

## On convection cells induced by surface tension

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### SUMMARY

A mechanism is proposed by which cellular convective motion of the type observed by H. Bénard, which hitherto has been attributed to the action of buoyancy forces, can also be induced by surface tension forces. Thus when a thin layer of fluid is heated from below, the temperature gradient is such that small variations in the surface temperature lead to surface tractions which cause the fluid to flow and thereby tend to maintain the original temperature variations. A small disturbance analysis, analogous to that carried out by Rayleigh and others for unstable density gradients, leads to a dimensionless number  $B$  which expresses the ratio of surface tension to viscous forces, and which must attain a certain minimum critical value for instability to occur. The results obtained are then applied to the original cells described by Bénard, and to the case of drying paint films. It is concluded that surface tension forces are responsible for cellular motion in many such cases where the criteria given in terms of buoyancy forces would not allow of instability.

### INTRODUCTION

Experiments have shown\* that drying paint films often display steady cellular circulatory flow of the same type as that observed in the case of fluid layers heated from below. In the latter case (that of the so-called Bénard cells†) the motion can usually be ascribed to the instability of the density gradient that would be present if the fluid were stationary. This cannot be the mechanism causing the flow in the former case, since the circulation is observed whether the free surface is made the underside or the top side of the paint layer, that is, even if the gravity vector is effectively reversed. Instead it will be shown that surface tension forces are sufficient to cause instability and are probably responsible for many of the cellular patterns that have been observed in cooling fluid layers with at least one free surface.

\* These were brought to my notice by Dr R. Cousens of the Research Department of I.C.I. Ltd., Paints Division, who put forward the basic idea of a phenomenon dominated by surface tension, and pointed out many of the relevant physical factors that are introduced in this paper. The analysis given stems largely from his earlier investigation.

† For a description of these see, for example, Prandtl (1952).

The essential physical features of the phenomenon spring from the fact that surface tension—in most fluids at most temperatures—is a monotone decreasing function of temperature and in the case of two constituents, a function of relative concentration. Thus if the free surface of a fluid layer is not at a uniform temperature or of uniform relative concentration, effective surface tractions are present and motion within the fluid must be expected to take place. This idea is a very old one and has been used in a qualitative sense by several authors to explain many otherwise puzzling phenomena.

If we consider for a moment the case of a homogeneous liquid layer cooling by radiation from the upper free surface and heated at the lower fixed surface, a simple qualitative explanation of the existence of steady cellular motion can be given. In the centre of the cells warm fluid is drawn towards the surface; this spreads across the surface, cooling as it does so until it reaches the edges of the cell where it descends towards the lower surface of the layer, and is there warmed. The decrease in temperature across the surface from centre to edge of cell is accompanied by an increase in surface tension and hence by surface tractions that tend to maintain the circulation. The amplitude of the motion will of course be determined by the physical parameters that characterize the particular fluid in question and by the temperature gradients involved. The driving force for the motion is provided by the flow of heat from the heated lower surface to the cooled upper surface.

As in the case of Bénard cells induced by density variations, certain minimum requirements must be satisfied in order that cells may develop under the action of surface tension forces. These are examined analytically by means of small-disturbance theory (analogous to that developed by Rayleigh, Jeffreys and others for buoyancy forces) in the following section. Critical values for a certain dimensionless number are derived, corresponding to the case of marginal stability. Associated with these critical values are critical wave-numbers which define the size of the marginally-stable cells.

In the concluding section an application of the results obtained to experimental observations on thin liquid films confirms the relevance of surface tension forces in many cases of instability. Somewhat surprisingly, it seems almost certain that many of the cells observed in molten spermaceti by Bénard himself were in fact caused by surface tension forces.

#### SMALL DISTURBANCE ANALYSIS

A small disturbance analysis will now be carried out for the particular case of an infinite homogeneous liquid layer of uniform thickness whose lower surface is in contact with a fixed plane and whose upper surface is free. The only physical quantities that are assumed to vary within the fluid are the temperature, the surface tension, which is regarded as a function of temperature only, and the rate of heat loss from the surface, also a function of temperature only. These are in fact the dominant factors in the cases

observed and a discussion of the relevance of this idealization will be given where required. For the case of a drying paint film, temperature variations can be replaced by concentration variations; the same analysis applies with only trivial redefinition of the parameters involved.

The treatment adopted will be closely parallel to that developed by Rayleigh (1916), Jeffreys (1926), Low (1929), and Pellew & Southwell (1940), for the case of density-induced instability, and many of their arguments will be taken over directly. (A good concise account is given by Lin (1955, §7.3).)

We start by defining the steady-state (unstable) equilibrium conditions that are to be perturbed, and we consider therefore a liquid layer whose bottom surface is given by the plane  $y = 0$ , whose free surface is given by the plane  $y = d$ , and whose temperature is a function of  $y$  only. If

$Q_0$  = rate of heat loss per unit area from the upper free surface in the unperturbed system,

$k$  = coefficient of heat conduction in the liquid, and

$T_{0B}$  = steady-state temperature of the lower surface in the unperturbed system,

then the unperturbed temperature distribution  $T_0$  in the liquid will be given by

$$T_0 = T_{0B} - \beta y, \quad (1)$$

where

$$Q_0 = k\beta, \quad (2)$$

since the rate of supply of heat to the surface from the liquid must equal the rate of loss of heat from the surface to its upper environment. In the relation (2), we suppose the magnitude of  $Q_0$  to be defined by the upper surface temperature  $T_{0S}$  and the nature of the environment; the method of heat transfer may be conduction, convection or radiation, or any combination of the three. We shall assume that the environment exerts no mechanical forces on the liquid, and serves only as a heat sink.

The temperature  $T_{0B}$  will itself depend on the nature of the liquid, the supply of heat to the bottom surface and the (equal) loss of heat from the top surface. However, we are not concerned here with a thorough analysis of the mechanism of heat transfer to and from the liquid layer, though these matters become relevant in the investigation of any particular physical phenomenon. Equations (1) and (2) provide sufficient information for our immediate purposes.

Next, we superpose an infinitesimal disturbance and linearize the equations of motion and heat conduction. We write

$\nu$  = kinematic viscosity of the liquid,

$\kappa$  = thermometric conductivity of the liquid,

$\rho$  = density of the liquid,

$t$  = time,

$v$  = velocity (supposed small) in the  $y$ -direction,

$S$  = surface tension of the liquid,

$Q$  = rate of heat loss per unit area from the upper free surface (now a function of  $x$  and  $z$ ),

$T$  = temperature distribution in the liquid (a function of  $x$ ,  $y$  and  $z$ ),

$T' = T - T_0$  is thus the perturbation temperature (also supposed small), and we write  $T'_s$  for its value at the surface.

The equations of motion and heat conduction become

$$\left(\frac{\partial}{\partial t} - \nu \nabla^2\right) \nabla^2 v = 0, \quad (3)$$

$$\left(\frac{\partial}{\partial t} - \kappa \nabla^2\right) \nabla^2 T' = \beta v. \quad (4)$$

It will be noted that the equation for  $v$  contains no buoyancy term and is thus much simpler than in the case considered by Rayleigh. We also write\*

$$S = S_0 - \sigma T'_s \quad (5)$$

where  $-\sigma = (\partial S / \partial T)_{T=T_{0S}}$  represents the rate of change of surface tension with temperature, evaluated at temperature  $T_{0S}$ , with  $S_0 = S(T_{0S})$ , and

$$Q = Q_0 + q T'_s, \quad (6)$$

where  $q = (\partial Q / \partial T)_{T=T_{0S}}$  represents the rate of change with temperature of the rate of loss of heat per unit area from the upper surface to its upper environment.  $Q_0$  is as defined before.  $\sigma$  is a function of the liquid only, while  $q$  is likely to be affected in a complicated way by the surface-environment relations. The relations (5) and (6) for  $S$  and  $Q$  are taken to depend linearly on  $T'$  because we are considering an infinitesimal disturbance theory and therefore need only the first two terms in a Taylor expansion.

The boundary conditions on the velocity are

$$v = \frac{\partial v}{\partial y} = 0, \quad (7)$$

when  $y = 0$ ,

$$v = 0, \quad \rho \nu \frac{\partial^2 v}{\partial y^2} = \sigma \nabla_1^2 T', \quad (8)$$

when  $y = d$ , where

$$\nabla_1^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}.$$

The second relation in (7) follows directly from the continuity condition. The necessity for the first of the relations (8), particularly in the case of neutral stability, is explained by Jeffreys. The second relation (8) equates the change in surface tension due to temperature variations across the

\* The boundary conditions (including (5) and (6)) are of crucial importance; by means of a suitable choice for these many physical phenomena may be very reasonably idealized. The aim in this account is not to provide an exhaustive description of these phenomena and their relevant idealizations, but rather to provide a general treatment that illustrates the fundamental surface tension mechanism and comprehends its many realizations. It is shown that the use of but three parameters suffices to describe the system.

surface to the shear stress experienced by the fluid at the surface, use being made of the continuity condition. The effect of the surface tension on the normal stress condition is ignored because its effects are small. (This same assumption is made in the conventional thermal convection problem.)

It is the boundary conditions on the temperature that need most careful explanation. It is worth considering in this respect the possible physical circumstances leading to the thermal equilibrium expressed by (1), (2), in order to understand the significance of the boundary conditions that will be applied to the perturbation temperature. The supply of heat to the bottom surface of the liquid may be from a material whose coefficient of heat conduction is either large or small compared with that of the liquid. If the boundary consists of a good conductor of large extent, then the temperature  $T_{0B}$  may be taken as a given fixed constant, and will lead, in the perturbed case, to the 'conducting' condition  $T' = 0$  at the lower boundary. If however, the bottom boundary of the liquid consists of a layer of a bad conductor itself in contact at its lower surface with a good conductor (for example, glass on metal), then the temperature gradient in the material bounding the liquid may be large compared with the temperature gradient in the liquid itself;  $T_{0B}$  will, in the steady unperturbed state, be a constant, though it will be determined by the thermal properties both of the badly-conducting solid and of the liquid, and of their respective thicknesses. A slight change in the bottom surface temperature will not affect the rate of heat conduction through the bad conductor by any appreciable amount. Hence the lower boundary condition on the perturbation temperature will be approximately  $\partial T'/\partial y = 0$ . This we shall define, illogically perhaps, but consistently with previous authors, as the 'insulating' boundary condition. The two cases chosen above are limiting cases of the general mixed boundary condition

$$T' = Y \frac{\partial T'}{\partial y}, \quad (9)$$

which we can assume applies, where  $Y$  is a constant depending on the thermal properties of boundary and liquid. By a suitable choice of materials all values of  $Y$  ranging from 0 to  $\infty$  may be obtained. For convenience we shall consider in detail only the two extreme values  $Y = 0$  and  $Y^{-1} = 0$ ; since we shall find that they do not lead to radically different results, an exhaustive solution for arbitrary values of  $Y$  will not be attempted. Because of some confusion which has arisen among previous authors it is worth pointing out that the case  $Y^{-1} = 0$  does not correspond *only* to a physically quasi-steady system in which the true insulating boundary condition,  $\partial T/\partial y = 0$ , strictly applies, but also to a strictly steady system in which the so-called 'insulating' boundary condition on the perturbation temperature is a limiting *approximation* to the exact boundary condition.

The balance between heat supply to and heat loss from the upper surface may exhibit similar characteristics. If, for simplicity, we consider a discrete jump in temperature as occurring at the free surface, then this

jump may be small or large compared with the drop in temperature across the liquid layer, depending on the efficiency of the processes for removing heat from the surface. Whatever the process, the equality

$$-k \frac{\partial T'}{\partial y} = qT' \quad (10)$$

must hold at  $y = d$ , using the relation (6) and the reasons given to justify the equality (2). If the temperature jump is large, then we expect  $q$  to be small, and vice versa. The particular value to be ascribed to  $q$  will depend on circumstances, and for this reason we shall retain it as a parameter in the subsequent analysis. It is worth noting that if  $q \rightarrow \infty$ , then we approach the 'conducting' boundary condition, and surface tension effects will not be present, whereas if  $q \rightarrow 0$ , we approach the 'insulating' boundary condition, as defined above, valid for perturbation of a strictly steady-state system.

A further application of this small-disturbance analysis to concentration gradients in a layer composed of a mixture of two liquids will show—if only by comparison with experiment—that predictions of instability are relevant for quasi-steady systems. If convection cells can be set up in a time small compared with that in which changes occur in the quasi-steady thermal gradient  $\beta$ , then the application of strict 'insulating' boundary conditions leads to meaningful results.

If we now introduce dimensionless variables

$$(\xi, \eta, \zeta) = \left( \frac{x}{d}, \frac{y}{d}, \frac{z}{d} \right), \quad \tau = \frac{t\kappa}{d^2}, \quad (11)$$

and suppose that

$$v = -\frac{\kappa}{d} F(\xi, \zeta) f(\eta) e^{\nu\tau}, \quad (12)$$

$$T' = \beta d F(\xi, \zeta) g(\eta) e^{\nu\tau}, \quad (13)$$

we find that

$$\frac{\partial^2 F}{\partial \xi^2} + \frac{\partial^2 F}{\partial \zeta^2} + \alpha^2 F = 0, \quad (14)$$

where  $\alpha$  is a dimensionless constant arising from the separation of variables; and that

$$[p - Pr(D^2 - \alpha^2)](D^2 - \alpha^2)f = 0, \quad (15)$$

$$[p - (D^2 - \alpha^2)]g = -f, \quad (16)$$

where  $D \equiv d/dy$  and  $Pr = \nu/\kappa$ . The particular choice of the forms (12), (13) for  $v$ ,  $T'$  is well explained by Pellew & Southwell (1940) who show that the constant  $\alpha$  is merely indicative of a periodic structure in the  $(\xi, \zeta)$ -plane. The shape of the cells associated with the solution obtained is not specified and a second-order theory would be required to select a particular cellular structure. Christopherson (1940) has given the solution of (14) for hexagonal cells.

The boundary conditions (7), (8) and (10) become\*

$$f(0) = f'(0) = 0; \quad f(1) = 0, \quad f''(1) = \alpha^2 B g(1), \quad g'(1) = -Lg(1); \quad (17)$$

where

$$B = \frac{\sigma\beta d^2}{\rho\nu k}, \quad (18)$$

and

$$L = \frac{qd}{k} \quad (19)$$

are dimensionless constants. Physically speaking, the number  $B$  is a dimensionless grouping of physical parameters expressing the relative importance of surface tension forces (caused by temperature variation) and of viscous forces, in any small disturbance responsible for both of them. The number  $L$  can be suitably interpreted in terms of the arguments given earlier with regard to relation (10).

As a last boundary condition, we have for the conducting case ( $Y = 0$  in (9)),

$$g(0) = 0, \quad (20)$$

and for the insulating case ( $Y^{-1} = 0$  in (9)),

$$g'(0) = 0. \quad (21)$$

The general boundary condition (9) would lead to the relation

$$g'(0) = Mg(0),$$

where  $M = Y/d$ , and although we shall not retain it as an independent parameter, we see that  $M$  forms with  $B$  and  $L$  a set of three parameters which suffice to describe the system for our purposes†.

In common with earlier workers, we look for solutions of the case of neutral stability when we put  $p = 0$ . Equations (15) and (16) become

$$(D^2 - \alpha^2)(D^2 - \alpha^2)f = 0, \quad (22)$$

$$(D^2 - \alpha^2)g = f. \quad (23)$$

The solution of (22), subject to the first three conditions (17), is

$$f = a \left( \sinh \alpha \eta + \frac{\alpha \cosh \alpha - \sinh \alpha}{\sinh \alpha} \eta \sinh \alpha \eta - \alpha \eta \cosh \alpha \eta \right), \quad (24)$$

and the solution of (23), subject to the last condition (17) and (20) or (21) becomes

$$g = a \left[ \frac{3}{4\alpha} \eta \cosh \alpha \eta + \frac{\alpha \cosh \alpha - \sinh \alpha}{4\alpha \sinh \alpha} \eta^2 \cosh \alpha \eta - \frac{1}{4} \eta^2 \sinh \alpha \eta - \frac{\alpha \cosh \alpha - \sinh \alpha}{4\alpha^2 \sinh \alpha} \eta \sinh \alpha \eta - \frac{\{(\alpha^2 \cosh^2 \alpha + \alpha \sinh \alpha \cosh \alpha + \sinh^2 \alpha) + L(\alpha^2 + \alpha \sinh \alpha \cosh \alpha + \sinh^2 \alpha)\}}{4\alpha^2 \sinh \alpha (\alpha \cosh \alpha + L \sinh \alpha)} \right] \times \sinh \alpha \eta \quad (25)$$

\* (') now denotes differentiation with respect to the single independent variable.

† It must be made clear that the evaluation of these three parameters in any physically observed circumstances is not necessarily easy; it is however a separate problem. A lengthy consideration of possible values to be expected, beyond that already given, would only obscure the explanation of the fundamental instability that is being analysed.

for the conducting case, and

$$g = a \left[ \frac{3}{4\alpha} \eta \cosh \alpha \eta + \frac{\alpha \cosh \alpha - \sinh \alpha}{4\alpha \sinh \alpha} \eta^2 \cosh \alpha \eta - \frac{1}{4} \eta^2 \sinh \alpha \eta - \frac{\alpha \cosh \alpha - \sinh \alpha}{4\alpha^2 \sinh \alpha} \eta \sinh \alpha \eta - \frac{3}{4\alpha^2} \sinh \alpha \eta - \left\{ \frac{(\alpha \cosh \alpha - \sinh \alpha)^2 + L(\alpha^2 + \alpha \sinh \alpha \cosh \alpha - 2 \sinh^2 \alpha)}{4\alpha^2 \sinh \alpha (\alpha \sinh \alpha + L \cosh \alpha)} \right\} \cosh \alpha \eta \right] \quad (26)$$

for the insulating case. Substitution into the fourth of the boundary conditions (17), namely the one involving both  $f$  and  $g$ , yields a relation between  $B$ ,  $L$  and  $\alpha$ . This is

$$B = \frac{8\alpha(\alpha \cosh \alpha + h \sinh \alpha)(\alpha - \sinh \alpha \cosh \alpha)}{(\alpha^3 \cosh \alpha - \sinh^2 \alpha)} \quad (27)$$

for the conducting case, and

$$B = \frac{8\alpha(\alpha \sinh \alpha + h \cosh \alpha)(\alpha - \sinh \alpha \cosh \alpha)}{(\alpha^3 \sinh \alpha - \alpha^2 \cosh \alpha + 2\alpha \sinh \alpha - \sinh^2 \alpha \cosh \alpha)} \quad (28)$$

for the insulating case. These are plotted in figures 1 and 2 for the various values of  $L$ . The curves obtained are neutral stability curves, and without repeating the analysis for  $p \neq 0$  it is clear which regions refer to growing disturbances and which to damped disturbances. All the curves asymptote to  $B = 8\alpha^2$  for large values of  $\alpha$ , whilst all display a critical (minimum) value of  $B$  corresponding to a particular value for  $\alpha$  for which stable disturbances are first possible. The case  $L = 0$  for the insulating boundary condition is particular in that the critical value of  $\alpha$  is zero,  $B = 48$ . Apart from this special case, the shape of the neutral stability curves is very similar in the conducting and insulating cases; in general larger positive values of  $L$  lead to greater stability. The values of  $L$  encountered in practice would depend on the thickness of the film and for very thin films would tend to zero. Detailed solutions for the more general boundary condition (9) with finite non-zero values of  $Y$  are not given but it is not expected that these would behave very differently from the two limiting cases  $Y = 0$ , and  $Y^{-1} = 0$ .

It is interesting to compare the dimensionless number  $B$ , defined by (18), which is relevant for the surface tension mechanism, with the Rayleigh number

$$A = \frac{g\gamma\beta d^4}{\nu\kappa},$$

where  $g$  is the gravitational acceleration and  $\gamma$  is the coefficient of thermal expansion of the liquid, which is relevant for the density-dependent mechanism. In particular we may compare the critical value  $B_{\text{crit}} = 80$  when



$L = 0$ , from figure 1, with the corresponding critical value  $A_{\text{crit}} = 571^*$  (see Jeffreys (1926), the case of one free 'insulating'† and one fixed conducting

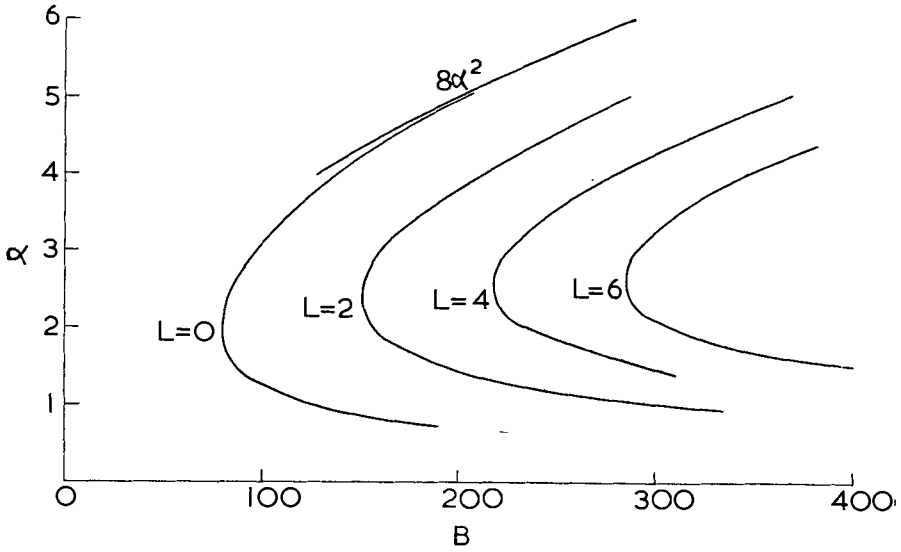


Figure 1. Neutral stability curves, conducting case.

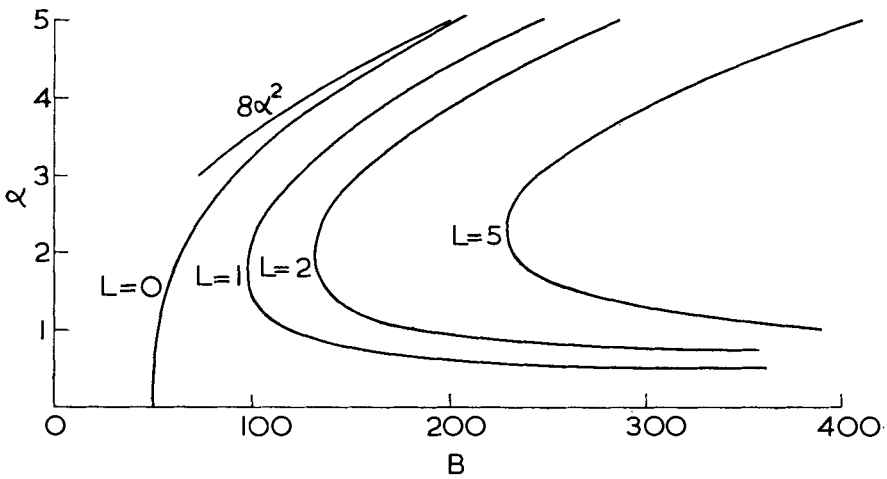


Figure 2. Neutral stability curves, insulating case.

\* This value is the best estimate that is available, and although it was calculated using erroneous boundary conditions, it is expected to be close to the correct result. Since we are using it for order of magnitude arguments, the discrepancy need not trouble us unduly.

† 'Insulating' as regards the perturbation temperature. It corresponds to a case of uniform heat flow, as does our case  $L = 0$ .

surface, and the amending paper Jeffreys (1928)). The former of these leads, for any given fluid layer, to a critical thickness

$$d_1 = \left( \frac{80\rho\nu\kappa}{\sigma\beta} \right)^{1/2}$$

and the latter to a thickness

$$d_2 = \left( \frac{571\nu\kappa}{g\gamma\beta} \right)^{1/4}.$$

These will be equal for a value  $d_{12}$  given by

$$d_{12}^2 = \frac{\sigma}{\rho g \gamma} \frac{571}{80}.$$

For most liquids at laboratory temperatures this relation leads to values for  $d_{12}$  of the order of 1 cm. For thicknesses less than  $d_{12}$ , then, we expect surface tension forces to be more effective than buoyancy forces in producing instability, and, for values of  $d$  as small as 1 mm, the onset of cellular motion could confidently be attributed to surface tension rather than to buoyancy. Since  $L$  will not be large for sufficiently small values of  $d$  and since  $B_{\text{crit}}$  does not vary very rapidly with  $L$ , the arguments are not altered greatly if non-zero values for  $L$  are assumed to apply.

#### COMPARISON WITH OBSERVATION AND EXPERIMENT

The original observations of Bénard (1900, 1901) provide a very suitable illustration of the instabilities considered above. For with spermaceti he achieved cells in layers less than  $\frac{1}{2}$  mm thick when the temperature of the lower surface was maintained at  $100^\circ\text{C}$ . Moreover, these cells persisted even when the temperature of the lower surface approached  $50^\circ\text{C}$ . Since spermaceti solidifies at rather above  $50^\circ\text{C}$  an upper value can be placed on the temperature variation across the layer and can only have been a degree or two, if that, in some cases. Bénard gives a value of  $7.7 \times 10^{-4}$  c.g.s. units for  $\gamma$  and, fortunately for our purposes, a value of nearly  $5 \times 10^{-2}$  c.g.s. units for  $\sigma$ . We can assume that the case of a lower rigid conducting and an upper free 'insulating' boundary applies approximately to his experiments since the lower surface was metallic and the temperature difference between the upper surface and its surroundings can be assumed large compared with the drop in temperature across the liquid layer. It would require detailed calculation to obtain an *accurate* estimate for  $L$  in this case, since the mechanism for heat transfer involves both convection and radiation. However, a rough calculation shows that  $L \ll 1$ —whether it be  $10^{-3}$  or  $10^{-1}$  is scarcely important since figure 1 shows that the critical value  $B$  necessary for instability only increases by a factor of 3 when  $L = 5$ —and we can therefore use the approximation  $L = 0$  as an initial approximation.

Even if we assume that  $\kappa$  was as small as  $10^{-4}$  and  $\nu$  as small as  $10^{-2}$ , the value obtained for  $A$  is still less than 571. On the other hand, for reasonable values of  $\kappa$  ( $5 \times 10^{-4}$ ) and  $\nu$  ( $5 \times 10^{-2}$ ), a value of  $B$  in excess of 80 is obtained even for a temperature drop of only  $1^\circ\text{C}$  across the layer. Furthermore the ratio of cell size to layer thickness quoted by Bénard

leads to values of  $\alpha$  lying between 2.1 and 2.5 which are in good agreement with the analysis given in the previous section, where  $\alpha_{\text{crit}} = 2.0$ . The equivalent value of  $\alpha_{\text{crit}}$  from the analysis of Jeffreys is 3.5, which even allowing for error is significantly different from the observed values. Thus we see that the buoyancy mechanism has no chance of causing convection cells, while the surface tension mechanism is almost certain to do so, and that observations support this. (Going back to the choice of  $L = 0$ , we see that this was not critical and hence that an exact analysis of the heat transfer at the surface is not necessary to sustain the argument.) An intimation that the instability theory based on buoyancy forces would not account for all of Bénard's results appears in a paper by Volkovisky (1939).

The allied problem of a liquid cooling by evaporation may be treated in a similar fashion. Although no strictly steady equilibrium state may be presupposed, owing to the loss of fluid from the surface, the effect of evaporation may be reasonably well represented by a given heat loss from the surface, using a value for  $L$  that depends on the rate of evaporation and the latent heat of vaporization. A quasi-steady value for  $\beta$  must be assumed to hold.

The application of the analysis to the case of a mixture of two liquids, one more volatile than the other, requires more explanation. Two factors tending to instability will now be relevant. The first, that due to temperature variations, has been treated already. The second is that due to relative concentration variations. This may be treated separately using a suitable interpretation of the analysis given above for temperature effects. For if the temperature  $T$  is interpreted as the concentration  $C$  of the volatile liquid  $\mathcal{L}_1$  in the non-volatile liquid  $\mathcal{L}_2$ , the constant  $k$  is interpreted as the coefficient of diffusion of  $\mathcal{L}_1$  in  $\mathcal{L}_2$  and the parameters  $\sigma$ ,  $q$  and  $\gamma$  refer to variations with concentration  $C$ , then the equations (3) and (4) are appropriate equations for describing small disturbances due to concentration variations in a layer whose equilibrium (or quasi-steady) concentration gradient is given by  $\beta$ —for the moment we regard  $\beta$  as some unspecified function of  $y$ . Previous work has shown—see for example Batchelor (1954)—that the most unstable case, for any given concentration drop across the layer, occurs when the gradient  $\beta$  is a constant\*. Consequently, although the instantaneous concentration across the layer for the case of surface evaporation of  $\mathcal{L}_1$  from a mixture of  $\mathcal{L}_1$  and  $\mathcal{L}_2$  would never be a linear function of  $y$ , we may safely use a value of

$$\beta = C_{\text{max}}/d$$

to obtain a lower limit for stability. The boundary conditions on the velocity, (7) and (8), would still apply; the relation (10) would also apply with suitable interpretation; but at the bottom surface the insulating condition would now be relevant. Hence the result (28), displayed in figure 2, can fairly reasonably be applied to describe the concentration effect. In

\* This has been verified analytically for the particular choice of  $\beta$ :  $\beta = C_0/bd$ ,  $d > y > d(1-b)$ ;  $\beta = 0$ ,  $d(1-b) \geq y \geq 0$ ;  $0 \leq b \leq 1$ . Instability is greatest for  $b = 1$ .

general terms the temperature and concentration effects are additive and for any given circumstances a joint criterion replacing either (27) or (28) could be calculated. This will not be carried out here because of the difficulty in prescribing the equilibrium concentration gradient.

A series of experiments carried out in this laboratory on thin layers of mixtures of liquid paraffin and ether have shown convection cells of polygonal type when evaporation of the ether takes place. Estimates of the buoyancy forces involved showed that these could not be responsible for the motion. On the other hand, the difference in surface tension between liquid paraffin (32 c.g.s. units) and ether (19 c.g.s. units), combined with their temperature variations, leads to surface tractions large enough to maintain the motion. For example, a 5% concentration of ether evaporating at room temperature (say, 15° C or less) showed cells down to a layer thickness of 0.5 mm, this critical thickness being highly reproducible; even allowing for a very high rate of evaporation, and adding the concentration and temperature effects on the density, a value of  $A$  of the order of 10 or less is obtained. Similarly crude estimates of  $B$  for the two effects suggest instability. The ratio of cell size to layer thickness proved to be relatively constant over a fair range of layer thickness and using the analysis of Christopherson (1940) a value of  $\alpha \sim 2.0$  was obtained, which is in reasonable agreement with our analysis.

Similar experiments using a wide range of both volatile and non-volatile liquids have been carried out by Dr Cousins. All his results are in excellent qualitative agreement with the ideas described here. In particular, by choosing a volatile fluid with higher surface tension than the non-volatile base, cellular motion was inhibited. The addition of a very small quantity of silicone oil to various mixtures also inhibited cell formation by reducing the surface tension overall.

The author wishes to thank Dr R. Cousins for pointing out the probable role of surface tension and for helpful discussion of the observations quoted. It is hoped to publish a joint paper on the specific application of the foregoing theory to paint films. The author is also grateful for many useful criticisms by the referees.

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