Marangoni convection in binary liquids

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We consider Marangoni convection in a binary liquid. The effect of crispation is considered and it is seen that above a certain critical crispation, only long wavelength rolls can be formed via the stationary instability. Oscillatory instability is allowed and hence a codimension-two point exists. In fact, by varying the crispation a line of codimension-two points can be generated but they do not terminate on a codimension-three point.

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I. INTRODUCTION

For a thin layer of fluid heated from below, the onset of convection is more likely to be surface tension driven than buoyancy driven. As the fluid layer thickness increases, the surface tension effect yields to the buoyancy effects. The surface tension driven convection is the Marangoni effect [1–3] and the stability of the fluid film is determined by the dimensionless Marangoni number M which is proportional to d^2, where d is the film thickness. The Rayleigh number is proportional to d^3, and hence for small values of d, the Marangoni effect dominates.

If the top surface of the fluid is free, then the fluctuations of the surface have an important effect on the stability. Its effect is estimated through a crispation number Cr and for Cr greater than a critical value, the long wavelength fluctuations dominate and the instability sets in as very long wavelength rolls [4–6]. The principle of exchange of stabilities is not proven but it is generally believed that, when heated from below, the instability is never oscillatory [2,3].

The problem of Marangoni convection in thermosolutal system with a free boundary has been tackled recently and it was found that the M vs a (a is the wave number at the onset of convection) can be quite interesting with the existence of crispation numbers Cr_1 and Cr_2 such that the convection was always in the form of long wavelength rolls for $\mathrm{Cr}>\mathrm{Cr}_2$ and the effect of crispation was completely absent if $\mathrm{Cr}<\mathrm{Cr}_1$. The various different situations have been studied by Dandapat and Kumar [7]. These authors addressed the question of Hopf bifurcation as well. It was generally concluded that for heating from below, it is not possible to have a Hopf bifurcation except possibly in a narrow band of frequency. The possibility of a meaningful codimension-two point consequently did not exist.

In this work, we consider the binary liquid mixture. The Soret effect becomes a very important factor and the separation parameter ψ which is a measure of the Soret effect in a parameter which can be varied externally. We find that for $\psi<0$, oscillatory Marangoni convection does indeed occur. The standard codimension-two point exists and in the presence of the free surface fluctuations, a line of codimension-two points are formed. However, this line of codimension-two points does not end in a codimension-three point. This is due to the fact that the high frequency branch does not correspond to positive Marangoni number.

In Sec. II we set up the governing equations and discuss the boundary conditions. The stationary instability is tackled in Sec. III. An approximate technique is developed in Sec. IV which helps us to discuss the oscillatory instability in Sec. V.

II. EQUATIONS AND BOUNDARY CONDITIONS

The governing hydrodynamic equations will be the Navier-Stokes equation for the velocity field and the diffusion equations for the temperature and concentration (of one of the components, which we take to be the lighter component) fields. These take the forms

$$\frac{\partial \mathbf{V}}{\partial t}+(\mathbf{V}\cdot\nabla)\mathbf{V}=-\frac{\nabla \mathbf{P}}{\rho}+\mathbf{g}+\nu\nabla^2\mathbf{V}\ , \tag{2.1}$$

$$\frac{\partial \mathbf{T}}{\partial t}+(\mathbf{V}\cdot\nabla)T=\lambda\nabla^2 T\ , \tag{2.2}$$

$$\frac{\partial c}{\partial t}+(\mathbf{V}\cdot\nabla)C=D\left[\nabla^2 C+\frac{k_T}{T_m}\nabla^2 T\right]\ , \tag{2.3}$$

where ∇, T, and C are the velocity, temperature, and concentration fields; ν, λ, and D are the kinematic viscosity, thermal diffusivity, and mass diffusion coefficient; k_T is the thermodiffusion coefficient; T_m is the mean temperature in the cell; P is the pressure; ρ the density; and $\mathbf{g}$ the acceleration due to gravity. We now have to supplement the equations of motion by constitutive relations [8–10]. To do so, we note that we are going to describe an instability which is being driven by surface tension forces and not by buoyancy forces. Consequently, the required relations involve the variation of surface tension S with temperature and concentration and we introduce the expansion

$$S=S_0+\left[\frac{\partial S}{\partial T}\right]_c \delta T+\left[\frac{\partial S}{\partial C}\right]_T \delta C+\cdots\ , \tag{2.4}$$

where S_0 is the surface tension at some reference temperature and concentration. The parameters α and β one then defines as

$$\alpha=-\frac{1}{S_0}\frac{\partial S}{\partial T}\ , \tag{2.5a}$$

$$\beta=-\frac{1}{S_0}\frac{\partial S}{\partial C}\ , \tag{2.5b}$$

and in general we expect α, $\beta>0$. The conduction state is described by

$$\mathbf{V}=\mathbf{0}\ , \tag{2.6}$$

the hydrostatic pressure distribution is

$$P=-\rho g z+\text{const}\ , \tag{2.7}$$

the no-mass current is

$$\mathbf{j}=-\left[\nabla C+\frac{k_T}{T}\nabla T\right]=0\ , \tag{2.8}$$

and linear profiles for temperature and concentration fields are

$$T=T_1+\beta_1 z\ , \tag{2.9}$$

$$C=C_1+\beta_2 z\ , \tag{2.10}$$

where β_1 and β_2 are constants and T_1 and C_1 are the concentrations at the lower plate which we take to be at $z=0$. To fix the constants β_1 and β_2, we need to consider the boundary conditions at the top surface, which we take at $z=d$. If the environment has a temperature T_0, the top surface a temperature T_2, and the heat flux at the top surface is H, then

$$\nabla T=-(T_2-T_0)H\hat{\mathbf{z}},\ \text{ at } z=d\ . \tag{2.11}$$

Using Eq. (2.9), $\nabla T=\beta_1\hat{\mathbf{z}}$, and hence

$$\beta_1=-(T_1+\beta_1 d-T_0)H\ ,$$

or

$$\beta_1=-\frac{H}{1+Hd}\Delta T=-\frac{\Gamma}{1+\Gamma}\frac{\Delta T}{d}\ , \tag{2.12}$$

where $\Delta T=T_1-T_0$ (the temperature difference between plates) and $\Gamma=Hd$. An insulating boundary corresponds to $\Gamma=0$. From Eq. (2.8), we are required to have

$$\frac{\beta_2}{\beta_1}=-\frac{k_T}{T_m}\ . \tag{2.13}$$

We now need to examine whether the above conduction state is stable to convective perturbations. The perturbations occur in velocity ($\mathbf{v}$), in temperature (δT), in concentration (δC) and in the height of the layer, i.e., fluctuations at the top surface which is free. These fluctuations we denote by η which is going to be a function of x, y, and t, and consequently the equation of the top surface becomes

$$z=d+\eta(x,y,t)\ . \tag{2.14}$$

The z component, w, of the velocity at the top surface must satisfy

$$w=\frac{\partial\eta}{\partial t}+u\frac{\partial\eta}{\partial x}+v\frac{\partial\eta}{\partial y}\ \text{ at the top surface}\ , \tag{2.15}$$

where u and v are the x and y components of the velocity.

Dimensionless variables are introduced by scaling all distances by d, time by d^2/ν, velocity by λ/d, δT by $(\Delta T)\Gamma/(1+\Gamma)$, and the variable $C+(k_T/T_m)T$ by

$$-\frac{k_T}{T_m}\frac{(\Delta T)\Gamma}{1+\Gamma}\ .$$

The dimensionless δT is denoted by θ and the dimensionless $\delta[C+(k_T/T_m)T]$ by ϕ in what follows, while we will adopt the convention that u, v, w, and η and also x, y, z, and t will be taken to be dimensionless whenever they appear henceforth. The bounding surfaces being infinite in extent, we expect the perturbations u, v, w, η, θ, and ϕ to be periodic with some wave number $\mathbf{k}$ (k_1,k_2).

If we linearize the equations of motion [(2.1)–(2.3)] about the conduction state, we find from Eq. (2.1) that

$$\left[\frac{\partial}{\partial t}-\nu\nabla^2\right]\mathbf{V}=-\frac{\nabla\delta P}{\rho}\ ,$$

since fluctuations in ρ are being dropped. Taking the curl of this equation twice and using the incompressibility condition leads to

$$\nabla^2\left[\frac{\partial}{\partial t}-\nu\nabla^2\right]w=0\ . \tag{2.16}$$

Straightforward manipulation of Eqs. (2.2) and (2.3) yield

$$\left[\sigma\frac{\partial}{\partial t}-\nabla^2\right]\theta=w\ , \tag{2.17}$$

$$\left[\frac{\sigma}{L}\frac{\partial}{\partial t}-\nabla^2\right]\phi=-\frac{1}{L}\nabla^2\theta\ , \tag{2.18}$$

where $L=D/\lambda$ is called the Lewis number and $\sigma=\nu/\lambda$ is the Prandtl number. The linear set of equations will support a time dependence of the form e^{pt} and thus the structure of w, θ, ϕ, and η will be (taking into account the periodicity in x and y)

$$\left.\begin{array}{l} u,v,w=U(z),V(z),W(z)\\ \theta=\Theta(z)\\ \phi=\Phi(z)\\ \eta=A \end{array}\right\}\times e^{pt}e^{i(k_1x+k_2y)}\ . \tag{2.19}$$

Inserting the above forms into Eqs. (2.16)–(2.18), we obtain the equations of linear stability analysis as $(D=d/dz)$

$$(D^2-a^2)[p-(D^2-a^2)]W=0\ , \tag{2.20}$$

$$[\sigma p-(D^2-a^2)]\Theta=W\ , \tag{2.21}$$

$$\left[\frac{\sigma}{L}p-(D^2-a^2)\right]\Phi=-\frac{1}{L}(D^2-a^2)\Theta\ . \tag{2.22}$$

The boundary conditions are now to be specified. On the lower plate (which is fixed and thermally conducting), we have

$$W = DW = \Theta = D\Phi = 0 \quad (z=0) . \tag{2.23}$$

On the top surface, we must have (boundary conditions, too, must be linearized in U, V, W, Θ, Φ, and A)

$$W = pA . \tag{2.24}$$

It is reasonable to assume that the mass flux across the surface is negligible and hence

$$D\Phi = 0 . \tag{2.25}$$

The stress tensor in a fluid is

$$T_{ij} = -P\delta_{ij} + \rho\nu \left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right] ,$$

and the force balance at the top surface yields, for directions normal to the surface,

$$T_{ij} n_i n_j = 2S/R ,$$

and for directions along the surface,

$$T_{ij} n_i t_j = \frac{\partial S}{\partial x_j} t_j ,$$

where $\{n_i\}$ is the unit normal, $\{t_i\}$ the unit tangent, and R the radius of curvature, which is given by

$$R^{-1} \simeq \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] \eta$$

to linear order accuracy. Using the force balance along the normal and the Navier-Stokes equation, we get, at the top surface,

$$\mathrm{Cr}(D^2 - 3a^2 - p)DW = a^2(B + a^2)A , \tag{2.26}$$

where $\mathrm{Cr} = \rho\nu\lambda/S_0 d$ is the crispation number and $B = \rho d^2 g/S_0$ is the Bond number. The tangential component of the force balance leads to

$$(D^2 + a^2)W + Ma^2(1+\psi)(\theta - A) + Ma^2\psi\Phi = 0 , \tag{2.27}$$

where ψ is the separation parameter $[\psi = -(k_T/T_m)(\beta/\alpha)]$ and the Marangoni number M is given by

$$M = \frac{\alpha S_0 d^2 \Delta T}{\rho\nu\lambda} , \tag{2.28}$$

S_0 being the value of the surface tension at $z=1$. The task is to solve the eigenvalue equation for p [Eqs. (2.20)–(2.22)] under the boundary conditions given in Eqs. (2.23)–(2.28). The conduction state will be unstable whenever $\mathrm{Re}p \geq 0$. If $\mathrm{Im}p = 0$ when $\mathrm{Re}p = 0$, we have a stationary instability, and if $\mathrm{Im}p \neq 0$ when $\mathrm{Re}p = 0$, we have a Hopf bifurcation or overstability.

III. STATIONARY INSTABILITY

In this case we ask for the condition which gives a zero eigenvalue for p in Eqs. (2.20)–(2.22). These equations now take the form

$$(D^2 - a^2)^2 W = 0 , \tag{3.1}$$

$$(D^2 - a^2)\Theta = -W , \tag{3.2}$$

$$(D^2 - a^2)\Phi = -\frac{W}{L} . \tag{3.3}$$

Using the boundary condition that $D = DW = 0$ for $z = 0$ and $W = 0$ on $z = 1$, Eq. (3.1) yields for W,

$$W = A_1 \left[\sinh az - az \cosh az + \frac{aC - S}{S} z \sinh az \right] , \tag{3.4}$$

where $C = \cosh a$ and $S = \sinh a$.

Solving for Θ from Eq. (3.2) and using the fact that $\Theta = 0$ on $z = 0$ and on $z = 1$ [from Eqs. (2.11) and (2.26)]

$$D\Theta + \Gamma\Theta = \Gamma A = \frac{\mathrm{Cr}}{a^2(B + a^2)}(D^2 - 3a^2)DW , \tag{3.5}$$

we arrive at

$$\Theta = B_2 \sinh az - A_1 \left[\frac{3}{2a}\cosh az - \frac{1}{4a}(az^2 \sinh az - z\cosh az) + \frac{aC - S}{S}\frac{1}{4a^2}(az^2\cosh az - z\sinh az) \right] , \tag{3.6}$$

where

$$B_2 = KA_1 , \tag{3.7a}$$

with

$$K = \frac{(B + a^2)[(a^2C^2 + S^2 + aCS) + \Gamma(a^2 + S^2 + aCS)] - 8a^4\Gamma\,\mathrm{Cr}}{4a^2 S(B + a^2)(aC + \Gamma S)} . \tag{3.7b}$$

From Eq. (3.3), we obtain, on using the boundary conditions $D\Phi = 0$ on $z = 0$ and $z = 1$,

$$\Phi = C_1 \cosh az + C_2 \sinh az - \frac{A_1}{L} \left\{ \frac{1}{2a} z\cosh az - \frac{1}{4a}(az^2 \sinh az - z\cosh az) + \frac{aC - s}{S}\frac{1}{4a^2}(az^2\cosh az - \sinh az \right\} , \tag{3.8}$$

with

$$C_2=\frac{3A_1}{4a^2L} \tag{3.9a}$$

and

$$C_1=\frac{A_1}{4a^3LS^2}(aC-S)^2 . \tag{3.9b}$$

Using the solutions obtained for W, Θ, and Φ, we now need to satisfy the boundary condition in Eq. (2.27) and this yields

$$8a(a-SC)(B+a^2)+\frac{M(1+\psi)}{aC+\Gamma S}[(S^3-a^3C)(B+a^2)+8a^5C\,\mathrm{Cr}]+\frac{\psi M}{L}\frac{B+a^2}{aS}\{C(aC-S)^2+aS(2S^2-a^2-aCS)\}=0 . \tag{3.10}$$

The critical Marangoni number for the onset of stationary convection is given by Eq. (3.10). For $\psi=0$, we obtain the standard result for the single component fluid, as expected.

Anticipating a long wavelength instability, we expand the various terms in powers of a, as follows:

$$a(a-SC)(B+a^2)(aC+\Gamma S)=-\tfrac{2}{3}Ba^5(1+\Gamma)\left[1+\frac{a^2}{5}+\frac{a^2}{B}+\frac{a^2}{2}\frac{1+\Gamma/3}{1+\Gamma}\right],$$

$$(S^3-a^3C)(B+a^2)+8a^5C\,\mathrm{Cr}=8a^5\mathrm{Cr}\left[1+\frac{a^2}{2}+\frac{a^2B}{120\,\mathrm{Cr}}+\cdots\right],$$

$$\frac{B+a^2}{aS}(aC+\Gamma S)\{C(aC-S)^2+aS(2S^2-a^2-aCS)\}=\frac{a^5}{9}B(1+\Gamma)\left\{1+\frac{3a^2}{10}+\frac{a^2}{3(1+\Gamma)}+\frac{a^2}{B}+\cdots\right\}.$$

This leads to (for $\Gamma=0$)

$$M=\frac{2}{3}\frac{B}{\mathrm{Cr}(1+\psi)+\dfrac{\psi B}{72L}}\left\{1+\frac{a^2}{5}+\frac{a^2}{B}+\frac{a^2}{2}\left[1-\frac{\dfrac{2B}{15}(1+\psi)+8(1+\psi)\mathrm{Cr}+\dfrac{2B\psi}{L}\left[\dfrac{1}{B}+\dfrac{19}{30}\right]}{8\,\mathrm{Cr}(1+\psi)+\dfrac{\psi B}{9L}}\right]+\cdots\right\}. \tag{3.11}$$

Clearly, the value of M at $a=0$ will be a minimum if

$$\mathrm{Cr}>\mathrm{Cr}_1=(B^2/120)\left[1+\psi-\frac{\psi}{9L}\right]\Big/(1+\psi)(1+B/5) .$$

This will be the onset point of convection if this is the only minimum or if it is the lower of the two possible minima—the other being at a finite value of a. This minimum is totally insensitive to the value of Cr for low Cr ($\lesssim 10^{-2}$) and is very well approximated by $80/(1+\psi+\psi/L)$ for $\Gamma=0$. Thus the convection occurs as long wavelength rolls (i.e., $a=0$) with the threshold M_s given by

$$M_s=\frac{2}{3}\frac{B}{\mathrm{Cr}(1+\psi)+\dfrac{B\psi}{72L}} , \tag{3.12}$$

provided $\mathrm{Cr}>\mathrm{Cr}_2$ is given by

$$\frac{2}{3}\frac{B}{\mathrm{Cr}_2(1+\psi)+\dfrac{B\psi}{72L}}=\frac{80}{1+\psi+\psi/L}$$

or

$$\mathrm{Cr}_2=\frac{B}{120}\left[1-\frac{2}{3}\frac{\psi}{L}\frac{\psi}{1+\psi}\right] .$$

Thus, we have the situation that if $\mathrm{Cr}<\mathrm{Cr}_1$, then there is only one minimum in the M vs a curve and $M_s=80/(1+\psi+\psi/L)$ with $a_c=1.99$; and if $\mathrm{Cr}>\mathrm{Cr}_2$, the only minimum is at M_s given by Eq. (3.12); and for $\mathrm{Cr}_1<\mathrm{Cr}<\mathrm{Cr}_2$, there are two minima, but the one given by $80/(1+\psi+\psi/L)$ is the lower and thus gives the threshold value of the Marangoni number.

IV. AN APPROXIMATION

In this section we will consider the stationary convection in an ordinary fluid and develop an approximation scheme that will turn out to be useful for the Hopf bifurcation and should also turn out to be very useful for treating the nonlinear problem. In the absence of the second fluid, the governing equations are given by Eqs. (3.1) and (3.2). The solution for W is, as before, given by Eq. (3.4). It is in the solution of Eq. (3.2) that we introduce the approximation by assuming that the solution for Θ can be expanded in a power series in z ($0\le z\le 1$), so that

$$\Theta=\sum_{n=0}^{\infty}B_nz^n , \tag{4.1}$$

and then restrict ourselves to only three terms so that the boundary conditions are met at $z=0$ and $z=1$ and Eq. (3.2) is satisfied in the mean. The boundary condition at $z=0$ leads to $B_0=0$. The boundary condition at $z=1$ leads to

$$(2+\Gamma)B_1B_2+B_1(1+\Gamma)=-\frac{2\Gamma\,\mathrm{Cr}\,a^2A}{S(B+a^2)} , \tag{4.2}$$

and the requirement of satisfying Eq. (3.2) in the mean leads to

$$\left[\frac{a^3}{3}-2\right]B_1B_2+\frac{a^2}{2}B_1=\frac{A}{a^2S}(S-a)^2 . \tag{4.3}$$

One now needs to satisfy the boundary conditions of Eq. (2.27) at $z=1$ (note in this case, $\psi=0$) and that leads to

$$M=\frac{4a(CS-a)\left[1+\frac{a^2}{3}+\frac{a^2\Gamma}{12}+\Gamma\right]}{(S-a)^2+4\left[1+\frac{a^2}{6}\right]\frac{\mathrm{Cr}\,a^4}{B+a^2}} . \tag{4.4}$$

This is to be compared with the exact answer that can be read off from Eq. (3.10) as

$$M_{\text{exact}}=\frac{8a(CS-a)(B+a^2)(aC+\Gamma S)}{(S^3-a^3C)(B+a^2)+8a^5C\,\mathrm{Cr}} . \tag{4.5}$$

If we consider the long wavelength instability, i.e., $a=0$, the expansions of the two expressions are as follows:

$$M=\tfrac{2}{3}(1+\Gamma)\frac{B}{\mathrm{Cr}}\left[1+\frac{a^2}{30}+\frac{a^2}{B}-\frac{a^2}{36}\frac{B}{\mathrm{Cr}}+\frac{a^2}{3(1+\Gamma)}+\frac{a^2}{12(1+\Gamma)}+\cdots\right], \tag{4.6}$$

$$M_{\text{exact}}=\tfrac{2}{3}(1+\Gamma)\frac{B}{\mathrm{Cr}}\left[1+\frac{a^2}{5}+\frac{a^2}{B}-\frac{a^2}{120}\frac{B}{\mathrm{Cr}}-\frac{\Gamma a^2/3}{1+\Gamma}+\cdots\right] . \tag{4.7}$$

So long as the instability acts as an infinite wavelength one, we see that the critical Marangoni number is the same in both cases. We now cross over to the other extreme, where $\mathrm{Cr}=0$. In this case (for $\Gamma=0$)

$$M=\frac{4a(CS-a)(1+a^2/3)}{(S-a)^2} , \tag{4.8}$$

leading to $a_c=2.11$ and $M_c=81.8$, while

$$M_{\text{exact}}=\frac{8a^2C(CS-a)}{(S^3-a^3c)} , \tag{4.9}$$

leading to $a_c=1.99$ and $M_c=80.1$. We have checked to see that over the entire range of parameters the approximate M obtained from Eq. (4.4) is within 5% of the exact M as given by Eq. (4.5).

V. OSCILLATORY INSTABILITY

In this section we make the usual approximation for the binary liquid, namely, $L\ll 1$ (the mass diffusion is less efficient than heat diffusion) and work to leading order in L. We also make the approximation that the Prandtl number $\sigma\gg 1$. This latter approximation is true for almost all binary mixtures except ^{3}He-^{4}He mixtures and even for the helium mixtures it is not a sensitive parameter if $|\psi|\ll 1$. The simplification obtained in this limit, on the other hand, is enormous and makes the results visually transparent. Returning to Eqs. (2.20)–(2.22), we note that if we scale p by σ, then $p\sigma\to p$ in Eqs. (2.21) and (2.22), while $p\to p/\sigma$ in Eq. (2.20). Consequently, to the lowest order in $1/\sigma$, the equation for W can be taken to be

$$(D^2-a^2)^2W=0 . \tag{5.1}$$

The Θ equation can be written as

$$(D^2-b^2)\Theta=-W , \tag{5.2}$$

where $b^2=a^2+i\omega$ (we have set $p=i\omega$), and for $L\ll 1$, the Φ equation becomes

$$i\omega\Phi=-(D^2-a^2)\Theta . \tag{5.3}$$

The governing set of equations for the oscillatory instability for $\sigma\gg 1$ and $L\ll 1$ are consequently given by Eqs. (5.1)–(5.3). The boundary conditions to be satisfied are, on $z=0$,

$$W=DW=\Theta=D\Phi=0 , \tag{5.4}$$

and on $z=1$,

$$\begin{aligned} &W=i\omega A ,\\ &\mathrm{Cr}(D^2-3a^2)DW=a^2(B+a^2)A ,\\ &D\Theta+\Gamma\Theta=A ,\\ &D\Phi=0 ,\\ &(D^2+a^2)W+Ma^2(1+\psi)(\Theta-A)+\psi Ma^2\Phi=0 . \end{aligned} \tag{5.5}$$

The solution of Eq. (5.1) satisfying the given boundary conditions on W is

$$W=A_1\left\{\sinh az-az\cosh az+\frac{aC-S}{S}z\sinh az\, f\right\} , \tag{5.6}$$

where

$$f=\frac{1+\frac{i\omega\,\mathrm{Cr}}{a^2(B+a^2)}\left[\frac{2a^4S-2a^3C}{aC-S}\right]}{1+\frac{2i\omega\,\mathrm{Cr}}{a^2(B+a^2)}\frac{a^3C}{S}} . \tag{5.7}$$

The solution of Eq. (5.2) is tried according to Sec. IV as

$$\Theta=B_1z+B_2z^2 . \tag{5.8}$$

The fourth equation of the set of Eq. (5.5) leads to

$$(1+\Gamma)B_1+(2+\Gamma)B_2=\Gamma A=\frac{\Gamma}{i\omega}W$$
$$=\frac{\Gamma}{i\omega}A_1[S-aC+f(aC-S)]$$
$$=\frac{\Gamma}{i\omega}A_1(f-1)(aC-S)\ . \tag{5.9}$$

The satisfying of Eq. (5.2) in the mean leads to

$$\left[\frac{b^2}{3}-2\right]B_2+\frac{b^2}{2}B_1=A_1\left[\frac{(S-a)^2}{a^2S}+(f-1)\frac{(aC-S)^2}{a^2S}\right]\ . \tag{5.10}$$

Thus,

$$\frac{B_1}{A_1}=\frac{\left[\frac{b^2}{3}-2\right]\frac{\Gamma}{1\omega}(aC-S)(1-f)+(2+\Gamma)\left[\frac{(a-S)^2}{a^2S}+(f-1)\frac{(aC-S)^2}{a^2S}\right]}{\frac{b^2}{2}(2+\Gamma)+(1+\Gamma)\left[2-\frac{b^2}{3}\right]}\ , \tag{5.11}$$

and

$$\frac{B_2}{A_1}=\frac{\frac{\Gamma}{i\omega}(aC-S)(1-f)\frac{b^2}{2}+(1+\Gamma)\left[\frac{(a-S)^2}{a^2S}+(f-1)\frac{(aC-S)^2}{a^2S}\right]}{\frac{b^2}{2}(2+\Gamma)+(1+\Gamma)(2-b^2/3)}\ . \tag{5.12}$$

To solve for Eq. (5.3) in the same style, we note that $D\Phi$ must vanish on the boundary $z=1$ and hence we use $\Phi=\text{const}\ (C_1)$ to the lowest order; now to satisfy Eq. (5.3) in the mean, we must have

$$i\omega C_1=-(2-a^2/3)B_2+\frac{a^2}{2}B_1\ . \tag{5.13}$$

The last of the boundary conditions in Eq. (5.5) now yields

$$(D^2+a^2)W|_{z=1}=\frac{Ma^2(1+\psi)}{\Gamma}D\Theta\Big|_{z=1}-\psi Ma^2\Phi|_{z=1}$$
$$=\frac{Ma^2(1+\psi)}{\Gamma}(B_1+2B_2)-\frac{\psi Ma^2}{i\omega}\left[\left[2-\frac{a^2}{3}\right]B_2-\frac{a^2}{2}B_1\right]\ , \tag{5.14}$$

leading to

$$M=\frac{\{2a(CS-a)+2a(1-f)[(a^2-1)SC+a]\}}{(1+\psi)a^2\frac{\left[2S\frac{1-f}{i\omega}(aC-S)\left[1+\frac{b^2}{3}\right]+\frac{(S-a)^2}{a^2}+(f-1)\frac{(aC-S)^2}{a^2}\right]}{2+\frac{2b^2}{3}+\Gamma\left[2+\frac{b^2}{6}\right]}}-\frac{\psi a^2}{A_1 i\omega}\left[\left[2-\frac{a^2}{3}\right]B_2-\frac{a^2B}{2}\right]\ . \tag{5.15}$$

For $\Gamma=0$, we get

$$M=\frac{4a\{(CS-a)+(1-f)[(a^2-1)SC+a]\}\left[1+\frac{b^2}{3}\right]}{(1+\psi)2Sa^2\frac{1-f}{1\omega}(aC-S)\left[1+\frac{b^2}{3}\right]+[(S-a)^2+(f-1)(aC-S)^2]}\left[1+\Psi+\frac{\psi}{i\omega}\left[1+\frac{a^2}{3}\right]\right]\ . \tag{5.16}$$

If $\mathrm{Cr}\rightarrow 0$, then $1-f\rightarrow 0$, and we have

$$M=\frac{4a\,(CS-a)\left[1+\frac{b^2}{3}\right]}{(S-a)^2\left[1+\psi+\frac{\psi}{i\omega}\left[1+\frac{a^2}{3}\right]\right]}\;. \tag{5.17}$$

Equating real and imaginary parts, the critical Marangoni number M_0 for the oscillatory convection can be written as

$$\omega^2=-3\psi(1+a^2/3)^2/(1+\psi)\;, \tag{5.18}$$

$$M_0=\frac{4a\,(CS-a)\left[1+\frac{a^2}{3}\right]}{(S-a)^2(1+\psi)}\;. \tag{5.19}$$

The critical Marangoni number for stationary convection when Cr=0 and $\Gamma=0$ is obtained from Eq. (3.10) as

$$M=\frac{8a^2(SC-a)CS}{(1+\psi)S(S^3-a^3C)+\frac{\psi}{L}[C^2(aC-S)^2+aSC(2S^2-a^2-aCS)]}\;. \tag{5.20}$$

As is obvious from Eq. (5.18), the oscillatory instability can occur only if $\psi<0$ and study of Eqs. (5.19) and (5.20) reveals that $\psi=0$ is the codimension-two point in the limit of $L\to 0$ (i.e., to the leading order in L). For $\psi<0$, the onset is oscillatory, with a critical wave number of 2.11, which leads to

$$\omega^2=-18.75\psi/(1+\psi)\;, \tag{5.21a}$$

$$M_0=\frac{81.8}{(1+\psi)}\;. \tag{5.21b}$$

As for the Rayleigh convection, M_0 increases as ψ becomes more negative and the codimension-two point is at $\psi=0$.

We now turn to the situation where $\mathrm{Cr}\neq 0$. Since $\mathrm{Cr}/(B+a^2)$ is always $\ll 1$, we can safely linearize in this variable and immediately we see that

$$1-f\simeq\frac{2i\omega\,\mathrm{Cr}\,a^2}{(B+a^2)S(aC-S)}\;, \tag{5.22}$$

$$\begin{aligned}M&=\frac{4a\,(CS-a)\left[1+\frac{a^2}{3}\right]}{(1+\psi)(S-a)^2}\left[\frac{1-\omega^2A_1}{1-B_1}\right]\\&=-\frac{4a}{3}\frac{\omega^2}{\psi}\frac{(CS-a)}{\left[1+\frac{a^2}{3}\right](S-a)^2}\left[\frac{1+B_2}{1+C_2+A_2\omega^2}\right]\;,\end{aligned} \tag{5.23}$$

where

$$A_1=\frac{2}{3}\frac{\mathrm{Cr}\,a^2[(a^2-1)SC+a]}{S(B+a^2)(aC-S)(CS-a)\left[1+\frac{a^2}{3}\right]}\;, \tag{5.24}$$

$$B_1=\frac{2\left[1+\frac{a^2}{3}\right]\mathrm{Cr}\,a^2(aC-S)}{S(B+a^2)(1+\psi)(S-a)^2}\;, \tag{5.25}$$

$$A_2=\frac{2\,\mathrm{Cr}\,a^2}{B+a^2}\frac{(1+\psi)}{(S-a)^2}\frac{aC-S}{S}\frac{1}{\psi}\frac{1}{1+a^2/3}\;, \tag{5.26}$$

$$B_2=\frac{6\,\mathrm{Cr}\,a^2}{(B+a^2)S}\frac{[(a^2-1)SC+a]\left[1+\frac{a^2}{3}\right]}{(aC-S)(CS-a)}\;, \tag{5.27}$$

$$C_2=\frac{4(1+\psi)\mathrm{Cr}\,a^4}{(B+a^2)\psi(S-a)^2}\;. \tag{5.28}$$

As is obvious, the shift in the actual threshold for the oscillatory convection and the change in the frequency is miniscale, but the change in the codimension-two point is significant. For all $\mathrm{Cr}<\mathrm{Cr}_2$ of Sec. III, we have the threshold for stationary convection given by Eq. (3.12). Thus, the codimension-two point occurs when this critical value matches that given in Eq. (5.21b), i.e., for

$$\frac{80}{1+\psi}=\frac{2}{3}\frac{B}{\mathrm{Cr}(1+\psi)+\frac{B}{72L}}\;,$$

or

$$\psi=\frac{1-120\,\mathrm{Cr}/B}{\frac{5}{3L}+\frac{120\,\mathrm{Cr}}{B}-1}\simeq\frac{3L}{5}\left[1-120\frac{\mathrm{Cr}}{B}\right]\;. \tag{5.29}$$

Thus for $\mathrm{Cr}>\mathrm{Cr}_2$, a line of codimension-two points is generated. However, this line does not terminate in a codimension-three point, since the second oscillatory branch does not correspond to a positive value of M.

To see the truth of the above statement, we note that Eq. (5.23) leads to a second real value of ω^2 for $A_2<0$, i.e., $\psi<0$. This real value is $O(A_1^{-1}A_2^{-1})$ and is a high frequency branch. We immediately infer from the first of Eq. (5.23) that M will become negative as $1-\omega^2 A_1$ is $O(1-A_2^{-1})$ and $A_2^{-1} \gg 1$.

To summarize, we have seen that, depending on system parameters, both stationary and oscillatory convection are possible in Marangoni convection in binary liquids. In a real situation, we will always have a combination of Marangoni and Rayleigh effects [11]. However, if the thickness of the fluid layer is very small, the Marangoni effect is expected to dominate. We also expect the Marangoni effect to dominate if the surface tension becomes a very sensitive function of temperature, e.g., when the fluid considered is close to a second order critical point. In the case of stationary instability, the crispation number plays an important role in determining whether long wavelength rolls will be formed or not. For a range of crispation numbers, the initial Marangoni numbers for zero and finite wave number convections are very close and thus should lead to an interesting pattern selection problem [12]. For the oscillatory instability, the changing crispation number leads to a line of codimension-two points.

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