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On convective instability induced by surface-tension gradients

By K. A. SMITH
Department of Chemical Engineering, Massachusetts Institute of Technology

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The linearized stability problem for steady, cellular convection resulting from gradients in surface tension is examined in some detail. Earlier work by Pearson (1958) and Sternling & Scriven (1959, 1964) has been extended by considering the effect of gravity waves. In order to avoid the use of an assumed coupling mechanism at the interface, the relevant dynamical equations were retained for both phases. It is shown that the existence of a critical Marangoni number is assured, and that for many situations this critical value is essentially that which is appropriate to the case of a non-deformable interface. Usually, surface waves are important only at very small wave-numbers, but they are dominant for unusually thin layers of very viscous liquids.

1. Introduction

The importance of surface-tension gradients as a cause of convective instability has now been so well established (Pearson 1958; Sternling & Scriven 1959; Scriven & Sternling 1964) that further discussion of this point is probably unnecessary. A striking illustration of its importance is the fact that the regular cellular convection observed by Bénard (1900, 1901) was almost certainly due to gradients in surface tension rather than to buoyancy forces, as originally supposed. Many observations such as Bénard's may be interpreted with the aid of existing analyses, but each analysis suffers from at least one deficiency.

The pioneering work of Pearson (1958) was motivated by the observation that drying paint films often exhibit an organized cellular motion which cannot be explained by buoyancy effects. In order to model this situation, Pearson assumed that the interface did not deform in the direction normal to itself, that the boundary condition on the free surface was that of constant heat-transfer coefficient, and that the air phase was essentially inviscid. The possibility of oscillatory instability was not considered. The results indicated the existence of a critical 'Marangoni number' of about 80 at a wave-number (made dimensionless with respect to film depth) of about 2·0. If the surface tension decreases with increasing temperature, then the liquid film is unstable only if it is heated from below; but, for the very unusual case in which surface tension increases with temperature, the heating must be from above.

The independent investigation of Sternling & Scriven (1959) was an attempt to understand similar effects that occur when mass is transferred across an interface between two immiscible liquid phases. Since the diffusion equations are the same for heat and for material transport, and since surface tension depends on concentration as well as temperature, it follows that the underlying problem is essentially the same as Pearson's. However, it is obviously not possible to neglect the dynamics of either liquid phase. Therefore, in order to simplify the problem, it was assumed that both phases were infinitely deep and that the interface did not deform in the direction normal to itself. On the other hand, the effect of surface viscosity was included, and the oscillatory modes were considered. Depending on the fluid properties and the direction of transfer, this model was either stable to all wave-numbers or unstable to a band of wave-numbers, and much of the analysis was devoted to determining those modes with the largest growth rates. If the solute diffusivity and the kinematic viscosity were both lower for one phase than for the other, instability was predicted for transfer in either direction.

Scriven & Sternling (1964) later returned to the problem first considered by Pearson, pointing out that certain observations did not seem to be compatible with Pearson's results. In their modification, the additional effects of surface viscosity were included. The surface was considered deformable and capillary waves were permitted, but gravity waves were not. The results showed that disturbances with zero wave-number were always unstable and hence that no critical Marangoni number existed. At higher wave-numbers, the solution for low values of the 'crispation group' (see end of § 2 for definition) was similar to Pearson's result, but for larger values of the crispation group the character of the solution was entirely different. In all cases, instability was possible for transfer in one direction only, as was found by Pearson. In a footnote, the authors indicate that Brooke Benjamin had pointed out to them that, for upward facing films, disturbances of zero wave-number would be stabilized by the action of gravity.

In sum, then, the best existing model of thin film behaviour shows an anomaly at zero wave-number and this difficulty is probably associated with the neglect of gravity waves. In contradiction with some experiments, this model also fails to show the possibility of instability to transfer in both directions. By contrast, the sole existing analysis for mass transfer between two liquid phases proceeds on rather different grounds and fails to show any critical condition for the onset of the instability. Yet this model can exhibit instability to transfer in either direction. In what follows, both physical problems are brought within the framework of the same theoretical analysis and some of these difficulties are resolved.

2. Mathematics

For simplicity, the problem is formulated in terms of steady, one-dimensional heat transfer between two fluid phases separated by a horizontal interface. Thus the unperturbed state is one of no motion, and within each phase the temperature varies linearly in the vertical direction. It is assumed that surface tension is the only physical property which varies with temperature. A linearized, normal-mode analysis is then employed to determine the state of marginal stability, but oscillatory modes are not considered.

The z-axis is taken to be in the vertical direction, so that the (x, y)-plane coincides with the mean position of the interfaces. Then, if u, v, w are the velocity components in the directions x, y, z, the linearized equations of motion become

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\nabla^2 u, \tag{1}$$

$$\frac{\partial v}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial y} + \nu\nabla^2 v, \tag{2}$$

$$\frac{\partial w}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\nabla^2 w, \tag{3}$$

where all quantities represent perturbations from the state of rest. Similarly, the continuity equation becomes

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \tag{4}$$

while the energy equation is

$$\partial\theta/\partial t = -\beta w + \kappa\nabla^2\theta, \tag{5}$$

in which β is the slope of the unperturbed temperature profile.

It is now assumed that the perturbations may be expressed in terms of their normal modes; thus

$$\left.\begin{aligned} u &= U(z)\exp(ik_x x + ik_y y + nt), \\ v &= V(z)\exp(ik_x x + ik_y y + nt), \\ w &= W(z)\exp(ik_x x + ik_y y + nt), \\ p &= P(z)\exp(ik_x x + ik_y y + nt), \\ \theta &= \Theta(z)\exp(ik_x x + ik_y y + nt). \end{aligned}\right\} \tag{6}$$

Similarly, since the equation of the undisturbed interface is simply $z = 0$, the perturbed interface is assumed to be given by

$$z = \zeta = \zeta_0 \exp(ik_x x + ik_y y + nt). \tag{7}$$

Now, with $k^2 = k_x^2 + k_y^2$ and with $n = 0$, the equations of motion and the energy equation reduce to

$$\left(\frac{d^2}{dz^2} - k^2\right)^2 W = 0, \tag{8}$$

and

$$\left(\frac{d^2}{dz^2} - k^2\right)\Theta = \beta W/\kappa. \tag{9}$$

The real part of n is set equal to zero because the purpose of this analysis is to consider those marginal disturbances which are neither amplified nor damped. For oscillatory disturbances of this kind, the imaginary part of n will not vanish and this paper is therefore restricted to a consideration of the stationary modes.

Let W_2 and Θ_2 be the solutions to these equations which are appropriate to the upper phase, and let W_1 and Θ_1 be the solutions for the lower phase. These are coupled to each other by the boundary conditions at the interface, which require continuity of velocity, temperature, and heat flux. Newton's third law places constraints on the tangential and normal stresses. Strictly, all of these conditions are to be applied at $z = \zeta$; but since ζ_0 is a small quantity, they may be applied at $z = 0$ consistently with the overall linearized approximation, together with a first-order correction in ζ if any should be needed. For instance, the interfacial temperature can be written

$$\theta_s = \theta_{1,z=0} + \beta_1 \zeta. \tag{10}$$

Continuity of velocity requires that

$$W_1 = W_2, \tag{11a}$$

but we have
$$\partial\zeta/\partial t = n\zeta = w,$$

so that
$$n\zeta_0 = W. \tag{11b}$$

For $n = 0$, (11a) and (11b) obviously require

$$W_1 = W_2 = 0. \tag{11c}$$

Also
$$U_1 = U_2, \quad V_1 = V_2. \tag{12a}$$

From equation (4), these lead to

$$dW_1/dz = dW_2/dz. \tag{12b}$$

For continuity of temperature, we must take

$$\Theta_1 + \beta_1 \zeta_0 = \Theta_2 + \beta_2 \zeta_0, \tag{13}$$

and for continuity of heat flux

$$k_1 \frac{d\Theta_1}{dz} = k_2 \frac{d\Theta_2}{dz}. \tag{14a}$$

But, in the unperturbed state,

$$k_1 \beta_1 = k_2 \beta_2;$$

hence
$$\frac{1}{\beta_1}\frac{d\Theta_1}{dz} = \frac{1}{\beta_2}\frac{d\Theta_2}{dz}. \tag{14b}$$

For tangential stress, the surface divergence of the continuity condition is

$$\nabla_{\text{II}}^2 \sigma = \mu_2\left(\nabla_{\text{II}}^2 w_2 - \frac{\partial^2 w_2}{\partial z^2}\right) - \mu_1\left(\nabla_{\text{II}}^2 w_1 - \frac{\partial^2 w_1}{\partial z^2}\right), \tag{15a}$$

where σ is the surface tension. Let σ vary in accordance with

$$\sigma = \sigma_0(1 - \epsilon\theta). \tag{15b}$$

Effects of surface viscosity and surface elasticity are not considered. With the surface temperature as given by equation (10), it follows that

$$\epsilon\sigma_0 k^2(\Theta_1 + \beta_1 \zeta_0) = \mu_1\left(\frac{d^2 W_1}{dz^2} + k^2 W_1\right) - \mu_2\left(\frac{d^2 W_2}{dz^2} + k^2 W_2\right). \tag{15c}$$

Finally, for the normal stress

$$(p_2 - p_1) + (\rho_1 - \rho_2) g\zeta + 2\mu_1 \frac{\partial w_1}{\partial z} - 2\mu_2 \frac{\partial w_2}{\partial z} = \sigma_0 \nabla_{\text{II}}^2 \zeta. \tag{16a}$$

In combination with the foregoing equations, this yields

$$\mu_2 \frac{d^3 W_2}{dz^3} - \mu_1 \frac{d^3 W_1}{dz^3} + 3(\mu_1 - \mu_2)\frac{dW_1}{dz} + (\rho_1 - \rho_2) g\zeta_0 = -\sigma_0 k^2 \zeta_0. \tag{16b}$$

The specification of the problem is completed by assuming that both phases are bounded by perfectly conducting rigid surfaces. Thus, at $z = d_2$

$$\Theta_2 = 0, \tag{17}$$

$$W_2 = 0, \tag{18}$$

and since $U_2 = V_2 = 0$, by continuity

$$dW_2/dz = 0. \tag{19}$$

Similarly, at $z = -d_1$

$$\Theta_1 = 0, \tag{20}$$

$$W_1 = 0, \tag{21}$$

$$dW_1/dz = 0. \tag{22}$$

The characteristic-value problem is now well posed and is seen to be simple in principle. Its solution proceeds in the usual tedious manner, leading to the following

$$\begin{aligned} N_M \Bigg\{ 1 - \frac{\kappa_1}{d_1}\frac{d_2}{\kappa_2}\frac{F_1(kd_1)}{F_1(kd_2)} - \frac{8N_{CR}}{N_G+(kd_1)^2} G_1(kd_1)\left[1+\frac{\tanh kd_1}{\tanh kd_2}\right] \\ \times \left[1-\frac{\mu_2}{d_2^2}\frac{d_1^2}{\mu_1}\frac{G_2(kd_1)}{G_2(kd_2)} + (kd_1)^2\left(1-\frac{\mu_2}{\mu_1}\right)G_2(kd_1)\right]\Bigg\} \\ = 8F_2(kd_1)\left[1+\frac{\beta_1}{\beta_2}\frac{\tanh kd_1}{\tank kd_2}\right]\left[1+\frac{\mu_2}{d_2}\frac{d_1}{\mu_1}\frac{F_3(kd_1)}{F_3(kd_2)}\right], \end{aligned} \tag{23}$$

where

$$F_1(\xi) = \frac{(1-(1/\xi^2)\sinh^2\xi)\sinh\xi}{\cosh\xi-(1/\xi^3)\sinh^3\xi},$$

$$F_2(\xi) = \frac{(1-(1/\xi)\sinh\xi\cosh\xi)\cosh\xi}{\cosh\xi-(1/\xi)^3\sinh^3\xi},$$

$$F_3(\xi) = \frac{1-(1/\xi^2)\sinh^2\xi}{1-(1/\xi)\sinh\xi\cosh\xi},$$

$$G_1(\xi) = \frac{\cosh\xi\sinh^2\xi}{\cosh\xi-(1/\xi^3)\sinh^3\xi},$$

$$G_2(\xi) = \frac{1-(1/\xi^2)\sinh^2\xi}{\sinh^2\xi}.$$

Of the dimensionless groups, N_M is the Marangoni number, N_{CR} has been named the crispation group by Scriven & Sternling (1964), and N_G is that group which occurs so frequently in problems involving both gravity waves and capillary ripples. Some authors refer to this last group as the Weber number. Specifically

$$N_M = \frac{\epsilon\sigma_0\beta_1 d_1^2}{\mu_1\kappa_1},$$

$$N_{CR} = \frac{\mu_1\kappa_1}{\sigma_0 d_1},$$

$$N_G = \frac{(\rho_1-\rho_2)gd_1^2}{\sigma_0}.$$

If the upper phase is of infinite depth, as in the case examined by Pearson, then equation (23) becomes

$$N_M\left\{1-\frac{\kappa_1}{\kappa_2}\frac{F_1(kd_1)}{kd_1}-\frac{8N_{CR}}{N_G+(kd_1)^2}G_1(kd_1)\left[\frac{(1+\tanh kd_1)(kd_1)^2}{\sinh^2 kd_1}\right]\right\}$$
$$=8F_2(kd_1)\left[1+\frac{\beta_1}{\beta_2}\tanh kd_1\right]\left[1+\frac{\mu_2}{\mu_1}kd_1F_3(kd_1)\right]. \quad (24)$$

3. Discussion

Physical interpretation

The formal process carried out above is roughly equivalent to posing and answering the following question: 'If mutually compatible temperature and velocity perturbations are introduced, then what must be the size and magnitude of β if these disturbances are to be maintained by the resulting perturbation in the tangential stress?' In short, equation (15*c*) is the key boundary condition. For this reason, the final results, equations (23) and (24), are given in a form which exactly parallels equation (15*c*). The first two terms on the left-hand side are proportional to the temperature perturbation at $z=0$; i.e. if $\beta_1=\beta_2$, then they represent the net effect of convection and diffusion. The third term is proportional to $\beta_1\zeta_0$ and is due solely to the action of surface waves. The right-hand side is obviously proportional to the sum of the viscous tractions which are applied to the interface. In order to examine the relative importance of these processes, it is convenient to examine the limiting cases of very short wavelengths and of very long wavelengths; that is, $kd_1\to\infty$ and $kd_1\to 0$.

Large wave-number

For $kd_1\to\infty$, equations (23) and (24) take the same form

$$N_M\left(1-\frac{\kappa_1}{\kappa_2}\right)\to 8\left(1+\frac{\beta_1}{\beta_2}\right)\left(1+\frac{\mu_2}{\mu_1}\right)(kd_1)^2 \quad (25)$$

and
$$W_1/V_s\to\frac{z}{d_1}\exp(kz),\quad W_2/V_s\to\frac{z}{d_1}\exp(-kz), \quad (26)$$

$$\frac{\Theta_1}{\beta_1 d_1}\to\frac{1}{4}\frac{1}{kd_1}\left[\left(\frac{z}{d_1}\right)^2-\frac{1}{kd_1}\left(\frac{z}{d_1}\right)+\frac{\beta_2}{\beta_1+\beta_2}\frac{1}{(kd_1)^2}\left(1-\frac{\kappa_1}{\kappa_2}\right)\right]\frac{V_s d_1}{\kappa_1}\exp(kz),$$

$$\frac{\Theta_2}{\beta_1 d_1}\to-\frac{1}{4}\frac{\kappa_1\beta_2}{\kappa_2\beta_1}\frac{1}{kd_1}\left[\left(\frac{z}{d_1}\right)^2+\frac{1}{kd_1}\left(\frac{z}{d_1}\right)+\frac{\beta_1}{\beta_1+\beta_2}\frac{1}{(kd_1)^2}\left(1-\frac{\kappa_1}{\kappa_2}\right)\right]\frac{V_s d_1}{\kappa_1}\exp(-kz),$$

where V_s is an arbitrary scale velocity. Since $kd_1\to\infty$ states that the transverse scale of the disturbance is very much less than the fluid depth, both phases are effectively infinitely deep. It may be surprising, therefore, that d_1 appears in each of the above equations. However, the definition of N_M is such that d_1 appears to the same power on both sides of equation (25). Similarly, in equation (26) the role of d_1 is one of units alone and results from using a scale velocity rather than an arbitrary time scale. As expected, equation (25) is equivalent to the condition obtained by Sternling & Scriven (1959) for the existence of a stationary marginal disturbance when both phases are infinitely deep, except that surface viscosity is not considered here and the notation is rather different. In this limit, energy transfer is largely by convection and lateral diffusion, diffusion in the direction normal to the interface being of secondary importance. Since convection is absent at the interface ($w = 0$ at $z = 0$), it follows that the temperature perturbation at $z = 0$ must be associated with this secondary effect. Hence, as shown above, the temperature perturbation at the interface varies as $(kd_1)^{-2}$ and is therefore two orders of magnitude smaller than the temperature perturbations occurring in the bulk of either phase. Even then, it depends on the asymmetry introduced via the difference in the thermal diffusivities.

As shown by Scriven & Sternling (1964), surface deformation plays no role whatsoever in this limit. For comparison with the limiting forms given in equation (26), the wave amplitude is given below

$$\frac{\zeta_0}{d_1} \to 8N_{CR}\left[1-\frac{\mu_2}{\mu_1}\left(\frac{d_2}{d_1}\right)^2 \exp\{2k(d_1-d_2)\}\right]\frac{V_s d_1}{\kappa_1}\exp\{(-2kd_1)\}. \tag{27}$$

Small wave-number, both phases of finite depth

By contrast, for $kd_1 \to 0$, the effects of depth are paramount, and equations (23) and (24) do not lead to the same result. For the case in which both phases are of finite depth, a first-order approximation to each term in equation (23) leads to

$$N_M\left\{\frac{\kappa_1}{\kappa_2}\left(\frac{d_2}{d_1}\right)^2 - 1 + \frac{120}{(\kappa d_1)^2}\frac{N_{CR}}{N_G}\left[1+\frac{d_1}{d_2}\right]\left[1-\frac{\mu_2}{\mu_1}\left(\frac{d_1}{d_2}\right)^2\right]\right\} \to \frac{80}{(kd_1)^2}\left[1+\frac{\beta_1 d_1}{\beta_2 d_2}\right]\left[1+\frac{\mu_2 d_1}{\mu_1 d_2}\right]. \tag{28}$$

Clearly, in the strict limit as $kd_1 \to 0$, the waves are of the gravity type (N_{CR}/N_G does not contain σ) and they are of overwhelming importance. The corresponding forms for the temperature perturbation and for the wave amplitude are

$$\left.\begin{aligned}
\frac{\Theta_1}{\beta_1 d_1} &\to -\frac{\beta_1 d_1}{\beta_1 d_1+\beta_2 d_2}\left(1-\frac{\beta_2}{\beta_1}\right)\left(\frac{z}{d_1}+1\right)\frac{\zeta_0}{d_1},\\
\frac{\Theta_2}{\beta_2 d_2} &\to -\frac{\beta_1 d_1}{\beta_1 d_1+\beta_2 d_2}\left(1-\frac{\beta_2}{\beta_1}\right)\left(\frac{z}{d_2}-1\right)\frac{\zeta_0}{d_1},\\
\frac{\zeta_0}{d_1} &\to 2\frac{N_{CR}}{N_G}\left[1-\frac{\mu_2}{\mu_1}\left(\frac{d_1}{d_2}\right)^2\right]\frac{V_s d_1}{\kappa_1}.
\end{aligned}\right\} \tag{29}$$

The temperature profiles are due solely to the waves, and are those simple solutions of the one-dimensional conduction equation which are required to maintain continuity of temperature and of heat flux at the interface. The situation is most clearly visualized when $\beta_1 = \beta_2 = \beta$ so that

$$\Theta_1 = \Theta_2 = 0.$$

Then the variation in temperature along the interface is simply

$$\theta_s \to \beta\zeta. \tag{30}$$

On the other hand, the value of N_{CR}/N_G may be so small as to make the third term of equation (28) unimportant at any wave-number of sufficient magnitude to be of interest. In this event, convection and diffusion are again of major significance and these processes are greatly altered by the relative depth. If N_{CR} is set equal to zero for definiteness, then the appropriate limiting forms are

$$\left.\begin{aligned}
&\frac{W_1}{V_s} \to \frac{1}{3}\frac{z}{d_1}\left(\frac{z}{d_1}+1\right)^2 (kd_1)^2,\\
&\frac{W_2}{V_s} \to \frac{1}{3}\frac{z}{d_1}\left(\frac{z}{d_2}-1\right)^2 (kd_1)^2,\\
&\frac{\Theta_1}{\beta_1 d_1} \to \frac{1}{60}\left(\frac{z}{d_1}+1\right)\left\{\frac{\beta_2 d_2}{\beta_1 d_1+\beta_2 d_2}\left[1-\frac{\kappa_1}{\kappa_2}\left(\frac{d_2}{d_1}\right)^2\right]\right.\\
&\qquad\left.+\frac{z}{d_1}\left[\left(\frac{z}{d_1}\right)^3+\frac{7}{3}\left(\frac{z}{d_1}\right)^2+\frac{z}{d_1}-1\right]\right\}(kd_1)^2\frac{V_s d_1}{\kappa_1},\\
&\frac{\Theta_2}{\beta_2 d_2} \to \frac{1}{60}\frac{\kappa_1}{\kappa_2}\left(\frac{d_2}{d_1}\right)^2\left(\frac{z}{d_2}-1\right)\left\{\frac{\beta_1 d_1}{\beta_1 d_1+\beta_2 d_2}\left[1-\frac{\kappa_2}{\kappa_1}\left(\frac{d_1}{d_2}\right)^2\right]\right.\\
&\qquad\left.+\frac{z}{d_2}\left[\left(\frac{z}{d_2}\right)^3-\frac{7}{3}\left(\frac{z}{d_2}\right)^2+\frac{z}{d_2}+1\right]\right\}(kd_1)^2\frac{V_s d_1}{\kappa_1}.
\end{aligned}\right\} \tag{31}$$

In this case, diffusion in the direction normal to the interface is a first-order process with both convection and diffusion depending on the ratio d_2/d_1, so that the significant grouping is

$$\frac{\kappa_1}{\kappa_2}\left(\frac{d_2}{d_1}\right)^2-1.$$

Unlike the situation for $kd_1 \to \infty$, the temperature perturbation here increases with kd_1 and a minimum for N_M may therefore be expected in the neighbourhood of $kd_1 = 1$ (at least if $N_{CR} = 0$).

Small wave-number, upper phase infinitely deep

In the event that $d_2 = \infty$, only the lower phase has a prescribed length scale. In the two limiting cases considered above, length scales were prescribed for both phases or for neither phase; so the present case should exhibit some of the features contained in each of the above. Using a first-order approximation to each term in equation (24) leads to

$$N_M\left[(kd_1)^2-5\frac{\kappa_1}{\kappa_2}+120\frac{N_{CR}}{N_G}\right] = 80. \tag{32}$$

The perturbation quantities are given by

$$\left.\begin{aligned}
&\frac{W_1}{V_s} \to \frac{1}{3}\frac{z}{d_1}\left(\frac{z}{d_1}+1\right)^2 (kd_1)^2,\\
&\frac{W_2}{V_s} \to \frac{1}{3}\frac{z}{d_1}\{\exp(-kz)\}(kd_1)^2,\\
&\frac{\Theta_1}{\beta_1 d_1} \to -\frac{1}{12}\left(\frac{z}{d_1}+1\right)\frac{\kappa_1}{\kappa_2}\frac{V_s d_1}{\kappa_1},\\
&\frac{\Theta_2}{\beta_1 d_1} \to -\frac{1}{12}\left(1+\frac{\beta_2}{\beta_1}\frac{z}{d_1}\right)\{\exp(-kz)\}\left(\frac{\kappa_1}{\kappa_2}\frac{V_s d_1}{\kappa_1}\right)+\left(1-\frac{\beta_2}{\beta_1}\right)\frac{\zeta_0}{d_1}\{\exp(-kz)\},\\
&\frac{\zeta_0}{d_1} \to \frac{2N_{CR}}{N_G}\frac{V_s d_1}{\kappa_1}.
\end{aligned}\right\} \tag{33}$$

In agreement with the postulate that this result would be a mixture of previous results, both convection and surface waves are found to be effective in causing a temperature perturbation in the upper phase, and this is reflected in the equation for the neutral curve. The lower phase is passive and merely responds to the temperature perturbation imposed on the interface by convection in the upper phase. Hence, the detailed dynamics of the upper phase may never be ignored at very small wave-numbers.

For many practical cases in which $d_2 = \infty$, N_{CR}/N_G and κ_1/κ_2 are extremely small, so equation (33) is of little interest at reasonable wave-numbers. If both of these parameters are set identically equal to zero, the temperature perturbations for $kd_1 \to 0$ are

$$\left.\begin{aligned} \frac{\Theta_1}{\beta_1 d_1} &\to \frac{1}{60}\left[\left(\frac{z}{d_1}\right)^5 + \frac{10}{3}\left(\frac{z}{d_1}\right)^4 + \frac{10}{3}\left(\frac{z}{d_1}\right)^3 + 1\right](kd_1)^2 \frac{V_s d_1}{\kappa_1}, \\ \frac{\Theta_2}{\beta_1 d_1} &\to \frac{1}{60}\{\exp(-kz)\}(kd_1)^2 \frac{V_s d_1}{\kappa_1}. \end{aligned}\right\} \tag{34}$$

In this case, the temperature perturbation is associated with convection in the lower phase and the upper phase is passive. Similarly, for $kd_1 \to \infty$, an examination of equation (26) shows that the temperature perturbation in the upper phase is again passive if $\kappa_1/\kappa_2 \ll 1$. Behaviour of this sort is implied by Pearson (1958) and by Scriven & Sternling (1964) in their use of a heat-transfer coefficient at the interface. These results show that the assumption is likely to be quite adequate, provided that very small wave-numbers are of no interest, that $\kappa_1/\kappa_2 \ll 1$, and that $N_{CR}/N_G \ll 1$.

Further comments on surface waves

Scriven & Sternling (1964) point out that if ζ_0 and $(dW_1/dz)_{z=0}$ have the same sign, then there is an upflow under depressions in the interface and a downflow beneath elevations. They further showed that within the confines of their analysis, the upflow is always beneath the depressions if the instability is driven by surface-tension gradients. Since the opposite is true for instabilities driven by buoyancy forces, this provides a simple experimental criterion for distinguishing between the two. For the analysis employed here, a convenient non-dimensional form of this criterion is

$$\begin{aligned}[N_G + (kd_1)^2]\frac{\zeta_0}{d_1}\Big/\frac{d_1^2}{\kappa_1}\left(\frac{dW_1}{dz}\right)_{z=0} \\ = \left(2\Big/\frac{1}{(kd_1)^2}\sinh^2 kd_1 - 1\right) - \left(2\frac{\mu_2}{\mu_1}\Big/\frac{1}{(\kappa d_2)^2}\sinh^2 kd_2 - 1\right).\end{aligned} \tag{35}$$

When $d_2 = \infty$, the second term on the right vanishes and the left-hand side is then positive definite. Thus, the result of Scriven & Sternling is unchanged by the inclusion of gravity waves, provided that

$$[N_G + (kd_1)^2] > 0.$$

If d_1 and d_2 are both finite, a simple criterion is not generally possible; but since the right-hand side can have no more than one zero, a sufficient condition may be determined by examining the extremities $k \to 0$ and $k \to \infty$. This approach shows that the sign is determined by the following groups

$$1-\frac{\mu_2}{\mu_1}\left(\frac{d_1}{d_2}\right)^2; \quad 1-\frac{d_1}{d_2}.$$

If both of these are positive, there is an upflow beneath surface depressions and, similarly, the upflow is beneath elevations if both are negative; again provided that

$$[N_G+(kd_1)^2] > 0;$$

otherwise the result is reversed. If one is positive and the other negative, equation (35) must be evaluated at the wave-number of interest.

The role of waves on inclined or inverted surfaces deserves special mention. If in all of the preceding equations, g is replaced by $g\cos\phi$, where ϕ is defined by $-\mathbf{g}.\mathbf{k} = g\cos\phi$ ($\mathbf{k}$ is the unit vector in the z direction) then these cases are formally included. However, on inclined surfaces there exists a mean flow in the unperturbed state and the above analysis is likely to fail unless

$$\frac{\overline{U}d}{\nu}kd \ll 1 \quad \text{and} \quad \frac{\overline{U}d}{\kappa}kd \ll 1,$$

where $\overline{U}$ is a velocity scale appropriate to the mean flow. Commonly, the phase adjacent to the surface will be rather viscous compared with the other phase and the constraints become

$$\{(g\sin\phi)\,d^3/\nu^2\}\,(kd) \ll 1 \quad \text{and} \quad \{(g\sin\phi)\,d^3/\nu\kappa\}\,(kd) \ll 1.$$

Another aspect is presented when $N_G < 0$, as would occur on inverted surfaces. In this case, equation (23) would seem to imply that Rayleigh–Taylor instability can be stabilized by the Marangoni effect, but this conclusion is unwarranted. The Rayleigh–Taylor problem is singular at the marginal condition $n = 0$. Thus the analysis describes the effect of gravity on stationary marginal instability driven by surface-tension gradients, but it contains no information with regard to the effect of surface-tension gradients upon gravitational instability. This provides an explanation for the manner in which N_G enters equation (23); namely that at large absolute values of N_G, the wave amplitude must be small if a marginal state is to exist. It does not deny the possibility of instability by another mechanism.

Finally, it is apparent that surface waves will not always play a significant role and it would be useful to have a criterion by which these cases could be recognized. This matter involves both the sign (direction of transfer) and the magnitude of the Marangoni number as separate matters, and there seems to be no simpler procedure than judicious use of the limiting formulae given above.

4. Numerical computations for sample cases

First consider a thin liquid layer which is horizontal and exposed to the atmosphere. The stability characteristics are governed by equation (24) which requires specification of five parameters. Values for four common liquids in contact with air at 20 °C are given in table 1. It is assumed that the liquid is

0·05 cm deep. Evidently, those terms of equation (28) which are connected with the quantities in the last three columns will play quite unimportant roles. By contrast, the importance of the term containing N_{CR} and N_G will vary widely; the

	N_{CR}	N_G	κ_1/κ_2	μ_2/μ_1	β_1/β_2
Water	4×10^{-6}	0·03	0·007	2×10^{-2}	0·04
Mercury	3×10^{-5}	0·07	0·2	1×10^{-2}	0·003
Glycerin	4×10^{-3}	0·05	0·005	1×10^{-5}	0·09
Silicone oil*	1·0	0·11	0·005	2×10^{-7}	0·16

* μ = 100,000 cp.

TABLE 1

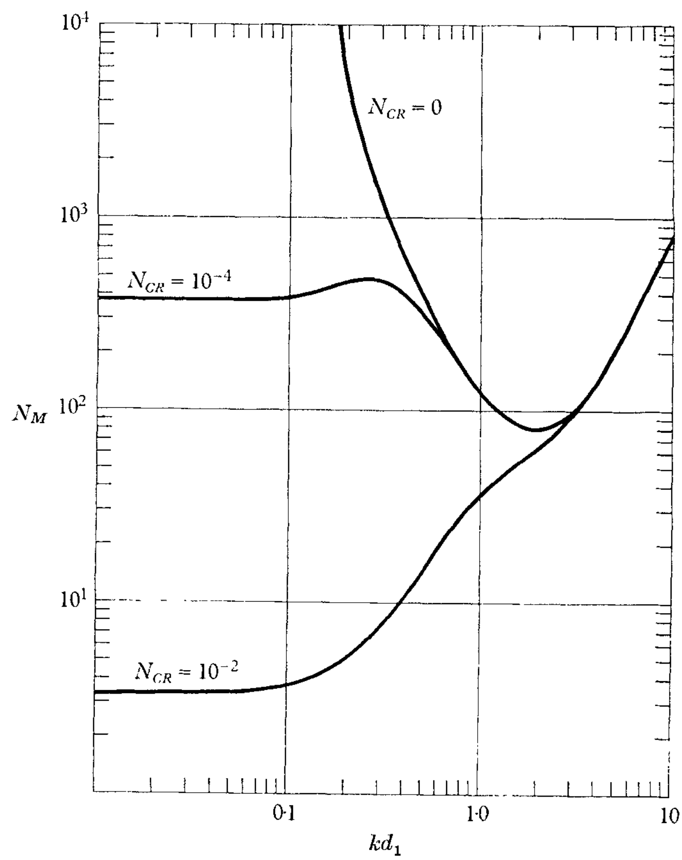

FIGURE 1. Neutral stability curves, upper phase infinitely deep.

wave phenomena being most important for very thin layers of very viscous liquids. For definiteness, figure 1 is based on

$$\mu_2/\mu_1 = \beta_2/\beta_1 = 0, \quad \kappa_1/\kappa_2 = 0{\cdot}005, \quad N_G = 0{\cdot}05.$$

The values of N_{CR} are given in the figure. If $N_{CR} = 0$, the results reproduce Pearson's conclusion that the critical value of the Marangoni number is about

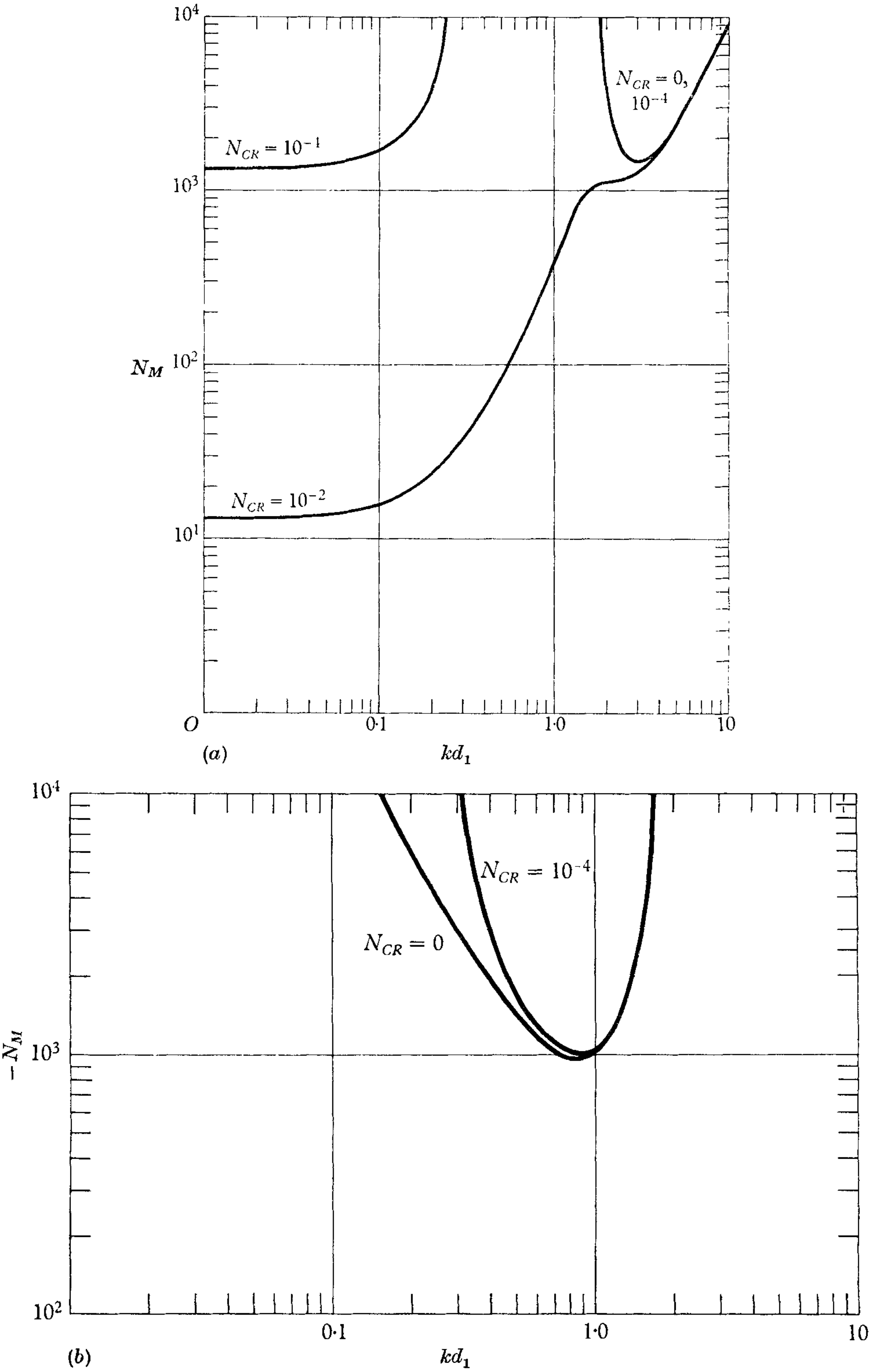

FIGURE 2. Neutral stability curves: (*a*) Positive half-plane, both phases finite; (*b*) negative half-plane, both phases finite.

80 and that it occurs at a wave-number of approximately 2·0. However, the very low wave-number portion of the curve lies in the negative half-plane and is not shown. This behaviour indicates that with liquids of low viscosity (and $\kappa_1/\kappa_2 > 0$) instability is possible for transfer in either direction. For larger values of N_{CR} ($> 10^{-5}$ in this case) surface waves become dominant at low values of kd_1 and the neutral curve lies entirely in the positive half-plane. At still higher values of N_{CR}, the entire character of the results begins to change and for $N_{CR} = 10^{-3}$ the minimum is extremely shallow. In this situation, classical excitation of the 'most unstable mode' is extremely unlikely. However, it should be noted that for many physical situations, the approximation $N_{CR} = 0$ is quite adequate for determining the critical value of N_M.

A rather different situation exists when the depth and properties of the two phases are similar. Let

$$\frac{\kappa_1}{\kappa_2} = \frac{d_1}{d_2} = \frac{\mu_1}{\mu_2} = \frac{1}{2}, \quad \frac{\beta_1}{\beta_2} = 1, \quad N_G = 0{\cdot}05.$$

A comparison of the limiting forms contained in equations (25) and (28) shows that for this choice of values, N_M is positive for $kd_1 \to \infty$; but for $kd_1 \to 0$, N_M is negative if $N_{CR} = 0$ and positive if $N_{CR} \neq 0$. Obviously, the temperature perturbation caused by convection and diffusion at low wave-numbers is out of phase with the perturbations which result from the other two limiting cases. Again then, instability is a possibility for transfer in either direction. For any particular value of N_{CR}, the full neutral curve is given by equation (23). The positive half-plane is shown in figure 2 (*a*) and the negative half plane is given in figure 2 (*b*); this awkward device being necessitated by the use of logarithmic plotting.

For $N_{CR} = 0$, surface waves do not occur and only two mechanisms are operative, leading to one curve in each half plane, as shown. For $N_{CR} = 10^{-4}$, all three mechanisms are significant. At very low wave-numbers, surface waves are dominant and lead to positive values of N_M. At somewhat higher wave-numbers, there remains a curve in the lower half-plane; but it is somewhat modified by the effects of surface deformation. At still higher wave-numbers, the result for $N_{CR} = 0$ is essentially unchanged. Finally, for $N_{CR} = 10^{-2}$, the entire behaviour is profoundly influenced by surface waves, the minimum is very shallow, and instability is possible only with positive values of N_M.

5. Conclusion

The above analysis achieves the objectives set for it in the introduction and provides numerical results which are broadly consistent with experimental observations. However, the oscillatory modes have not been considered and their role may be significant, particularly with regard to the question of instability for transfer in either direction.

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