh number for steady onset is

$$R_1^{\rm s,crit} = \frac{27\pi^4}{4} - \frac{R_2}{\tau_2} - \frac{R_3}{\tau_3},\tag{2.6}$$

where it is clearly necessary to consider only n = 1.

For oscillatory onset ω is non-zero, which requires $f_2 = 0$ in (2.4), giving

$$y_n \frac{Pr+1}{k^2 Pr} - R_2 \frac{\tau_2 - 1}{\tau_2^2 y_n^2 + \omega^2} - R_3 \frac{\tau_3 - 1}{\tau_3^2 y_n^2 + \omega^2} = 0.$$

This can be rewritten as a dispersion relation which is quadratic in ω^2 :

$$\begin{split} \omega^4 y_n(Pr+1) + \omega^2 \left\{ y_n^3(Pr+1)(\tau_2^2 + \tau_3^2) + k^2 Pr\left[R_2(1-\tau_2) + R_3(1-\tau_3)\right] \right\} \\ + y_n^2 \left\{ y_n^3(Pr+1) \tau_2^2 \tau_3^2 + k^2 Pr\left[R_2(1-\tau_2) \tau_3^2 + R_3(1-\tau_3) \tau_2^2\right] \right\} = 0 \\ \text{abolically as} \qquad \alpha(k^2) \, \omega^4 + \beta(k^2) \, \omega^2 + \gamma(k^2) = 0. \end{split}$$
(2.7)

or sym

2.2. Topology of the neutral curves

Equation (2.7) implies that if $\beta(k^2) < 0$ and $\gamma(k^2) > 0$ for some wavenumber, then there may exist two real positive values of ω^2 , corresponding to two different onset frequencies for that value of k. To each such frequency there corresponds a Rayleigh

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number R_1^0 on the oscillatory neutral curve. The necessary conditions for the existence of two frequencies are then

$$0 < R_3(1 - \tau_3)(\tau_2 - \tau_3) \tag{2.8a}$$

$$0 < R_2(1 - \tau_2)(\tau_3 - \tau_2), \tag{2.8b}$$

which are found from the conditions $\beta(k^2) < 0$ and $\gamma(k^2) > 0$.

We note that for fixed τ_2 and τ_3 satisfying $(1-\tau_2)(1-\tau_3)(\tau_2-\tau_3) \neq 0$, (2.8a, b) will be satisfied in exactly one quadrant of the (R_2, R_3) -plane. The condition that the diffusivities be distinct from unity and each other simply requires that the fluid be really triply diffusive. Moreover, we note from (2.8a, b) that for $R_2 < 0$ and $R_3 < 0$, we cannot have two onset frequencies at the same k. That is, at least one of these stratifying agencies must be stabilizing.

To find the extremal value(s) or R_1^0 , we begin by setting $\sigma = i\omega$ and rewriting the real and imaginary parts of (2.3) as

$$\omega^4 y_n - \omega^2 [y_n^3 f_1 - k^2 Pr(R_1^0 + f_2)] + y_n^2 Pr[y_n^3 f_3 - k^2 (R_1^0 f_3 + f_4)] = 0 \qquad (2.9a)$$

$$-\omega^3 y_n^2 f_5 + \omega y_n \left[y_n^3 f_6 - k^2 \Pr(R_1^0 f_7 + f_8) \right] = 0, \qquad (2.9b)$$

where y_n has been defined and

$$\begin{split} f_1 &= \tau_2 \tau_3 + (Pr+1)(\tau_2 + \tau_3) + Pr, \quad f_2 = R_2 + R_3, \quad f_3 = \tau_2 \tau_3, \quad f_4 = R_2 \tau_3 + R_3 \tau_2, \\ f_5 &= Pr + 1 + \tau_2 + \tau_3, \quad f_6 = \tau_2 \tau_3 (Pr+1) + Pr(\tau_2 + \tau_3), \quad f_7 = \tau_2 + \tau_3, \\ f_8 &= R_2 (1 + \tau_3) + R_3 (1 + \tau_2). \end{split}$$

On the oscillatory neutral curve, ω vanishes only at the bifurcation points, so elsewhere (2.9b) can be divided by ω to yield

$$\omega^2 = \frac{y_n^3 f_6 - k^2 Pr(R_1^0 f_7 + f_8)}{f_5 y_n}.$$
(2.10)

Substituting (2.10) into (2.9a), we obtain

$$\frac{y_n^6}{k^4}f_9 + \frac{y_n^3}{k^2}Pr(f_{10}R_1^0 + f_{11}) + Pr^2(R_1^0f_7 + f_8)(R_1^0f_{12} + f_{13}) = 0, \qquad (2.11)$$

where

and

and

$$\begin{split} f_9 &= f_6^2 - f_1 f_5 f_6 + Pr f_3 f_5^2, \quad f_{10} &= -2 f_6 f_7 + f_5 f_6 + f_1 f_5 f_7 - f_3 f_5^2, \\ f_{11} &= -2 f_6 f_8 + f_2 f_5 f_6 + f_1 f_5 f_8 - f_4 f_5^2, \quad f_{12} &= f_7 - f_5, \quad f_{13} &= f_8 - f_2 f_5. \end{split}$$

Equation (2.11), which is satisfied on the oscillatory neutral curve, can be written as $F_1(k, R_1^0) = 0$, so that at the extremal values of R_1^0 , we have $\partial F_1/\partial k = F_1 = 0$, which gives

$$\frac{2y_n^2(3k^2-y_n)}{k^5}[2f_9y_n^3+k^2Pr(f_{10}R_1^0+f_{11})]=0.$$

Thus, the extremal values of R_1^0 occur at either

$$3k^2 - y_n = 0 \tag{2.12a}$$

$$2f_9 y_n^3 + k^2 Pr(f_{10} R_1^0 + f_{11}) = 0. (2.12b)$$

or

For the first case, (2.12*a*) yields $y_n^3/k^2 = 27n^4 \pi^4/4$, which is substituted into (2.11) to obtain

$$Pr^{2}f_{7}f_{12}(R_{1}^{0})^{2} + \left[Pr^{2}(f_{7}f_{13} + f_{8}f_{12}) + \frac{27n^{4}\pi^{4}}{4}Prf_{10}\right]R_{1}^{0} + \frac{729n^{8}\pi^{8}}{16}f_{9} + \frac{27n^{4}\pi^{4}}{4}Prf_{11} + Pr^{2}f_{8}f_{13} = 0. \quad (2.13)$$

For fixed values of τ_2 , τ_3 , R_2 , R_3 , and Pr, (2.13) is a quadratic in R_1^0 which has zero, one, or two real solutions. For each solution, the sign of ω^2 in (2.10) must be checked to see whether the frequency is real. Thus, there may be zero, one, or two physically meaningful extremal values of R_1^0 on the oscillatory neutral curve for $k = n\pi/\sqrt{2}$ (corresponding to $3k^2 - y_n = 0$).

In the other case, rearrangement of (2.12b) followed by substitution into (2.11) yields

$$(R_1^{\rm o})^2 (4f_7f_9f_{12} - f_{10}^2) + R_1^{\rm o}[4f_9(f_7f_{13} + f_8f_{12}) - 2f_{10}f_{11}] + 4f_8f_9f_{13} - f_{11}^2 = 0.$$
(2.14)

Equation (2.14) may have zero, one, or two physically meaningful ($\omega^2 \ge 0$) extremal solutions at wavenumbers other than $k = n\pi/\sqrt{2}$. By defining

$$f_{14} = -\Pr(f_{10}R_1^0 + f_{11})/(2f_9),$$

we can rewrite (2.12b) as

$$(n^2 \pi^2 + k^2)^3 - k^2 f_{14} = 0. (2.15)$$

It can be shown that (2.15) must have zero or two positive roots. Thus, for each physically meaningful value of R_1° satisfying (2.12b), there are two extrema on the oscillatory neutral curve with $k \neq n\pi/\sqrt{2}$. If there are two extrema ($k \neq n\pi/\sqrt{2}$) at one R_1° and two extrema at $k = n\pi/\sqrt{2}$, then it can be shown that the oscillatory neutral curve is heart-shaped (figure 1). This result differs from the other known case in which two frequencies and Rayleigh numbers exist on the neutral curve for the same wavenumber (Pearlstein 1981), in which case the closed oscillatory neutral curve was found to have a single minimum and a single maximum.

Three types of neutral curves in the (R_1, k) -plane can exist:

(i) a stationary neutral curve with no oscillatory neutral curve,

(ii) a stationary neutral curve accompanied by an oscillatory neutral curve to which it is connected at one or two bifurcation points, and

(iii) a stationary neutral curve accompanied by a closed oscillatory neutral curve having no bifurcation points.

In this context, a bifurcation point on the stationary neutral curve is one at which the oscillatory neutral curve intersects the stationary neutral curve and the frequency on the oscillatory neutral curve approaches zero as the intersection is approached. These points are to be distinguished from those in the (R_1, k) -plane at which the stationary and oscillatory neutral curves intersect but at which the frequency on the oscillatory curve does not approach zero at the intersection (see §3). The latter points merely correspond to coincidental crossings of the stationary and oscillatory neutral curves, as discussed earlier (Pearlstein 1981).

As in the rotating doubly diffusive problem, the closed oscillatory neutral curves were found by a non-iterative method, the key feature of which is its ability to analytically decide the existence question for these closed curves without actually searching for them in the (R_1, k) -plane. This is accomplished by first locating any bifurcation points and points of infinite slope on the oscillatory neutral curve. The existence of bifurcation points is decided by setting $\omega = 0$ in (2.7) and considering the



FIGURE 1. Topology of a heart-shaped oscillatory neutral curve.

equation $\gamma(k^2) = 0$. It is easily shown that there are either zero or two distinct positive values of k^2 that satisfy this equation, corresponding to either zero or two bifurcation points.

Points of infinite slope occur at those wavenumbers where the number of branches on the oscillatory neutral curve changes from zero to two and vice versa. At these points, the number of allowable frequencies changes from zero to two; thus we compute the wavenumbers at the points of infinite slope by solving $\beta^2(k^2) - 4\alpha(k^2)\gamma(k^2) = 0$ from (2.7). Although this equation can be satisfied for zero, two, or four positive values of k^2 , it can be shown that $\beta(k^2)$ is negative (and hence $\omega^2 > 0$) at no more than two values of k^2 at which the discriminant of (2.7) vanishes.

If there are no bifurcation points and no points of infinite slope, then no oscillatory neutral curve exists, because such a curve must be either connected to the stationary neutral curve (at the bifurcation points) or closed (and have two points of infinite slope).

If there are two bifurcation points and no points of infinite slope, then the neutral curves have the topology shown in figure 2(a). The oscillatory neutral curve is a single-valued function of k and exists only between the wavenumbers k_{b1} and k_{b2} of the two bifurcation points.

In the event that there are two bifurcation points and two points of infinite slope, the neutral curves have the topology shown in figure 2(b). The oscillatory neutral curve exists between the wavenumbers k_{s1} and k_{s2} at which its slope is infinite; it is double-valued between k_{s1} and k_{b1} and between k_{b2} and k_{s2} , and single-valued between k_{b1} and k_{b2} .

If there are two points of infinite slope and no bifurcation points, the neutral curves will have the topology shown in figures 2(c) or 2(d). The oscillatory neutral curve is now closed and may be connected to (figure 2c) or disconnected from (figures 1 and 2d) the stationary neutral curve.



FIGURE 2. One route to disconnectedness. (a) Oscillatory neutral curve connected to stationary neutral curve at two bifurcation points; one frequency per wavenumber. (b) Same as (a), except that oscillatory neutral curve has two frequencies at some wavenumbers. (c) Oscillatory neutral curve is closed (two frequencies at each wavenumber) but is still connected to stationary neutral curve. (d) Oscillatory neutral curve is closed and disconnected from the stationary neutral curve.

2.3. Topology of the stability boundaries

It follows from the topology of the disconnected neutral curves, as shown in figures 1 and 2(d), that there exist combinations of R_2 , R_3 , Pr, τ_2 and τ_3 for which three values of R_1 are required in order to specify linear stability criteria. Clearly, one has stability for $R_1 < R_{1,1}$ and for $R_{1,2} < R_1 < R_{1,3}$, and instability otherwise. Thus, the stability boundary in the (R_1, R_2) - or (R_1, R_3) -plane (with all other parameters held fixed) may be a multivalued function of R_2 or R_3 , as observed earlier (Pearlstein

1981). In what follows, we shall discuss the case where R_3 , Pr, τ_2 , and τ_3 are held fixed, and the stability boundary in the (R_1, R_2) -plane is computed.

In all of the results that follow, the vertical wavenumber n is set to 1 for the oscillatory neutral curves. Although the validity of this assumption has not been established conclusively for the triply diffusive case, it has been proved that consideration of n = 1 is sufficient for the Rayleigh-Bénard problem (Chandrasekhar 1961), the rotating Rayleigh-Bénard problem (Chandrasekhar 1961), and the doubly diffusive case (Baines & Gill 1969). Also, for the rotating doubly diffusive case (Pearlstein 1981), exhaustive numerical work proved that n = 1 was the only relevant case for all parameter values examined.

For each R_2 , we use (2.6) to compute $R_1^{\text{s.crit}}$ for the onset of steady convection. We then establish whether oscillatory instability can occur at a lower value of R_1 . To do this, we determine the existence of any bifurcation points (k_{b1}, k_{b2}) or points of infinite slope (k_{s1}, k_{s2}) in the (R_1, k) -plane and, as appropriate, compute the real solution(s) R_1^0 , if any, of (2.13) and (2.14). For each such real solution lying below $R_1^{\text{s.crit}}$, we compute ω^2 from (2.10), using $k = \pi/\sqrt{2}$ for the solution(s) of (2.13), and the solutions of (2.15) for k (with n = 1) for the values of R_1^0 satisfying (2.14). It is clear from (2.15) and the discussion subsequent thereto that $f_{14} > 27\pi^4/4$ is a necessary condition for the existence of meaningful (k > 0) solutions of (2.14). Then, according to the number of real values of R_1^0 to which there correspond a real frequency and a real wavenumber, we may have one or three critical values of R_1 for each R_2 . Stability boundaries in the (R_1, R_3) -plane are obtained in a similar manner.

3. Results

Certain triply diffusive systems exhibit behaviour qualitatively different from that seen in singly or doubly diffusive cases. One example, discussed later in this section, is that of a triply diffusive layer for which three critical Rayleigh numbers are required to specify linear stability criteria. For other parameter values, not only are three critical Rayleigh numbers required to specify the linear stability criteria, but also the oscillatory neutral curve is heart-shaped. These two results have important consequences and will be discussed in this section.

In previous work on the triply diffusive problem, Griffiths (1979a) described stability boundaries which require a single critical value of R_1 to determine linear stability or instability when the transport property ratios and R_2 and R_3 are fixed. He overlooked the case for which three critical values of R_1 are needed, as well as the existence and implications of closed, disconnected, and heart-shaped oscillatory neutral curves. The stability boundaries we discuss below are clearly not parts of a surface in Rayleigh number space which 'is very closely approximated by its planar asymptotes'.

The case where the fluid layer's transport property ratios are set at Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$ leads to some interesting results. Figure 3(a) shows the stability boundary R_1^{crit} as a function of R_2 for fixed $R_3 = 814.1119$. This boundary can be examined separately in three regions of R_2 . To the left of the cusp (A) lies a range of (simple) oscillatory onset, which, for these values of Pr, τ_2 , τ_3 , and R_3 , occurs for $R_2 < -944.55$. Here, oscillatory instability sets in at a lower value of R_1 than does stationary instability, and there is a single critical value of R_1 . To the right of the point of infinite slope (B), for $R_2 > -943.15$, is a region in which the onset of motion is predicted to occur via monotonically growing disturbances and there is a single



FIGURE 3. (a) (R_1, R_2) -stability boundary for $R_3 = 814.1119$, with Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$. (b) Expanded view of the multivalued region.

critical value of R_1 . The intervening region is the most interesting and is shown enlarged in figure 3(b). It is seen that the single-valued stationary ($R_2 > -943.15$) and oscillatory ($R_2 < -944.55$) portions of the stability boundary do not merely intersect, but instead give rise to a multivalued ($R_1^{\rm crit}, R_2$)-curve. For $-944.55 < R_2$ < -943.15, three critical values of R_1 are needed to specify the linear stability criteria. Thus, in this range of R_2 , as R_1 passes from below through the lower (oscillatory) branch of the stability boundary, the layer becomes unstable, regains its stability (on a linear basis) upon crossing the middle (oscillatory) branch, and finally becomes unstable again above the uppermost (steady onset) branch of the stability boundary.

Moreover, the stability boundary in figure 3(a) is qualitatively different from the multivalued (R_1^{crit}, R_2) -stability boundaries found in the rotating doubly diffusive problem (Pearlstein 1981) in that in the latter case, multivalued stability boundaries correspond to either three values of R_1^{crit} for a given R_2 or three values of R_2 for a given R_1 . In no case examined were both Rayleigh numbers found to be multivalued functions of the other. In the triply diffusive case, however, each of R_1 and R_2 can be a multivalued function of the other, for R_3 , Pr, τ_2 , and τ_3 fixed. This is of interest from the standpoint of a laboratory experiment and will be discussed in §4.

Figure 4(a) shows the (R_1, R_3) -stability boundary for $R_2 = -943$ and the same values of Pr, τ_2 , and τ_3 . Figure 4(b), which enlarges the multivalued portion of figure 4(a), clearly shows that three critical values of R_1 are needed to specify the linear stability criteria in a finite range of R_3 .

Figure 5(a-i) shows the evolution of neutral stability curves for the same transport property ratios (Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$). Here, R_3 has been fixed at 814.1119 and R_2 is varied. Figure 5(a-c) shows that the oscillatory neutral curve is connected to the stationary neutral curve at two bifurcation points which move closer together as R_2 is increased, as in the doubly diffusive case with (Pearlstein 1981) and without (Baines & Gill 1969) rotation. In figure 5(c), the oscillatory neutral curve loses its single-valued character, which has no physical significance because the



FIGURE 4. (a) (R_1, R_3) -stability boundary for $R_2 = -943$, with Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$. (b) Expanded view of the multivalued region.

single critical R_1 remains at the minimum of the oscillatory neutral curve. At a value of R_2 between those shown in figures 5(c) and 5(d), the bifurcation points move together and coalesce, resulting in the formation of a closed, heart-shaped oscillatory neutral curve which has become disconnected from the stationary curve.

In figures 5(e) and 5(f), the twin maxima $(R_1^o vs. k)$ of the closed, heart-shaped, disconnected, oscillatory neutral curve move below the minimum of the stationary neutral curve. The significance of the heart-shaped neutral curve in figure 5(f) is twofold. First, as in the rotating doubly diffusive case (Pearlstein 1981), three critical values of R_1 are needed to specify the stability criteria. Second, as R_1 decreases below the minimum on the stationary neutral curve and approaches the twin maxima on the oscillatory neutral curve, the onset of oscillatory instability occurs at two different wavenumbers and, as discussed later, at two different frequencies, at the same value of R_1 . As R_2 is changed in figure 5(f-h), the closed oscillatory neutral curve loses its heart shape and becomes a closed convex curve. Three critical values of R_1 are still required, however. At a value of R_2 between those shown in figures 5(h)and 5(i), the closed oscillatory neutral curve collapses to a point and subsequently disappears, leaving only the stationary neutral curve. It is easily shown that the collapse occurs at $k = \pi/\sqrt{2}$.

Figure 6 is a schematic description of how the critical values of R_1 and k change as R_2 is varied, with the values of Pr, τ_2 , τ_3 , and R_3 corresponding to those employed in figure 5(a-i). The lower curve AB shows the lowest point on the oscillatory neutral curve, which, in this range of R_2 , is still connected to the stationary neutral curve at the two bifurcation points. Points E, G, and F correspond to the value of R_2 at which the twin maxima of the heart-shaped oscillatory neutral curve and the minimum of the stationary neutral curve occur at the same value of R_1 . The curves ED and FD correspond to the maxima of the heart-shaped oscillatory neutral curve which approach each other and coalesce at D, yielding a closed convex oscillatory neutral curve. At C, the oscillatory neutral curve collapses to a point and, as R_2 is increased, ceases to exist. The ray beginning at G and passing through H corresponds









FIGURE 6. Schematic description of the relation between R_1^{crit} , R_2 , and k_{crit} for $R_3 = 814.1119$, Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$.



FIGURE 7. Onset frequencies for a range of R_2 , with $R_3 = 814.1119$, Pr = 10.2, $\tau_2 = 0.22$, and $\tau_3 = 0.21$.

to the minimum of the stationary neutral curve on the semi-infinite range of R_2 for which steady onset can occur. Figure 5(f) shows the cross-section in the plane P for $R_2 = -944.3$, $R_3 = 814.1119$, Pr = 10.2, $\tau_2 = 0.22$, $\tau_3 = 0.21$.

For the same values of R_3 , Pr, τ_2 , and τ_3 , figure 7 shows the onset frequency in the range of R_2 in which three critical values of R_1 are required to specify the linear stability critera. Point B corresponds to the onset frequency at the R_2 at which the disconnected oscillatory neutral curve collapses to a point. The branch BE is the onset frequency at the maximum of the closed, convex oscillatory neutral curve found in this region of R_2 . At E, the closed, convex oscillatory neutral curve flattens





FIGURE 9. (R_1, R_2) -stability boundary for $R_3 = 80$, with Pr = 625, $\tau_2 = 0.8125$, $\tau_3 = 0.28125$.

out at the top and then becomes heart-shaped as R_2 is decreased. The curves EC and ED correspond to the different onset frequencies at the twin maxima of the heart-shaped neutral curve. The points C and D occur at the R_2 for which the twin maxima of the heart-shaped neutral curve move above the minimum of the stationary neutral curve, beyond which point there is only one critical value of R_1 and only one onset frequency, both corresponding to the minimum of the oscillatory neutral curve. This is the branch BA.

Another interesting case occurs when the transport property ratios are set at $Pr = 2, \tau_2 = 2$, and $\tau_3 = 0.666666$, with $R_2 = 7874$. Figure 8(a, b) shows the oscillatory neutral curve, at each wavenumber lying below the stationary neutral curve, to which it is attached at two bifurcation points which move toward each other as R_{a} increases. When R_3 is increased further (figure 8c), the two bifurcation points coalesce and part of the closed oscillatory neutral curve lies above the stationary neutral curve. In figure 8(c), the upper branch of the oscillatory neutral curve closely follows the stationary neutral curve and remains largely above it, as shown on an expanded scale in figure 8(d). As R_3 is increased (figure 8e), the oscillatory neutral curve loses its heart shape and becomes a closed convex curve; part of it remains above the stationary neutral curve. Figure 8(c-e) shows that one may have a closed oscillatory neutral curve that is not disconnected from the stationary neutral curve. The points at which the oscillatory and stationary neutral curves intersect are not bifurcation points, as the frequency on the closed oscillatory neutral curve vanishes nowhere. In figure 8(f), the oscillatory curve moves below the minimum of the stationary curve so that three critical values of R_1 are now needed to specify the linear stability criteria. If R_3 is increased further, the oscillatory neutral curve eventually collapses to a point and disappears.

The values of the transport property ratios and Rayleigh numbers discussed so far were chosen so as to allow for a clear graphical presentation of the results. Heartshaped neutral curves lying below the minimum of the steady neutral curve can also be obtained for the values of Pr, τ_2 , and τ_3 appropriate to the isothermal KCl-NaCl-sucrose-H₂O system studied theoretically and experimentally by Griffiths



(1979a-c). Figure 9 shows an (R_1, R_2) -stability boundary for Pr = 625 (corresponding to the Schmidt number for NaCl in H_2O), $\tau_2 = 0.8125$, and $\tau_3 = 0.28125$, for $R_3 = 80$. In the range of R_2 for which the stability boundary is not a single-valued function of R_2 , the oscillatory neutral curve is disconnected from the steady neutral curve, as shown in figure 10(a). Over a smaller part of that range, the oscillatory neutral curve is heart-shaped and lies entirely below R_1^{crit} , as shown in figure 10(b, c).

4. Discussion

The present analysis reveals a number of striking features not found in the doubly diffusive case or in the previous work on the triply diffusive problem. These include:

(i) the existence of a finite range of linearly stable R_1 , in addition to the usual semiinfinite range;

(ii) the onset of oscillatory instability at a given value of R_1 for two different values of the critical wavenumber and two different onset frequencies; and

(iii) the existence of stability boundaries in the (R_1, R_3) (or R_1, R_2)-plane that are multivalued functions of both R_1 and R_3 (or R_1 and R_2).

Result (i) was previously obtained for a rotating doubly diffusive fluid layer (Pearlstein 1981) and is associated with the fact that both the triply diffusive layer and the rotating doubly diffusive layer can each support two 'overstable' instability mechanisms (and, hence, two non-zero frequencies at the same wavenumber when one examines the neutral stability curve).

Result (ii) requires the existence of a heart-shaped oscillatory neutral curve (not seen in the rotating doubly diffusive case) and is of special interest because it offers the possibility of observing fairly complicated dynamics at the onset of instability. Referring to figure 1, (or figure 5(f), we consider an experiment in which R_1 is reduced from a (linearly) stable value between $R_{1,2}$ and $R_{1,3}$ to an unstable value lying between $R_{1,1}$ and $R_{1,2}$. If the onset of instability at $R_{1,2}$ occurs via the growth of infinitesimally small disturbances, then two distinct disturbances with different frequencies and wavenumbers simultaneously become unstable. Thus, in contrast to the usual Hopf bifurcation in which a pair of complex-conjugate eigenvalues cross the imaginary axis into the right half-plane, we shall in this case have two pairs of eigenvalues crossing. As shown in figure 7, the two frequencies (each corresponding to the absolute value of the imaginary parts of a set of complex-conjugate eigenvalues) are unequal along branches EC and ED, and are in general incommensurable. By analogy to the nomenclature of Moroz (1989), we shall refer to this as a 'Hopf-Hopf' bifurcation.

This raises the possibility of bifurcating solutions that are quasi-periodic in time and space at the onset of motion. Previous studies in which two distinct pairs of complex-conjugate eigenvalues simultaneously cross the imaginary axis and lead to 'quasi-periodic bifurcation' directly from a steady solution include systems of firstorder nonlinear ordinary differential equations (Bauer, Keller & Reiss 1975; Cohen 1977; Steen & Davis 1982) and a model problem for the Navier–Stokes equations (Iooss 1976). Quasi-periodic bifurcation can also occur in a rotating conducting fluid layer subjected to a vertical magnetic field (A. J. Pearlstein & F. H. Busse, unpublished). In the language of Bauer *et al.*, the value of R_1 at the twin maxima is a multiple primary bifurcation point and is so called because at this R_1 the (motionless) base state bifurcates into two primary states and thus has a multiplicity (as a bifurcation point) of two. The dynamical behaviour possible in the triply diffusive problem is potentially richer than that inherent in the previous cases of quasi-periodic bifurcation in several respects. The most remarkable is that the two pairs of temporal eigenvalues that cross the imaginary axis in the present case are associated with two different (and generally incommensurable) horizontal wavenumbers. Thus the (temporally) quasi-periodic bifurcation may also be quasi-periodic in space. Moreover, as discussed in §2.2, when the oscillatory neutral curve has twin maxima, they always occur at the same value of the bifurcation parameter R_1 (which of course depends on the control parameters, R_2 , R_3 , τ_2 , τ_3 , and Pr). Thus, if 'quasi-periodic onset' does occur, it will still be a codimension-one bifurcation and will occur over a range of the control parameters. In the previous cases, the simultaneous crossing of the imaginary axis by four eigenvalues occurred via the tunable coalescence of two primary bifurcation points of multiplicity one. Thus the multiple primary bifurcation point occurred at a codimension-two point and could be realized only by proper choice of two control parameters.

If one is interested in looking at bifurcation in the triply diffusive case under 'resonance' conditions on either the frequencies or wavenumbers, this should be achievable by proper tuning of two control parameters. That is, it should be possible to adjust either the two wavenumbers or the two frequencies so that they are commensurable. By proper tuning of three control parameters, it should be possible to make both the frequencies and wavenumbers commensurable.

Result (iii) implies that the onset of convection may occur on a path in the (R_1, R_3) (or R_1, R_2)-plane with R_2 (or R_3) fixed, along which the constant gradients of both of the other stratifying agencies are simultaneously changed in such a way that they are individually made *more* hydrostatically stable. Like results (i) and (ii), this cannot occur in the doubly diffusive case and was not observed in the previous work on the triply diffusive problem.

4.1. Experimental considerations

In this section, we consider some of the factors that will determine the physical realizability of the predictions of the foregoing linear stability analysis. We begin by discussing the parameter space in which experiments might need to be conducted.

We first note that $\tau_1 = 1$ and τ_2 and τ_3 are positive, so that only a single (τ_2, τ_3) quarterplane in the positive octant of the (τ_1, τ_2, τ_3) -space need be considered. From (2.3), the entire problem is seen to be invarant under any permutation of the indices, so that results in one half (say, $\tau_2 > \tau_3$) of this quarterplane are obtainable from results in the other half (say, $\tau_2 < \tau_3$).

From (2.8a, b), we see that if stratifying agency 3 is the most rapidly diffusing $[\tau_3 > \max(\tau_2, \tau_1 = 1)]$, then two frequencies (and a closed disconnected neutral curve in the (R_1, k) -plane can exist only if R_3 is positive (i.e., agency 3 is destabilizing). Similarly, we require $R_3 > 0$ if agency 3 is the slowest diffusing. By like reasoning, we must have $R_2 > 0$ if species 2 is the fastest or slowest diffusing. Finally, if agency 2 (or 3) has an intermediate diffusivity (between those of the other two agencies), then we must have $R_2 < 0$ (or $R_3 < 0$). In any case, we observe (from §2.2) that for any triply diffusive fluid, the necessary conditions for the existence of a closed and disconnected neutral curve are satisfied in exactly one of the first, second, or fourth quadrants of the (R_2, R_3) -plane. Of course, these are only necessary conditions for the existence the existence of closed, disconnected neutral curves (see, e.g. figures 5c and 8a-e).

This discussion and the numerical results (cf. figures 3 and 4 for $\tau_2 = 0.22$,

 $\tau_3 = 0.21$, and figure 8 for $\tau_2 = 2$, $\tau_3 = 0.66666$) are consistent with the hypothesis that a necessary condition for the existence of two frequencies at the same wavenumber (i.e. a necessary condition for a disconnected neutral curve) is as follows. When the stratifying agencies are ordered by decreasing diffusivity (with $\tau_1 \equiv 1$), then the Rayleigh numbers, when arranged with their indices in the same order as the indices of the diffusivities, must alternate in sign, with the fastest diffusing agency being destabilizing. Thus, for example, with $\tau_2 = 0.22$ and $\tau_3 = 0.21$, we get $R_1 > 0$, $R_2 < 0$, and $R_3 > 0$. The alternating Rayleigh number hypothesis and its natural extension to an N-tuply diffusive fluid are entirely consistent with the analytical and numerical results for a quintuply diffusive fluid layer (Terrones 1987), in which one may obtain two disconnected oscillatory neutral curves (corresponding to four frequencies at the same wavenumber).

From these considerations and the numerical results, it appears that multivaluedness puts no restrictions on the values of τ_2 and τ_3 , other than that they be unequal and different from unity. This is to be contrasted with the rotating doubly diffusive case (Pearlstein 1981), for which it was shown (from conditions analogous to (2.8*a*, *b*)) that multivaluedness could occur only for Pr < 1 < Sc or Sc < 1 < Pr. (Here, we discuss the rotating doubly diffusive case in terms of a fluid in which the two stratifying agencies are heat and a solute, and Sc is the Schmidt number of the latter.) This restriction had the effect of limiting the search for multivalued stability boundaries to binary liquid metals. In the triply diffusive case, no such limitation occurs, and multivaluedness can be found for Pr > 1 with $Sc_2 > 1$ and $Sc_3 > 1$, where $Sc_i = Pr/\tau_i$ (see figures 3-5).

Given a fluid layer with values of Pr, τ_2 , and τ_3 appropriate for the existence of a multivalued stability boundary in some part of the (R_1, R_2, R_3) -space, we shall now discuss the other factors that determine the experimental realizability of the multivaluedness, as well as the quasi-periodic bifurcation from the motionless state discussed in §4.

One of the factors to be considered is the assumption of stress-free boundaries at the top and bottom of the layer. From previous comparisons of the linear stability theory for convective stability problems with stress-free and rigid boundaries, we expect that the qualitative features predicted for the stress-free case should carry over to the more realistic rigid case. Thus, we would expect that the existence of multivalued stability boundaries will be a feature of the linear analysis for rigid boundaries. As for the quasi-periodic onset, this is a characteristic associated with the heart shape of the disconnected oscillatory neutral curves. Although we expect the heart shape to persist, there is no assurance that the twin maxima (at $R_1 = R_{1,2}$) in the schematic figure 1; see also figure 5(f) will occur at the same value of R_1 in the rigid case. This question is the subject of a separate investigation (A. J. Pearlstein, A. R. Lopez, and L. A. Romero, unpublished).

A related issue is the effect of alternative boundary conditions on the stratifying agencies at the upper and lower walls. The most serious problem in an experimental realization of the basic state considered herein, and earlier by Griffiths (1979a) and Moroz (1989), is that of prescribing the concentrations of one or more diffusing species at a boundary. This might be done by making the horizontal walls from a semipermeable membrane, through which solute can pass into the working fluid volume. If the fluid on the other side of the membrane was maintained at a constant concentration, and there were no significant mass transfer limitations normal or tangential to the membrane, then the concentration boundary conditions prescribed in the present analysis could be realized to within a good approximation.

Experiments employing such a membrane have been conducted by Krishnamurti & Howard (1983).

A final point concerning the boundary conditions is the imposition of thermal boundary conditions other than the constant-temperature ones considered here. Constant-flux conditions (corresponding to adiabatic conditions on the disturbance) in the doubly diffusive case in a two-dimensional box are known to lead to degenerate bifurcations involving two incommensurable frequencies and two commensurable wavenumbers (Leibovich, Lele & Moroz 1989), with important consequences for the nonlinear development of convection. Given that the isothermal conditions considered herein support a 'Hopf-Hopf' bifurcation, it seems likely that other thermal boundary conditions will lead to even more complicated behaviour.

A second factor to be considered is the possible onset of motion via disturbances of finite amplitude. To observe the multivaluedness of the stability boundary, it is essential that below the minimum of the stationary neutral curve there exists a finite range of R_1 in which the layer is stable with respect to those finite-amplitude disturbances to which it is subject. With reference to figure 1, it is necessary that some part of the linearly stable range $R_{1,1} \leq R_1 \leq R_{1,2}$ be stable with respect to disturbances of some non-vanishing magnitude.

Recently, Moroz (1989) has conducted a nonlinear stability analysis of a triply diffusive fluid layer, with the same boundary conditions and basic state considered herein. She has used an expansion in Fourier modes to derive a set of nonlinear ordinary differential equations for the modal amplitudes. The centre manifold and normal form theorems were then used to study several multiple bifurcations. The dynamical behaviour near the Hopf-Hopf point can be treated by a similar formulation (capable of dealing with modes at two different wavenumbers), but is beyond the scope of the present work.

Finally, bifurcating solutions that are quasi-periodic in space and time will be observable only if they are stable as R_1 is reduced below $R_{1,2}$. This question, and the issue of subcritical instability discussed above, remain to be investigated.

4.2. Nature of the instability mechanism

As explained elsewhere (Turner 1973, 1974) instability can occur in a hydrostatically stable doubly diffusive fluid that is 'bottom-heavy' in the more slowly diffusing (stratifying) agency and 'top-heavy' in the more rapidly diffusing agency. The mechanism of the instability can be described in terms of the existence of an overly large restoring force on a displaced fluid parcel.

From the above discussion, it might seem useful to discuss the triply diffusive case in terms of *pairs* of stratifying agencies. In the present case, there are three such pairs. That there are only two overstable diffusive modes might be ascribed to the fact that the stratifying agencies cannot be arranged so that more than two pairs are bottom- and top-heavy with, respectively, the slower and faster diffusing agency of the pair. One might suppose that, as in the rotating doubly diffusive case, the frequency of one of the overstable mechanisms can be 'tuned' by the other, so that it operates more efficiently (i.e. leads to instability at a smaller Rayleigh number) than would otherwise be the case. This could then lead to destabilization by a nominally 'stabilizing' force, as discussed by Acheson (1980), and to non-monotonic (R_1, R_2) (or R_1, R_3)-stability boundaries (Pearlstein 1981).

Unfortunately, an explanation of the disconnected neutral curves in terms of two diffusive modes interacting with each other is not tenable in the triply diffusive problem because of the relationship between the diffusivities and the Rayleigh numbers discussed in §4.1. We showed there that when a disconnected neutral curve occurs, the arrangement of the stratifying agencies is such that the fluid is top-heavy in the fastest diffusing agency, bottom-heavy in the next fastest agency, and topheavy in the slowest diffusing agency. Thus, it is not possible to select two pairs of 'diffusive' modes. Hence, we conclude that the existence of a closed, disconnected, oscillatory neutral curve, and the consequences that follow therefrom, is not simply the result of the interaction of a pair of independent 'diffusive' modes, one of which 'tunes' the other, as in the rotating double diffusive case.

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REFERENCES

- ACHESON, D. J. 1980 'Stable' density stratification as a catalyst for instability. J. Fluid Mech. 96, 723–733.
- BAINES, P. G. & GILL, A. E. 1969 On thermohaline convection with linear gradients. J. Fluid Mech.
 37, 289–306.
- BAUER, L., KELLER, H. B. & REISS, E. L. 1975 Multiple eigenvalues lead to secondary bifurcation. SIAM Rev. 17, 101-122.
- CHANDRASEKHAR, S. 1961 Hydrodynamic and Hydromagnetic Stability. Clarendon.
- CHEN, F. & CHEN, C. F. 1988 Onset of finger convection in a horizontal porous layer underlying a fluid layer. Trans. ASME C: J. Heat Transfer 110, 403-409.
- COHEN, D. S. 1977 Bifurcation from multiple complex eigenvalues. J. Math. Anal. Appl. 57, 505-521.
- CORIELL, S. R., MCFADDEN, G. B., VOORHEES, P. W. & SEKERKA, R. F. 1987 Stability of a planar interface during solidification of a multicomponent system. J. Cryst. Growth 82, 295-302.
- GIAMEI, A. F. & KEAR, B. H. 1970 On the nature of freckles in nickel base superalloys. *Metall.* Trans. 1, 2185-2192.
- GRIFFITHS, R. W. 1979a The influence of a third diffusing component upon the onset of convection. J. Fluid Mech. 92, 659-670.
- GRIFFITHS, R. W. 1979b A note on the formation of "salt-finger" and "diffusive" interfaces in three-component systems. Intl J. Heat Mass Transfer 22, 1687–1693.
- GRIFFITHS, R. W. 1979c The transport of multiple components through thermohaline diffusive interfaces. Deep-Sea Res. 26A, 383-397.
- HARRIS, R. M. 1985 The onset of instability in a triply-diffusive fluid layer. M.S. thesis, University of Arizona.
- HUPPERT, H. E. & TURNER, J. S. 1981a Double-diffusive convection. J. Fluid Mech. 106, 299-329.
- HUPPERT, H. E. & TURNER, J. S. 1981b A laboratory model of a replenished magma chamber. Earth Planet. Sci. Lett. 54, 144-152.
- Iooss, G. 1976 Direct bifurcation of a steady solution of the Navier-Stokes equations into an invariant torus. In *Turbulence and Navier Stokes Equations* (ed. R. Teman). Lecture Notes in Mathematics, vol. 565. Springer.
- KIM, H. 1966 Procedures for isothermal diffusion studies of four-component systems. J. Phys. Chem. 70, 562-575.
- KIM, H. 1969 Combined use of various experimental techniques for the determination of nine diffusion coefficients in four-component systems. J. Phys. Chem. 73, 1716-1722.

- KIM, H. 1970 Gravitational stability in isothermal diffusion experiments of four-component liquid systems. J. Phys. Chem. 74, 4577-4584.
- KRISHNAMURTI, R. & HOWARD, L. N. 1983 Double-diffusive instability: Measurement of heat and salt fluxes. Bull. Am. Phys. Soc. 28, 1398.
- LEAIST, D. G. & NOULTY, R. A. 1985 An eigenvalue method for determination of multicomponent diffusion coefficients. Application to NaOH+NaCl+H₂O mixtures. Can. J. Chem. 63, 476-482.
- LEIBOVICH, S., LELE, S. K. & MOROZ, I. M. 1989 Nonlinear dynamics in Langmuir circulations and in thermosolutal convection. J. Fluid Mech. 198, 471-511.
- McDougall, T. J. 1983 Double-diffusive convection caused by coupled molecular diffusion. J. Fluid Mech. 126, 379-397.
- MILLER, D. G. & VITAGLIANO, V. 1986 Experimental test of McDougall's theory for the onset of convective instabilities in isothermal ternary systems. J. Phys. Chem. 90, 1706-1717.
- MOROZ, I. M. 1989 Multiple instabilities in a triply diffusive system. Stud. Appl. Maths (in press).
- NOULTY, R. A. & LEAIST, D. G. 1987 Quaternary diffusion in aqueous KCl-KH₂PO₄-H₃PO₄ mixtures. J. Phys. Chem. 91, 1655-1658.
- PEARLSTEIN, A. J. 1981 Effect of rotation on the stability of a doubly diffusive fluid layer. J. Fluid Mech. 103, 389-412.
- PEARLSTEIN, A. J. & HARRIS, R. M. 1984 Disconnected heart-shaped neutral curves in the triply diffusive problem. Bull. Am. Phys. Soc. 29, 1537.
- PLATTEN, J. K. & LEGROS, J. C. 1984 Convection in Liquids. Springer.
- POULIKAKOS, D. 1985 The effect of a third diffusing component on the onset of convection in a horizontal porous layer. *Phys. Fluids* 28, 3172-3174.
- RUDRAIAH, N. & VORTMEYER, D. 1982' The influence of permeability and of a third diffusing component upon the onset of convection in a porous medium. Intl J. Heat Mass Transfer 25, 457-464.
- SCHECHTER, R. S., VELARDE, M. G. & PLATTEN, J. K. 1974 The two-component Bénard problem. Adv. Chem. Phys. 26, 265–301.
- STEEN, P. H. & DAVIS, S. H. 1982 Quasiperiodic bifurcation in nonlinearly-coupled oscillators near a point of strong resonance. SIAM J. Appl. Maths 42, 1345-1368.
- TERRONES, G. 1987 The onset of convection in a quintuply diffusive fluid layer. M.S. thesis, University of Arizona, Tucson.
- TURNER, J. S. 1973 Buoyancy Effects in Fluids. Cambridge University Press.
- TURNER, J. S. 1974 Double-diffusive phenomena. Ann. Rev. Fluid Mech. 6, 37-56.
- TURNER, J. S. 1985 Multicomponent convection. Ann. Rev. Fluid Mech. 17, 11-44.
- WELLS, J. D. 1986 Solvent fluxes, coupled diffusion, and convection in concentrated ternary solutions. J. Phys. Chem. 90, 2433-2440.