7. R. J. GOLDSTEIN and E. R. ECKERT, The steady and transient free convection boundary layer, *Int. J. Heat Mass Transfer* **4**, 208 (1960).
8. K. BRODOWICZ, An analysis of laminar free convection around isothermal vertical plate, *Int. J. Heat Mass Transfer* **11**, 201–209 (1968).
9. J. GRYZAGORIDIS, Effects of pressure reduction on the free convective heat transfer coefficient from a heated vertical plate in air, argon and helium, Ph.D. Thesis to be submitted at the University of Cape Town, South Africa.
10. E. M. SPARROW and J. L. GREGG, The variable fluid-property problem in free convection, *Trans. Am. Soc. Mech. Engrs* **80**, 879–886 (1958).
11. E. M. SPARROW and J. L. GREGG, Laminar free convection from a vertical plate with uniform surface heat flux, *Trans. Am. Soc. Mech. Engrs* **78**, 435–440 (1956).
12. M. G. SCHERBERG, Natural convection near and above thermal leading edges on vertical walls, *Int. J. Heat Mass Transfer* **5**, 1001–1010 (1962).

Int. J. Heat Mass Transfer. Vol. 14, pp. 165–169. Pergamon Press 1971. Printed in Great Britain

ON THE BREAK-UP OF THIN LIQUID LAYERS FLOWING ALONG A SURFACE

E. RUCKENSTEIN

Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

(*Received* 10 *March* 1970 *and in revised form* 25 *June* 1970)

NOMENCLATURE

- c, concentration of the more volatile component;
- Δc, concentration difference between that at the free interface far from the leading edge and at the leading edge;
- g, acceleration of gravity;
- k, thermal conductivity;
- q, heat flux;
- T_b, boiling temperature;
- ΔT, temperature difference between that at the free interface far from the leading edge of the rivulet and the wall;
- u, velocity component in the direction of the main flow;
- x, mole fraction of the more volatile component;
- y, distance from the wall;
- α, proportionality constant, α_0—value of α for $\theta = 0$;
- Γ, volumetric flow rate per unit perimeter;
- Γ_c, critical value of Γ;
- δ, film thickness;
- δ_0, film thickness far from the leading edge of a patch or rivulet;
- η, viscosity of the liquid;
- ν, kinematic viscosity of the liquid;
- ρ, liquid density;
- σ, liquid–gas surface tension;
- σ_{sg}, solid–gas surface tension;
- σ_{ls}, liquid–solid surface tension;
- τ_0, shear stress;
- θ, dynamic angle (see Figs. 2 and 3);
- θ_e, static angle (See Fig. 1).

INTRODUCTION

THE PROBLEM of break-up of thin liquid films flowing along a surface has been examined in the literature from two different points of view. Some of the authors have given attention to the occurrence of a dry patch [1–3] and have established equations for the minimum flow-rate at which the surface is completely wetted. In this case the surface tension has an important part. Other authors have explained the occurrence of rivulets in conditions of heat or mass transfer by means of the Marangoni effect (surface tension gradient) [4–7] but have treated the problem in a qualitative manner. There exists a single paper [8] in which the Marangoni effect is taken into account in a quantitative manner but only for correcting the results obtained in connection with the stability of a dry patch. In the present paper both the stability of patches and that of rivulets will be examined.

Experiment shows that, when a thin liquid film is flowing in isothermal conditions along a vertical wall, dry patches can form if the flow-rate is sufficiently small. A significant contribution concerning the analysis of stability of a dry patch is due to Hartley and Murgatroyd [1] and Murgatroyd [2]. The stability condition of a patch is obtained by equating the surface forces and upstream kinetic energy of the liquid. Using for the surface forces the expression $\sigma(1 - \cos\theta)$

they write

$$\sigma(1 - \cos\theta) = \tfrac{1}{2}\rho \int_0^{\delta_0} u^2 \mathrm{d}y. \tag{1}$$

For laminar motion there results

$$\Gamma = 1{\cdot}69\left(\frac{\nu}{g}\right)^{\frac{1}{5}}\left(\frac{\sigma(1 - \cos\theta)}{\rho}\right)^{\frac{3}{5}}. \tag{2}$$

The minimum flow rate necessary for complete wetting of the surface may be calculated by using equation (2). The mentioned authors have also established an equation for Γ valid in turbulent conditions. Concerning the angle θ, it was considered [1–3] that it is the real angle which is formed when a dry patch occurs (Fig. 1) and that it is equal to the static one (angle formed when a drop is located on a horizontal surface of the same material). Equation (2) seems to show that there exists a single flow-rate for which a patch is stable and that for a larger or smaller flow-rate the patches are unstable (a continuous film being formed for larger flow-rates and rivulets for smaller). The following internal contradiction of the above theory seems to exist: the angle θ has a finite value, equal to the static one, at the minimum wetting flow-rate and is zero immediately above this minimum. For this reason we have re-examined the problem of stability of a patch and arrived at the conclusion that the surface and dynamic forces must be expressed in a somewhat different manner than that used by Hartley and Murgatroyd. Equation (2) in which θ is now the static angle is obtained for the minimum flow-rate. The dynamic angle corresponding to this minimum wetting flow-rate is however zero, and the patches are stable for all lower flow-rates (in these situations the dynamic angle is larger than zero but smaller than the static one).

If the flow of the film is accompanied by heat or mass transfer, the phenomena observed experimentally are much more complex. They have been described by Bond and Donald [4], Zuiderweg and Harmens [5], Danckwerts *et al.* [6] and Ford and Missen [7]. Ford and Missen have introduced as a quantitative criterion the derivative $\mathrm{d}\sigma/\mathrm{d}\delta$. If

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\delta} < 0, \text{ the film is stable} \tag{3}$$

and if

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\delta} > 0, \text{ the film is unstable.} \tag{4}$$

Indeed, in the first case, in the regions of small thickness the surface tension is larger and, consequently, owing to the Marangoni effect, the regions of smaller surface tensions (large thicknesses) are expanding and those of larger surface tension are contracting; the film is stable. If in the regions of small thickness the surface tension is smaller the film is unstable. For instance, when a pure substance is condensed the thin layers are colder (surface tension larger) and the film is stable; when it is evaporated, the thin layers are warmer (surface tension smaller) and the film is unstable. For a binary mixture which is condensing the sign of $\mathrm{d}T_b/\mathrm{d}\delta$ is positive (as for a pure component), however the sign of $\mathrm{d}\sigma/\mathrm{d}T_b$ depends upon the nature of the mixture and may be positive or negative. The film is unstable in the first case and stable in the second. The same criteria may explain the results obtained for distillation by Zuiderweg and Harmens, or for absorption by Bond and Donald. In distillation, thin spots become richer in the less volatile component, because, for a given rate of mass transfer, their change of composition is larger. Therefore for distillation $\mathrm{d}x/\mathrm{d}\delta > 0$. If $\mathrm{d}\sigma/\mathrm{d}x < 0$ the film is stable and if $\mathrm{d}\sigma/\mathrm{d}x > 0$ it is unstable. It will be shown that the Marangoni effect is not very important in the stability of patches but is very important in the stability of rivulets and the stability of rivulets will be analysed by means of an equilibrium condition between surface forces and those due to the Marangoni effect. The criteria obtained in this manner for the stability of thin flowing films are more complete than the qualitative ones mentioned above.

The flow along a vertical plate without heat or/and mass transfer

Let us first consider a static drop as in Fig. 1. Under equilibrium conditions one gets the well known Young equation

$$\sigma_{sg} - \sigma_{ls} - \sigma\cos\theta_c = 0. \tag{5}$$

Equation (5) is a result of a thermodynamic treatment (the extremum of the free energy). This equation is however usually obtained by assuming that the surface tensions are forces per unit length acting along the corresponding interfaces and by writing an equilibrium between the components along the solid surface. The mentioned interpretation is useful, though it was clearly stressed by Gibbs [9] that the surface tension gas–solid cannot be regarded as expressing the tension of the surface.

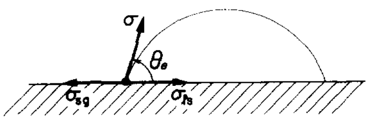

FIG. 1. Static equilibrium of surface tensions for a drop.

For the dynamical conditions which exist when a thin liquid film is flowing along a solid surface the statical Young equation must be replaced by a dynamical one. There exists however no general procedure for writing such an equation so that an intuitive approach, based on the interpretation of the surface tensions as forces per unit length, will be used. Consequently an equilibrium condition will be written at the leading edge of the patch (Fig. 2) by taking into account besides the usual surface tensions also the pressure excess arising in this stagnation point because of the conversion of the upstream kinetic energy into static pressure. For the average of this excess of pressure the expression

$$\frac{\rho}{2}\frac{1}{\delta_0}\int_0^{\delta_0} u^2\,\mathrm{d}y$$

may be used. Considering a curvature radius proportional to δ_0, one may write that the "excess of surface tension" due to this excess of pressure is proportional to

$$\frac{\rho}{2}\int_0^{\delta_0} u^2\,\mathrm{d}y.$$

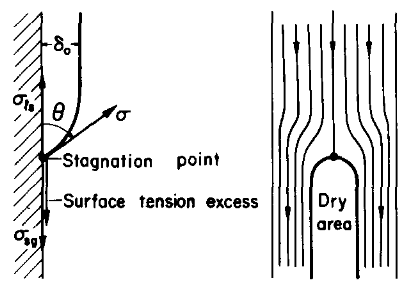

FIG. 2. Dynamic equilibrium of forces for a patch.

For the patch in Fig. 2 one may consider that it is stable if at the leading edge the surface forces are equal to the excess of surface tension due to the excess of pressure arising from the conversion of the upstream kinetic energy into static pressure. Hence, one may write*

$$\sigma\cos\theta + \sigma_{ls} - \sigma_{sg} = \alpha\frac{\rho}{2}\int_0^{\delta_0} u^2\,\mathrm{d}y \tag{6}$$

where α may be a function of the dynamic angle θ. Eliminating $\sigma_{sg} - \sigma_{ls}$ between equations (5) and (6) one obtains

$$\sigma(\cos\theta - \cos\theta_e) = \alpha\frac{\rho}{2}\int_0^{\delta_0} u^2\,\mathrm{d}y. \tag{7}$$

For laminar motion

$$u = \frac{g\delta_0^2}{\nu}\left[\frac{y}{\delta_0} - \frac{1}{2}\left(\frac{y}{\delta_0}\right)^2\right] \tag{8}$$

and since the flow-rate per unit perimeter is given by

$$\Gamma = \int_0^{\delta_0} u\,\mathrm{d}y, \tag{9}$$

one gets

$$\Gamma = 1{\cdot}69\left(\frac{\nu}{g}\right)^{\frac{1}{5}}\left[\frac{\sigma(\cos\theta - \cos\theta_e)}{\rho\alpha}\right]^{\frac{3}{5}}. \tag{10}$$

Equation (10) differs from that of Hartley and Murgatroyd only by $(\cos\theta - \cos\theta_e)$ which replaces $(1 - \cos\theta)$ and by the occurrence of $\alpha = \alpha(\theta)$. The new equation has, however, the following important physical consequences:

(a) The dynamic angle θ is smaller than the static one θ_e;
(b) Stable patches occur for all dynamic angles in the range $0 < \theta < \theta_e$, and not only for θ_e;
(c) There exists a limiting value of Γ, the minimum wetting flow rate Γ_c, for which the film is continuous. In that case the dynamic angle θ is zero.

Consequently, stable patches exist if

$$0 < \Gamma < \Gamma_c$$

where

$$\Gamma_c = 1{\cdot}69\left(\frac{\nu}{g}\right)^{\frac{1}{5}}\left[\frac{\sigma}{\rho\alpha_0}(1 - \cos\theta_e)\right]^{\frac{3}{5}} \tag{11}$$

and $\alpha_0 = \alpha(0) = \text{const.}$

A possible explanation for the smaller values obtained experimentally [2, 3] may be linked to the fact that only situations with a dynamic angle differing from zero can be observed and the corresponding values obtained for the flow-rates are smaller than Γ_c.

The flow of a film of liquid along a horizontal plate under the action of a co-current flow of gas without heat and/or mass transfer

Denoting by τ_0 the shear stress at the liquid–gas interface, one may write, for laminar motion, that

$$u = \frac{\tau_0 y}{\eta} \tag{12}$$

and that

$$\Gamma = \frac{\tau_0}{\eta}\frac{\delta_0^2}{2} \tag{13}$$

---

* Equation (1) used by the other authors is based on a momentum-force analysis applied to a control volume and does not lead in the limiting case of no flow to equation (5). As was stressed above the quantities σ_{sg}, σ_{ls} and σ are thermodynamic quantities and equation (5) is a consequence of thermodynamic equilibrium. The above quantities are not forces acting per unit length, but the final result [equation (5)] can be interpreted as if the components along the solid surface (and only along the solid surface) of three forces are in equilibrium. The present intuitive procedure is based on the concept of forces, but takes into account the fact that in the limiting case of no flow equation (5) must be valid.

or

$$\delta_0 = \left[\frac{2\eta\Gamma}{\tau_0}\right]^{\frac{1}{2}}. \tag{14}$$

Equation (7) leads in this case to

$$0{\cdot}47\left(\frac{\tau_0}{\eta}\right)^{\frac{1}{2}} \rho\alpha\Gamma^{\frac{3}{2}} = \sigma(\cos\theta - \cos\theta_e). \tag{15}$$

The patches are stable for those values of the product $\tau_0^{\frac{1}{2}}\Gamma^{\frac{3}{2}}$ for which

$$0 < \theta < \theta_e.$$

The limiting value of the product $\tau_0^{\frac{1}{2}}\Gamma^{\frac{3}{2}}$ is given by

$$0{\cdot}47\,\rho\alpha_0\eta^{-\frac{1}{2}}(\tau_0^{\frac{1}{2}}\Gamma^{\frac{3}{2}})_c = \sigma(1 - \cos\theta_e). \tag{16}$$

For values larger than this critical value the solid surface will be completely wetted.

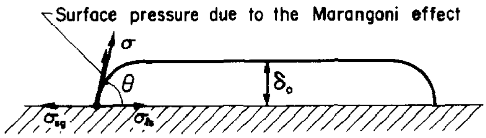

FIG. 3. Stability of a rivulet.

Now a comment which will be useful in the following section: The equilibrium condition on which the above considerations are based was applied to the most critical point. However, the angle θ will not be the same along the whole leading edge of the patch. For instance, parallel to the surface but in a direction normal to the direction of main flow, the angle θ will be equal to the equilibrium angle θ_e, because the velocity component of the liquid in that direction is equal to zero (or in any case much smaller than that in the main direction of the flow).

The flow of a thin film accompanied by heat and/or mass transfer

As discussed in the introduction, in these cases the effect of surface tension gradient (Marangoni effect) is very important. The stability of a dry patch occurring in thin films flowing over heated surfaces was examined by Zuber and Staub [8] who have introduced in the Hartley and Murgatroyd equation a term which takes into account the effect of thermocapillarity. Their numerical evaluations have shown that the effect is of importance for liquid metals or for highly wetting liquids. However, numerous experiments in absorption, distillation, condensation of binary mixtures, and vaporization of a pure liquid or of a binary mixture have proved that the effect is much more important. In our opinion this is due to the fact that in these situations quasi-parallel rivulets flowing along the wall are formed and in their stability the excess of pressure due to the conversion of kinetic energy is of secondary importance (because the velocity component in the plane of the surface but normal to the main direction of motion is small or zero). Only the competition between the surface wetting forces and those due to the Marangoni effect are of primary importance. In this manner even "small forces" become very active towards contributing to the rupture of the film. One may stress the fact that because the hydrodynamic forces do not play an important part the rivulets may appear at any flow-rate and not only at small ones as for patches.

Let us consider a liquid flowing non-isothermally along a vertical plate and let us analyze the stability of rivulets. The intuitive procedure based on the concept of forces suggests to write that a rivulet is stable if the surface pressure $\Delta\sigma$ due to the Marangoni effect equals the resultant "surface forces"

$$\sigma_{sg} - \sigma_{ls} - \sigma\cos\theta = \frac{d\sigma}{dT}\Delta T\cos\theta \,\text{(rivulet stability)} \tag{17}$$

where ΔT represents the temperature difference between the free interface in the region far from the leading edge of the rivulet and the wall. Since

$$q = -\frac{k}{\delta_0}\Delta T \tag{18}$$

equation (17) may be written, if $\sigma_{sg} - \sigma_{ls}$ is eliminated by using equation (5), in the form

$$\sigma\cos\theta_e = \left(\sigma - \frac{d\sigma}{dT}\frac{\delta_0 q}{k}\right)\cos\theta. \tag{19}$$

For pure liquids $d\sigma/dT < 0$ and, consequently, if heat is added ($q > 0$; the liquid is evaporating) an angle θ larger than θ_e may form. Even for liquids which are completely wetting the solid surface a rivulet may be stable. If $q < 0$ (condensation) an angle θ smaller than θ_e forms. Certainly this is not possible for a completely wetting liquid. In the last situation a rivulet is not stable. However for a partially wetting liquid a rivulet may or may not be stable depending on the number of rivulets and on their interaction. It is, however, reasonable to consider that the rivulets arising from the oscillations of the film will be, in the last case, most likely unstable. For a binary mixture, depending on the nature of the mixture, the sign of $d\sigma/dT$ may be negative or positive and several possibilities exist. The possible situations are given in Table 1.

Table 1.

$d\sigma/dT$	q	θ
−	+	$\theta > \theta_e$
−	−	$\theta < \theta_e$
+	+	$\theta < \theta_e$
+	−	$\theta > \theta_e$

When mass transfer instead of heat transfer takes place, equation (17) must be replaced by

$$\sigma_{sg} - \sigma_{ls} - \sigma \cos\theta = \frac{d\sigma}{dc}\Delta c \cos\theta, \qquad (20)$$

where Δc represents the difference in concentration between the free surface far from the leading edge and at the leading edge.

$$\sigma \cos\theta_e = \left(\sigma + \frac{d\sigma}{dc}\Delta c\right)\cos\theta. \qquad (21)$$

In the distillation of a binary mixture $\Delta c > 0$ because thin spots become richer in the less volatile component. Consequently,

$$\theta > \theta_e \text{ for } \frac{d\sigma}{dc} > 0 \qquad (22)$$

$$\theta < \theta_e \text{ for } \frac{d\sigma}{dc} < 0. \qquad (23)$$

Though precise assertions concerning the stability of a group of rivulets resulting from the oscillations of the film cannot be made, it is clear that it is more likely that they would be stable when $d\sigma/dc > 0 (\theta > \theta_e)$ than in the opposite case.

The equilibrium criteria, equations (17) and (20), may be written in the following more condensed form

$$\sigma_{sg} - \sigma_{ls} - \sigma \cos\theta = \frac{d\sigma}{d\delta}\delta_0 \cos\theta, \qquad (24)$$

or taking into account equation (5), in the form

$$\sigma \cos\theta_e = \left(\sigma + \frac{d\sigma}{d\delta}\delta_0\right)\cos\theta. \qquad (25)$$

Hence if $\frac{d\sigma}{d\delta} < 0$ then

$$\theta < \theta_e \qquad (26)$$

and if $\frac{d\sigma}{d\delta} > 0$ then

$$\theta > \theta_e \qquad (27)$$

In the first situation [equation (26)] the film is stable for completely wetting liquids. For partially wetting liquids the dynamic wetting angle θ is smaller than the static one and it is probable that the film would be stable. In the second situation [equation (27)] the probability of the rupture of the film is certainly much larger than in the first case.

Compared to the criteria of Ford and Missen [equations (3) and (4)] the criteria established above take into account the wetting properties.

CONCLUSIONS

The stability of two situations, dry patches and rivulets, were examined for obtaining information concerning the break-up of thin liquid films. In the first case the hydrodynamic conditions are of primary importance and it is the competition between the surface tensions on one hand and the excess of surface tension due to the conversion of the kinetic energy of the liquid into static pressure on the other hand which determines the stability of a patch. The second situation arises when the Marangoni effect is acting (i.e. when heat and/or mass transfer takes place). Only the competition between the surface tensions and the surface pressure due to the Marangoni effect is important for the stability of a rivulet. The first situation occurs at sufficiently small flow-rates, while the second, not being affected too much by hydrodynamic conditions, occurs at any flow-rate.

ACKNOWLEDGMENT

The author is indebted to L. Derzansky for useful comments.

REFERENCES

1. D. E. Hartley and W. Murgatroyd, Criteria for the break-up of thin liquid layers flowing isothermally over a solid surface, *Int. J. Heat Transfer* **7**, 1003 (1964).
2. W. Murgatroyd, The role of shear and form forces in the stability of a dry patch in two phase film flow, *Int. J. Heat Mass Transfer* **8**, 297 (1965).
3. A. B. Ponter, G. A. Davies, W. Beaton and T. K. Ross, The measurement of contact angles under conditions of heat transfer when a liquid film breaks on a vertical surface, *Int. J. Heat Mass Transfer* **10**, 1633 (1967).
4. J. Bond and M. D. Donald, The effect of absorption on the wetted area of absorption towers, *Chem. Engng Sci.* **6**, 237 (1957).
5. F. J. Zuiderweg and A. Harmens, The influence of surface phenomena on the performance of distillation columns, *Chem. Engng Sci.* **9**, 89 (1958).
6. P. V. Danckwerts, H. Sawistowski and W. Smith, The effect of heat transfer and interfacial tension in distillation, *Int. Symp. on Distillation*, p. 7. Institution of Chemical Engrs, London (1960).
7. J. D. Ford and R. W. Missen, On the conditions for stability of falling films subject to surface tension disturbances; the condensation of binary vapors, *Can. J. Chem. Engng* **46**, 309 (1968).
8. N. Zuber and F. W. Staub, Stability of dry patches forming in liquid films flowing over heated surface, *Int. J. Heat Mass Transfer* **9**, 897 (1966).
9. J. W. Gibbs, *Collected Works*, Vol. 1, p. 315. Dover Publ. (1961).