PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Drops, liquid layers and the Marangoni effect

The Royal Society

Phil. Trans. R. Soc. Lond. A 1998 **356**, 829-844
doi: 10.1098/rsta.1998.0190

Drops, liquid layers and the Marangoni effect

By Manuel G. Velarde
Instituto Pluridisciplinar, Universidad Complutense de Madrid,
Paseo Juan XXIII, n.1, 28040-Madrid, Spain

An overview is given of recent results about the onset and development of steady and time-dependent flow motions past an instability threshold induced by the Marangoni effect. First, I consider the case of a liquid drop immersed in another immiscible liquid when (endo- or exothermic) reaction, heat and/or mass transfer at/across the drop surface, etc., leads to self-propelled drop motion, overcoming viscous drag. Then I recall salient features about the spreading of an immiscible or a dissolving drop (with surfactant) on the surface of another liquid. Finally, I consider Bénard layers when either steady convective patterns or waves are produced by appropriate heat or mass transfer across the open surface.

Keywords: interfacial instability; spreading; Bénard patterns; interfacial waves; dissipative solitons; drop motions

1. Introduction

When there is an open surface or an interface exists between two liquids, the interfacial tension, σ, accounts for the jump in normal stresses proportional to the surface curvature across the interface; hence this Laplace force affects its shape and stability. Gravity competes with it in accommodating equipotential levels with curvature. Their balance defines, for instance, the stable equilibrium of spherical drops or bubbles. If the surface tension varies with temperature or composition, and, eventually, with position along an interface, its change takes care of a jump in the tangential stresses. Hence its gradient acts like a shear stress applied by the interface on the adjoining bulk liquid (Marangoni stress), and thereby generates flow or alters an existing one (Marangoni effect). Surface tension gradient-driven flows are known to affect the evolution of growing fronts, and measurements of transport phenomena. The variation of surface tension along an interface may be due to the existence of a thermal gradient along the interface or perpendicular to it. In the former case we have instantaneous convection while in the latter flow occurs past an instability threshold (Levich 1965; Levich & Krylov 1969; Scriven & Sternling 1960; Ostrach 1982; Davis 1987). The Marangoni effect is the engine transforming physicochemical energy into flow, whose form and time dependence for standard liquids rests on the sign of the thermal gradient and the ratios of viscosities and diffusivities of adjacent fluids.

2. Drops and bubbles

(a) ‘Passive’ drops

To place in context our recent findings and the difficulties still existing ahead of us, let me recall how the hydrodynamic force on a drop has been estimated since the

Phil. Trans. R. Soc. Lond. A (1998) **356**, 829–844
Printed in Great Britain

TEX Paper

pioneering work of Newton and Stokes (Levich 1965; Levich & Krylov 1969; Happel & Brenner 1965; Edwards *et al.* 1991). From Newton's experiments in 1710, and later observations, the magnitude of the drag force of a viscous fluid on a solid sphere (a drop, in a first approximation) in steady motion was given as

$$F_{\mathrm{D}} = 0.22\pi R^2 \rho U^2, \tag{2.1}$$

where U is the relative velocity between particle and fluid, R is the particle radius and ρ is the fluid density. This relation is for 'large' values of U, for which inertial (kinetic theory) effects are dominant.

Stokes, in 1850, suggested that at very low relative velocities all inertial effects are so small that they can be omitted from the Navier–Stokes equations (creeping flow approximation). Under this condition, the drag on a sphere is

$$F_{\mathrm{D}} = 6\pi R\eta U, \tag{2.2}$$

with μ denoting the dynamic or shear viscosity of the fluid. Oseen pointed out that at a great distance from the sphere the inertia terms become more important than the viscous terms, and suggested a possible improvement of the Stokes's law (2.2) by taking inertial terms partly into consideration. He obtained a drag force,

$$F_{\mathrm{D}} = 6\pi R\eta U(1 + \tfrac{3}{16}\mathit{Re}), \tag{2.3}$$

where ν is the kinematic viscosity of the fluid and $\mathit{Re} = (2R)U/\nu$. Neither Stokes's nor Oseen's laws are *uniformly* valid, and the latter is not really an improvement of the former. Rather Stokes's analysis is valid in a small enough neighbourhood of the sphere and Oseen's analysis, though valid far from the sphere, is not valid when approaching the sphere. Oseen's approximation, although incorporating inertial terms, is a linear theory and Stokes's approximation is a steady-state theory.

The mathematical problems solved by Stokes and Oseen come from different approximations to the Navier–Stokes equations, together with appropriate initial and boundary conditions. As for the axisymmetric motion of a sphere there is always a stream function, Ψ, with (r, θ, ϕ) coordinates and the hydrodynamic equations reduce to (Levich 1965; Happel & Brenner 1965)

$$\frac{\partial}{\partial t}(E^2\Psi) + \frac{1}{r^2\sin\theta}\frac{\partial(\Psi, E^2\Psi)}{\partial(r,\theta)} - 2\frac{E^2\Psi}{r^2\sin^2\theta}\left(\frac{\partial\Psi}{\partial r}\cos\theta - \frac{1}{r}\frac{\partial\Psi}{\partial\theta}\sin\theta\right) = \nu E^4\Psi, \tag{2.4}$$

with

$$\frac{\partial(f,g)}{\partial(r,\theta)} = \begin{pmatrix} \dfrac{\partial f}{\partial r} & \dfrac{\partial f}{\partial\theta} \\ \dfrac{\partial g}{\partial r} & \dfrac{\partial g}{\partial\theta} \end{pmatrix}$$

and

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right).$$

The Stokes aproximation is the reduction of equation (2.5) to

$$E^4\Psi = 0. \tag{2.5}$$

Equation (2.6) with the appropriate non-penetration no-slip/stick BC and suitable asymptotic behaviour for large r, yields

$$\Psi(r,\theta) = (-\tfrac{1}{4}U(R^3/r) + \tfrac{3}{4}URr - \tfrac{1}{2}Ur^2)\sin^2\theta, \tag{2.6}$$

hence the hydrodynamic drag force (2.2). Note that from (2.6) it follows that the disturbance of the sphere extends to infinity as $1/r$, and the presence of a boundary or another drop can modify the flow appreciably even when placed at a distance of many diameters from the drop. It was not until the fifties that Stokes's and Oseen's results were properly put in context and generalized.

In 1911–12, Rybczynski and Hadamard, independently, solved the Stokes problem for a liquid drop with flows outside and inside (Levich 1965; Happel & Brenner 1965). Their extension of equation (2.2) is

$$F_{\mathrm{D}} = 6\pi\eta_0 UR\left[1+\frac{\frac{2}{3}\mu}{1+\mu}\right], \tag{2.7}$$

with $\mu = \eta_{\mathrm{i}}/\eta_{\mathrm{o}}$ ($\eta_{\mathrm{i}} = \eta_{\mathrm{drop}}$). The limit η_{i} going to infinity yields Stokes's law (2.2), while $\eta_{\mathrm{o}} \gg \eta_{\mathrm{i}}$ yields the corresponding law for a bubble, with 4 rather than 6 in equation (2.2).

In 1957, Proudman & Pearson (1957) considered Stokes's solution as a local (or inner) solution of the problem and Oseen's as the regular (or outer) solution. The former was assumed to be valid in a spherical region of radius $1/Re$ around the sphere while the outer solution was valid from infinity down to the $1/Re$ neighbourhood. In the overlapping zone both solutions were accepted as valid; hence the need to appropriately match them. Proudman & Pearson found that for non-vanishing albeit low Reynolds number flows ($Re \ll 1$) the hydrodynamic drag on the sphere is

$$F_{\mathrm{D}} = 6\pi\eta UR(1+\tfrac{3}{16}Re + Re^2 + \tfrac{9}{160}Re^2\ln Re + \cdots), \tag{2.8}$$

which shows the non-analytic form of the expansion.

Subramanian (1981) used matched asymptotic expansions to obtain the hydrodynamic force on a drop including convective terms in the heat equation while maintaining the Stokes approximation for the velocity field. With

$$M = -\left(\frac{\partial\sigma}{\partial T}\right)\frac{\mathrm{d}\delta T}{\kappa\eta},$$

where κ is the thermal diffusivity of the drop, T denotes temperature and ΔT is the temperature contrast over a length scale d (this scale may be taken as R), his series expansion in terms of the Marangoni (as a Péclet, $Pe = 2RU_{\mathrm{T}}/\kappa$, $U_{\mathrm{T}} = -(\partial\sigma/\partial T)\Delta T/\eta$) number, and subsequent improvement by his collaborator Merritt, did not show any logarithmic term (Merritt & Subramanian 1988; Subramanian 1992; Wozniak et 1988). This was due to the way the outer solution was treated.

Taylor & Acrivos (1964) obtained the contribution of the deformation of the sphere in terms of the capillary number. At $Re = 0$, a drop or a bubble remains spherical irrespective of the low or high value of the (constant) surface tension. However, deformation may be relevant even when inertial effects are ignored if the surface tension σ is not constant. If over the spherical surface $\Delta\sigma$ is small compared to the value of σ, the capillary number will be small, and the drop or bubble may be asummed spherical with negligible error.

Young *et al.* (1959) were the first to realize the possibility of levitating a drop or a bubble by Marangoni stress. They showed that a drop or a bubble placed in another fluid where a temperature gradient exists instantaneously tends to move towards the hotter point. This is the motion of the drop relative to the flow induced along its surface by the lowering of surface tension at its leading pole (hotter than the rear pole). Using the Stokes–Rybczynski–Hadamard approximation they also computed the terminal velocity of a drop or a bubble in the field of gravity, and experimentally checked the theoretical prediction within reasonable accuracy (within 20%) with an experiment using rising bubbles in a liquid layer heated from below (diameters $2R = 10^{-3}$–22×10^{-3} cm; $\nabla T = \mathrm{d}T/\mathrm{d}z = 10$–$90$ K cm^{-1}; z denotes the vertical coordinate). Using neutrally buoyant liquid water at 4 °C, Bratukhin *et al.* (1979, 1982) did a similar experiment with rising bubbles in a laterally heated vertical liquid layer.

In their experiment, Young *et al.* (1959) used a tiny open liquid bridge. An improvement eliminating wetting and capillary convection at the open sides was carried out by Hardy (1979). He used a closed cavity with silicone oil and air bubbles ($2R = 5$–25×10^{-3} cm; $\mathrm{d}T/\mathrm{d}z = 40$–$140$ K cm^{-1}). Hardy discussed the role of contamination at the surface of the bubble, earlier suggested by Levich (1965; Levich & Krylov 1969). Further improvement came with an experiment by Merritt & Subramanian (1988). Experimentalists started using drops rather than bubbles. Barton & Subramanian (1989) used neutrally buoyant drops ($2R = 20$–600 mm, $\mathrm{d}T/\mathrm{d}z = 2.4$ K mm^{-1}). Recent Earth-based and low-g work by Braun *et al.* (1994) on thermocapillary migration of drops provided the most accurate verification of the prediction by Young *et al.* (1959). Their Marangoni (Péclet) number was in the range 10^{-5}–10^{-6}, but with a a non-standard liquid of surface tension increasing with the increase of temperature (2 butoxyethanol-water mixture with liquid–liquid phase separation at 61.14 °C on the lower branch of the closed miscibility gap; $2R = 11$ µm, $\mathrm{d}T/\mathrm{d}z = 36.9$ K m^{-1}, $\mathrm{d}\sigma/\mathrm{d}T > 0$).

For the Young, Goldstein and Block problem the balance between capillary, buoyancy and hydrodynamic forces is

$$F_\sigma + F_\mathrm{g} = AU, \tag{2.9}$$

with the (Marangoni) capillary force

$$F_\sigma = \frac{4\pi R^2}{(1+\mu)(1+\delta)} \left(\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right) (\nabla T)_\infty \tag{2.10}$$

and the buoyancy force

$$F_\mathrm{g} = \tfrac{4}{3}\pi R^3 g(\rho_\mathrm{i} - \rho_\mathrm{o}). \tag{2.11}$$

As

$$A = 4\pi\eta_0 \frac{1+\frac{3}{2}\mu}{1+\mu} R > 0, \tag{2.12}$$

the hydrodynamic force AU represents drag. $\delta = \lambda_\mathrm{i}/\lambda_\mathrm{o}$ is the ratio of thermal conductivities (drop to surrounding fluid). Clearly, AU embraces both Stokes's law ($\eta_\mathrm{i} \to \infty$, $\mu \to \infty$) and the Rybzcynski–Hadamard law ($[\nabla_\mathrm{T}]_\infty = 0$).

(*b*) *'Active' drops*

The work on drops and bubbles so far recalled, refers to 'passive' drops. Now I turn to some recent findings about 'active' drops obtained with A. Ye. Rednikov and Yu. S. Ryazantsev (Rednikov *et al.* 1994*a*–*e*, 1995*a*; Velarde *et al.* 1996). By an 'active' drop or bubble I mean a drop or a bubble with internal volume heat sources, with a surface where chemical reactions may occur, or there is drop dissolution with heat release, etc. Take, for example, a drop at rest in a homogeneous medium and assume that there is (uniform) internal heat generation or a surface chemical reaction. Let us evaluate how the state of rest can be made unstable. Consider, for instance, the latter case with given uniform composition far off the drop. A composition fluctuation at the surface of the drop brings the Marangoni effect which yields flows inside and outside the drop. They can be sustained if the Marangoni effet is strong enough relative to viscous drag and heat diffusion, i.e. past an instability threshold. Indeed, as the drop moves the flow brings to the leading pole the higher solute at the surface, it makes the concentration far off the drop higher than that in its vicinity. Alternatively, if a velocity fluctuation tending to move the drop in a certain direction spontaneously occurs, it breaks the initial spherical symmetry in composition; hence the possibility of bringing strong enough Marangoni stresses which in turn can help sustain the velocity fluctuation past an instability threshold. If the initial state is that of a uniform constant drop velocity or there is an externally imposed temperature or composition gradient, as in the experiment of Young *et al.* (1959), then instability is also possible leading to a different drop motion. These are not the only possible instabilities as the effects due to deformability and time dependence may come into play.

To illustrate how we have proceeded along the path set by the earlier mentioned authors dealing with passive drops, now I consider the case of a spherical drop moving with constant velocity in a temperature and composition-homogeneous infinitely extended surrounding fluid. Both the inner and outer fluids are taken immiscible. The surface tension is assumed to vary linearly with temperature. The outer fluid is assumed to have a uniform concentration of a solute which is allowed to react exo- or endothermally at the surface of the drop. Far off the drop both the temperature and concentration of the solute are constants; hence there is no external gradient. Stefan flow is negligible (convective flow of the reacting components in a direction normal to the surface where the reaction is taking place; it is generally a small effect for most chemical reactions and is normally important only in the presence of strong ablation or condensation). Let us consider the low Reynolds and Péclet number approximations with, however, $M\,Pe = 1$ (M is defined as earlier for the drop while Pe is defined using the far-field reference velocity, U, as for the earlier used Reynolds number, with indeed κ replacing ν). In dimensionless form the steady equation (2.4) becomes

$$\frac{Re}{\nu^* r^2}\left\{\frac{\partial(\psi_{\mathrm{i}}, E^2\psi_{\mathrm{i}})}{\partial(r,\delta)} + 2E^2 L_{\mathrm{r}}\psi_{\mathrm{i}}\right\} = E^4\psi_{\mathrm{i}}, \tag{2.13}$$

which is nonlinear. It is considered together with the corresponding nonlinear heat and mass diffusion equations, and appropriate BC. Here Re is defined with the constant drop velocity, $\delta = \cos\theta$, ν^* refers to (kinematic) viscosity ($i = 1$, outer fluid, $\nu^* = 1$; $i = 2$, drop, $\nu^* = \nu$), and L_{r} corresponds to the operator appearing in the third term of equation (2.4).

The linear solution of equation13) yields the hydrodynamic force (Rednikov *et al.* 1994*a*–*c*; Velarde *et al.* 1996).

$$F = -4\pi\eta_1 rAU. \tag{2.14}$$

If A is negative we have drag while if A is positive there is thrust; hence self-propulsion and autonomous motion of the drop in a medium originally uniform. We have

$$A = -[1 + \tfrac{3}{2}\mu + 3m]/(1 + \mu + m), \tag{2.15}$$

with $\mu = \eta_1/\eta_2$ and m a suitably scaled Marangoni number accounting for a balance between $\mathrm{d}\sigma/\mathrm{d}T$, the chemical reaction rate, and (viscous and heat) dissipation. For further details and the various cases studied see Rednikov *et al.* (1994*a*–*e*, 1995*a*) and Velarde *et al.* (1996). We see that at $m = m_1 = -\frac{1}{3} - \frac{1}{2}\mu$ we have $A = 0$, where, as at $m = m_2 = -1-\mu$, A diverges to infinity. Clearly, the study of both cases demands nonlinear analyses. Before referring to this we note that for $A = 3$, the Marangoni effect combined with the chemical reaction yields the possibility of self-propulsive thrust, while for $A = -1$ we have drag, as well as for $A = -\frac{3}{2}$. In the later case, the flow inside the drop completely stagnates as if it were a solid sphere. For $A = -3$ there is enhanced drag due to the appearance of recirculating backflow around the drop and flow reversed in the drop.

The weakly nonlinear result for $(m - m_1)$ (> 0, $\ll 1$) provides the value of the hydrodynamic force

$$F = -4\pi\eta_1 R[A + B(RU/\nu_1)]U, \tag{2.16}$$

with

$$B = -\tfrac{1}{4}A^2 + \tfrac{1}{2}\,Pr[m(6 + 3L - AL)/(1 + \mu + m)], \tag{2.17}$$

where here $Pr = \nu_1/\kappa_1$, and $L = \kappa_1/D$ is the (inverse) Lewis number of the homogeneous surrounding medium. A representation of F versus U straightforwardly shows that for $(m - m_1) < 0$ $(A > 0)$ there are three possible values of U for zero hydrodynamic force; hence, possible autonomous motion of the drop. The addition of an external force field like buoyancy, or an externally imposed thermal gradient like in the experiment by Young *et al.* (1959) provides the possibility of three genuinely different non-zero velocities for a given force field strength. We have multiplicity of steady states of motion which cannot all actually be realizable.

For $m < m_2$, there are three possible values of the hydrodynamic force for zero velocity; hence three possible coexisting levitation levels of which one cannot be stable. Levitation or motion is a consequence of the nonlinearity in the flow coupled to the Marangoni stress, and not a consequence of some external thermal gradient as in the case treated by Young *et al.* (1959).

Complete stability analyses, respectively, for m around m_1 and m around m_2, have not been carried out. They demand the inclusion of the time-dependent term in equation (2.4) and explicit use of the convective state, which is a formidable task. However, ad hoc quasi-stability analyses have confirmed the results reported here. For further details see Rednikov *et al.* (1994*a*–*c*).

Finally, addition of a time-varying gravity field as it occurs in space (g-jitter) and in some Earth-based experiments, leads to a time-dependent weakly nonlinear vector-form Landau equation for the velocity of the drop (Rednikov *et al.* 1995). This equation can be used not only to find the stationary regimes and analyse their stability, but also to consider time-varying motions. In the simplified case of a small amplitude buoyancy force changing sinusoidally with time the result found is that an *active* drop capable of *autonomous* motion actually tends to move in a direction orthogonal to the time-varying force.

3. Spreading of a drop on another liquid under Marangoni stress

(*a*) *Insoluble surfactant*

With de Ryck and Starov (Starov *et al.* 1997), I have recently considered the spreading of an insoluble drop of surfactant over a thin viscous layer (e.g. less than a millimeter depth). The experiment and theory refer to a case where diffusion is a much slower process than convection due to the Marangoni effect. For concentrations above CMC (about 3 μl of an aqueous solution of SDS at $c = 20$ g l^{-1}; CMC is 4 g l^{-1}) the spreading process involves two stages. First, there is a rather fast stage when the surfactant concentration is determined by the dissolution of micelles, with a duration fixed by the initial amount of micelles. Then it follows a second slower stage when the surfactant concentration drastically changes in the original center position of the drop but as the total mass of surfactant remains constant a hole, a dry spot is created in the liquid layer.

As the drop circularly spreads due to the dominant role played by the nonlinearity, the percursor film develops a shock-like front whose time evolution according to theory follows a power law in time; first about $\frac{1}{2}$ (experimentally, $t^{0.6}$) and subsequently $\frac{1}{4}$ (experimentally, $t^{0.17}$). The radius of the inner hole at the centre expands, also with a power law $t^{1/4}$ (theory and experiment). Further theoretical developments for the more general case when diffusion takes on a time scale comparable to Marangoni convection can be found in Starov *et al.* (1997), Borgas & Grotberg (1988) and Gaver & Grotberg (1990, 1992).

(*b*) *Soluble surfactant*

Another interesting experiment with, however, a dissolving drop of nitroethane deposited over a liquid water layer has been recently conducted by Santiago-Rosanne *et al.* (1997). Nitroethane has a much lower surface tension (39 mN m^{-1}) than water being only partially miscible in it in proportions lower than 5% at room temperature. Here too the Marangoni effect plays a dramatic role in creating shock-like fronts as well as smooth solitary-like waves. Indeed, the deposition of the nitroethane drop induces a sudden local change of surface tension at the circular periphery; hence the dramatic outward front motion. The interplay of Marangoni stresses and gravity creates daisy-like patterns which are in fact time-dependent structures. The daisy flower petals result from collisions of wave crests. Wave profiles and the kinematics of collisions of both the smooth solitary-like waves and the shocks have been studied and qualitative agreement exists with the theory I have recently developed, leading to dissipative Marangoni-driven Boussinesq–Burgers–Korteweg-de Vries (KdV) equations. Further below I return to this problem when discussing wave motions in Bénard layers. Details of the experiments with good diagrams and theory can be found in Santiago-Rosanne *et al.* (1997).

4. Bénard layers: convective patterns

The onset of patterned convective motions in heated fluid layers with a free upper surface has been extensively studied since the original experiments by Bénard (Koschmieder 1993; Velarde & Normand 1980; Normand *et al.* 1977). Depending on the depth of the layer, d, one distinguishes two basic mechanisms of instability. In sufficiently deep layers or in containers where the fluid is confined between rigid horizontal plates, the convective motion settles when buoyancy forces overcome viscous forces and heat dissipation (Rayleigh–Bénard problem) (Normand *et al.* 1977). Alternatively, in shallow enough layers with an open surface, inhomogeneity in the surface tension, hence the Marangoni effect is responsible for the onset of motion (Bénard–Marangoni problem). In both cases, the characteristic wavelength of the convective structure is about the depth of the cell or much larger, depending on whether or not the horizontal boundaries are good thermal conductors. Close to the instability threshold the system may be described by amplitude equations whose coefficients depend on the dimensionless numbers of the problem containing fluid properties, boundary conditions and the external forcing. Most of these numbers have been earlier defined. If the Biot number, $Bi = hd/\kappa$, where h is the thermal surface conductance, its infinite value corresponds to a perfectly conducting boundary while a zero value corresponds to a poorly conducting surface.

To the Navier–Stokes, continuity and energy equations, in the Boussinesq approximation (Normand *et al.* 1977), we add the boundary conditions. At the lower uniformly heated rigid plate, $v = 0$ and $\partial T/\partial z = Bi\, T$. At the top open surface, $w = 0$, $\partial\sigma/\partial z = \eta(\partial u/\partial z)$, $\partial\sigma/\partial y = \eta(\partial v/\partial z)$ and $\partial T/\partial z = -\, Bi\, T$, where w is the vertical velocity component.

To study the transition between the motionless state and convection, and the dynamics of the structures that define this convective state, a multiple scale perturbation theory has been developed in the vicinity of the onset of convection (Bragard *et al.* 1996; Bragard & Velarde 1997, 1998, where reference is also given of related recent work by other authors). A small parameter allows separation of the fast variables that describe the instability and the slow variables that describe the pattern dynamics. For instance, the temperature can be written as

$$T = T(z)[A_1(X,Y,\tau)\exp(\mathrm{i}k^{(1)}\cdot r) + A_2\exp(\mathrm{i}k^{(2)}\cdot r) + A_3\exp(\mathrm{i}k^{(3)}\cdot r) + \text{c.c.}], \tag{4.1}$$

where $k^{(i)}$ denotes three linearly critical wave vectors oriented at 120° in the horizontal plane. The amplitude equations in the horizontal plane are (e.g. for A_1)

$$\begin{aligned}\alpha_{\mathrm{t}}\partial_{\mathrm{t}}A_1 = \alpha_{\mathrm{t}}\mathit{\Delta}A_1 &+ \alpha_{\mathrm{q}}A_2^*A_3^*\\ &-\alpha_{\mathrm{cs}}A_1|A_1|^2 - \alpha_{\mathrm{ci}}A_1(|A_2|^2+|A_3|^2)\\ &+\alpha_{\mathrm{d}}(k^{(1)}\cdot\nabla_x)^2A_1 + \mathrm{i}\beta_1(K^{(1)}\cdot\nabla_x)(A_2^*A_3^*)\\ &+\mathrm{i}\beta_2[A_2^*(k^{(2)}\cdot\nabla_x)A_3^* + A_3^*(k^{(3)}\cdot\nabla_x)A_2^*]\\ &+\mathrm{i}\beta_3[A_3^*(k^{(2)}\cdot\nabla_x)A_2^* + A_2^*(k^{(3)}\cdot\nabla_x)A_3^*],\end{aligned} \tag{4.2}$$

where $\alpha_1 = 0.0038$, $\alpha_{\mathrm{t}} = 0.05 + 0.013\,Pr^{-1}$, $\alpha_{\mathrm{q}} = 0.0203 - 0.0046\,Pr^{-1}$, $\alpha_{\mathrm{cs}} = 0.016 + 0.0049\,Pr^{-1} + 0.00077\,Pr^{-2}$, $\alpha_{\mathrm{ci}} = 0.0217 + 0.003\,Pr^{-1} + 0.0018\,Pr^{-2}$, $\alpha_{\mathrm{d}} = 0.0021$, $\beta_1 = \beta_2 = \beta_3 = \beta = 0.0016 - 0.0041\,Pr^{-1}$ and $\mathit{\Delta} = M - M_{\mathrm{c}}$. Similar equations appear for A_2 and A_3 (with circular permutation of the indices) (Bragard & Velarde 1997, 1998). The numbers correspond to the specific case of a poor conducting upper surface and good conducting lower plate as in standard experiments. These equations are generalized Ginzburg–Landau equations with advective terms with nonvanishing β coefficients. In general, for these equations there is no Lyapunov functional; hence for some value of the β we may observe no steady behaviour. $\mathit{\Delta}$ and β measure the (sub/supercritical) distance to the threshold and the strength of the advective terms, respectively. In the simpler case of $Pr \to \infty$ we define

$$\mathit{\Delta}_{\mathrm{c}} = -\frac{\alpha_{\mathrm{q}}^2}{4\alpha_1(\alpha_{\mathrm{cs}} + 2\alpha_{\mathrm{ci}})} \approx -0.456, \tag{4.3}$$

$$\mathit{\Delta}_1 = -\frac{\alpha_{\mathrm{q}}^2\alpha_{\mathrm{cs}}}{\alpha_1(\alpha_{\mathrm{cs}} - \alpha_{\mathrm{ci}})^2} \approx -53.4, \tag{4.4}$$

$$\mathit{\Delta}_2 = -\frac{\alpha_{\mathrm{q}}^2(2\alpha_{\mathrm{cs}} + \alpha_{\mathrm{ci}}}{\alpha_1(\alpha_{\mathrm{cs}} - \alpha_{\mathrm{ci}})^2} \approx 179.2. \tag{4.5}$$

Computations and stability analysis show two hysteresis cycles; hence coexistence and bistability appears in the intervals $[\mathit{\Delta}_{\mathrm{c}}, 0]$ and $[\mathit{\Delta}_1, \mathit{\Delta}_2]$, respectively.

As an illustration, for a square container starting from random initial conditions (cases (i)–(iv)) or rolls (v) we have the following results.

(i) ($\Delta = 50$, $\beta = 0.1$). The system evolves to a stationary hexagonal pattern. Relative to the case $\beta = 0$ an increase of β only slightly distorts the pattern. The fluid rises in the centre of the cells in accordance with experimental observations. No defects are observed.

(ii) ($\Delta = 75$, $\beta = 0$). The system is in a bistable region of hexagons and rolls.

(iii) ($\Delta = 150$, $\beta = 0$). The rolls are the preferred structure. At boundaries the rolls tend to be perpendicular to the sidewalls.

(iv) ($\Delta = 150$, $\beta = 0.1$). The system does not reach a steady state. Besides the roll structure, defects appear moving through the system.

(v) ($\Delta = 150$, $\beta = 0.1$). Here the computation is with the same parameter values as in (iv) but with rolls plus noise added as an initial condition. First, the structure evolves to rolls without defects, but as time goes on the rolls start to bend leading to a ‘zig-zag’-like instability (Manneville 1990). The system does not show evolution to a steady state, but rather tends to a labyrinthine structure and possibly interfacial ‘turbulence’.

5. Bénard layers: overstability and waves

Let us consider now the liquid layer heated from the air side or open to suitable mass adsorption from a vapor phase above, with subsequent absorption in the bulk; hence creating a (stabilizing) thermal gradient inside the liquid layer. Contrary to the case of a layer heated from the liquid side, here the layer is stably stratified and the problem refers to oscillatory motions, waves, and not to Bénard cells (Levchenko & Chernyakov 1981; García-Ybarra & Velarde 1987; Chu & Velarde 1988).

(*a*) *Oscillatory flow motions (transverse and longitudinal waves, surface and internal waves and their mode mixing)*

Generally, the Bénard problem with Marangoni stresses, gravity and buoyancy involves several time scales. On one hand we have the viscous and thermal scales, $t_{\mathrm{vis}} = d^2/\nu$, $t_{\mathrm{th}} = d^2/\kappa$, respectively. There also exist two time scales associated with gravity and surface tension (Laplace force) that tend to suppress surface deformation, $t_{\mathrm{gr}} = (d/g)^{1/2}$, $t_{\mathrm{cap}} = (\rho d^3/\sigma)^{1/2}$ (g is gravity acceleration and ρ is density or density contrast; other quantities as earlier defined). The time scale related to the Marangoni effect is $t_{\mathrm{Mar}} = (\rho d^2/|\sigma_{\mathrm{T}}\beta|)^{1/2}$ ($\sigma_{\mathrm{T}} = \mathrm{d}\sigma/\mathrm{d}T < 0$, $\beta = \Delta T/d$, $\beta > 0$ when heating from below). There is also another time scale related to buoyancy due to the stratification imposed by the temperature gradient, $t_{\mathrm{st}} = (1/(|\alpha\beta|g))^{1/2}$ (α is the thermal expansion coefficient, positive in the standard case). The ratios of the time scales give rise to the dimensionless groups

$$Pr = \frac{t_{\mathrm{th}}}{t_{\mathrm{vis}}} = \frac{\nu}{\kappa}, \quad M = \sigma_{\mathrm{T}}\frac{t_{\mathrm{th}}t_{\mathrm{vis}}}{t_{\mathrm{st}}^2} = -\frac{\sigma_{\mathrm{T}}\beta d^2}{\eta\kappa}, \quad R = \frac{t_{\mathrm{th}}t_{\mathrm{vis}}}{t_{\mathrm{st}}^2} = \frac{\alpha\beta g d^1}{\nu\kappa},$$

$$G = \frac{t_{\mathrm{th}}t_{\mathrm{vis}}}{t_{\mathrm{gr}}^2} = \frac{gd^3}{\nu\kappa}, \quad B = \frac{t_{\mathrm{cap}}^2}{t_{\mathrm{gr}}^2} = \frac{\rho g d^2}{\sigma},$$

which heuristically are the earlier introduced Prandtl, Marangoni, Rayleigh, Galileo and (static) Bond numbers, respectively.

These time scales are not always of the same order (accordingly, Pr, M, R, G and

B are not always of order unity). For example, for the Pearson problem (Pearson 1958), i.e. the onset of the monotonic instability in a liquid layer with undeformable surface, we have $M \approx 1$, but $G \gg 1$ for gravity to be able to keep the surface practically level, whatever flows and thermal inhomogeneities exist, and $R \ll M$ for buoyancy to be neglected. The characteristic time scale of the problem is essentially $t_{\mathrm{th}} \approx t_{\mathrm{vis}} \approx t_{\mathrm{Mar}}$ (at $Pr \approx 1$).

Thus, for monotonic instability there exists a finite limit of the critical Marangoni number as $G \to \infty$ given just by Pearson's (1958) results. However, this is not the case for the oscillatory instability waves, where the critical Marangoni number tends to infinity with $G \to \infty$. Indeed, oscillatory instability does not appear in the one-layer problem with undeformable surface. Thus the critical Marangoni number should better be scaled with G, as G becomes very large ($G \to \infty$).

It is also known that for high enough values of G an oscillatory mode is the capillary-gravity wave. The time scales t_{gr} and t_{cap} associated with this wave are much smaller than the viscous and thermal time scales (at least for $Pr \approx 1$, $B \approx 1$). Then dissipative effects are weak and hence the wave is very much the inviscid liquid capillary-gravity wave with the dispersion relation $\omega^2 = G\,Pr\,k(1+(k^2/B))\tanh(k)$ (to non-dimensionalize ω the thermal time scale is used hereafter; k is the dimensionless wave number in units of d^{-1}). Then the problem of oscillatory instability partly reduces to the question whether the Marangoni effect can sustain this otherwise damped wave. Clearly, the higher the G (and the wave frequency), the stronger should be the work of the Marangoni stresses (i.e. the critical Marangoni number) to sustain it, in agreement with the argument of the previous paragraph. An oscillatory instability can indeed be associated with the capillary-gravity wave. For a standard liquid layer, σ_{T}, this instability appears when heating the liquid layer from the air side ($M < 0$), as expected.

However, when the Marangoni number is high enough (and negative), there exists another high-frequency oscillatory mode. Indeed when a liquid element rises to the surface, it creates a cold spot there. Then, the surface tension gradient acts towards this spot, pushing the element back to the bulk, leading to overstability. High values of M ensure that the oscillations exist. Their characteristic time scale is t_{Mar}. The corresponding wave is called 'longitudinal' as it is due to the Marangoni stresses along the surface in contrast to capillary-gravity waves with essentially transverse motion of the surface. Lucassen made the theoretical (and experimental) discovery of this wave mode (Lucassen 1968).

Calculation yields the following expression for the frequency of the longitudinal wave (in the limit $M \to -\infty$):

$$\omega^2 = -M\frac{Pr}{Pr^{1/2}+1}k^2.$$

Although this longitudinal wave has a genuinely dissipative nature, the damping rate proves to be asymptotically smaller, $O(|M|^{1/4})$, than its frequency. In practical terms the flow field accompanying the longitudinal wave is qualitatively similar to that for the capillary-gravity wave. Potential flow can be assumed in the bulk of the layer, while vorticity is present only in boundary layers at the bottom rigid plate and at the upper free surface. The boundary layer thickness is of the order $O(|M|^{-1/4})[O(G^{-1/4})]$ for the capillary-gravity wave. However, there is a significant difference, as already noted by Lucassen (1968). For the longitudinal wave the horizontal velocity field in the surface boundary layer is much more intense than the potential flow in the bulk (by $O(|M|^{1/4})$) at variance with the capillary-gravity wave. Thus, the longitudinal motion is really concentrated near the surface. Furthermore, it appears that with an undeformable surface ($1 \ll |M| \ll G$), the longitudinal mode is always damped. Indeed, oscillatory instability does not appear in the one-layer Marangoni problem without surface deformability. However, if the longitudinal wave is accompained by non-negligible surface deformation ($|M| \geqslant G$), it can be amplified, a striking result (Rednikov *et al.* 1998*a*).

Thus, at $G \gg 1$, the oscillatory Marangoni instability is associated with two high-frequency wave modes; capillary-gravity and longitudinal. The damping rate of one wave mode cannot be drastically changed, or even converted into amplification (oscillatory instability), if the underlying framework for the other wave mode does not operate. As already stated, to sustain the longitudinal wave one needs surface deformability. It also occurs that to sustain a capillary-gravity wave one needs the Marangoni effect. This is the coupling between capillary-gravity and longitudinal waves. The latter necessarily implies viscous effects. Presumably, the most dramatic manifestation of this coupling occurs at resonance, when the frequencies (2.1) and (2.2) are equal to each other. Near resonance there is mode-mixing. Namely, the capillary-gravity mode in the parameter half-space from one side of the resonance manifold is swiftly converted into the longitudinal mode when crossing the manifold, and vice versa. Another feature of resonance is that the damping/amplification rates are drastically enhanced here ($O(G^{3/5})$ versus $O(G^{1/4})$ far from resonance) (Rednikov *et al.* 1998*a*).

If the liquid layer is deep enough and has an undeformable surface the possibility also exists of coupling longitudinal waves to internal (negative buoyancy-driven) waves with $|R| \ll G$. This is the Rayleigh–Marangoni problem. Indeed, the role of the capillary-gravity wave is now played by the Brunt–Väisälä internal wave of frequency

$$\omega^2 = -R\,Pr\,\frac{k^2}{k^2+\pi^2 n^2} \quad (n = 1, 2, \ldots),$$

whose existence is due to the stable stratification induced by heating the layer from above. The oscillatory instability comes again from wave–wave coupling, now between internal and longitudinal waves. Note that in the absence of the Marangoni effect, no oscillatory motion via instability is possible, which again stresses the crucial role played by the coupling. This instability is studied in detail in Rednikov *et al.* (1998*b*).

Although general features of mode coupling are similar in the two problems, there are differences. In the Rayleigh–Marangoni case we have a countable number ($n = 1, 2, \ldots$) of internal wave modes, and the longitudinal wave can be coupled to each of them; hence there is a countable number of marginal stability conditions. The form of the marginal curves is qualitatively different. Furthermore, there exists the minimally possible Rayleigh number (in absolute value), below which there is no oscillatory instability. No such bound was found for the Galileo number in the first problem (at least in the region where G remains high).

(*b*) *Nonlinear waves*

(i) *Nonlinear theory for long wavelength motions in shallow layers*

The nonlinear evolution past threshold of either capillary-gravity or longitudinal waves poses formidable tasks. Let us then concentrate on a simplified analysis, which is still amenable to experimental test. If we restrict consideration to just long wave oscillatory instability it has been shown (Chu & Velarde 1991; Velarde *et al.* 1991; Garazo & Velarde 1991; Nepomnyashchy & Velarde 1994) that in the particular case of one-sided (left to right) moving waves they are describable by a dissipation-modified KdV equation:

$$h_{\mathrm{t}} + (h^2)_y + h_{yyy} + \delta[h_{yy} + h_{yyy} + D(h^2)_{yy} + \alpha h] = 0, \tag{5.1}$$

where $h(y,t)$ is a scaled elevation of the surface in the study of one-side steadly propagating waves. The coefficient D can be either positive or negative, while α and δ are non-negative. Equation (5.1) underlies the energy balance sustaining, say, a solitary wave. Indeed, multiplying equation (5.1) by h, and integrating over the appropriate space, if the mean value of h along the layer is zero (mass conservation), then the energy $E = \frac{1}{2}\int h^2$ is governed by the balance

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \delta\biggl(\int h_x^2\,\mathrm{d}x - \int h_{xx}^2\,\mathrm{d}x + 2D\int hh_x^2\,\mathrm{d}x - \alpha\int h^2\,\mathrm{d}x\biggr), \tag{5.2}$$

whose value vanishes for a steadily travelling wave. The first term on the right-hand side of (5.2) describes the energy input at rather long wavelengths due to instability, the second and fourth terms describe energy dissipation on short and long wavelengths, respectively, and the third term accounts for nonlinear (feedback) correction to long-wave energy input (for h positive, positive if D is positive and negative otherwise). In the absence of dissipation and continuous energy supply, equation (5.1) reduces to the standard KdV equation and solitary waves or cnoidal waves (periodic wave trains) are still possible thanks to the disperion-nonlinearity balance also existing in equation (5.1). When dissipation plays a negligible role in experiment they can be excited from appropriate initial conditions either numerically or in water tanks where viscosity can be neglected. In the present case the situation is different. Indeed, at variance with the (integrable, dissipation-less) KdV equation where a one-parameter family of solutions exists, and hence as a consequence of initial conditions all possible amplitudes and corresponding velocities exist, the input–output energy balance (5.2) selects a single wave or a single amplitude periodic wave train, a bound state or an erratic/chaotic wave train (Christov & Velarde 1995; Nekorkin & Velade 1994; Velarde *et al.* 1995; Rednikov *et al.* 1995*b*).

On the other hand, when considering the three-dimensional problem (Nepomnyashchy & Velarde 1994) phase shifts following collision or reflection at walls depend upon the incident angle, α_{i} (e.g. measured front-to-front or twice the value front-to-wall, i.e. by $\frac{1}{2}\pi - \alpha_{\mathrm{i}}$; a reflection is like a collision with a mirror image wave). At the approximate value of $\frac{1}{2}\pi$ no phase shift is expected while for lower collision angles the phase shift has the sign of phase shifts upon head-on collisions. Higher values than $\frac{1}{2}\pi$ (or $\alpha_{\mathrm{i}} < \frac{1}{4}\pi$) lead to a change of sign in the phase shift and the formation of a Mach stem, i.e. a third wave evolving phase locked with the post collision or reflected front, a phenomenon discovered a century ago by Russell (1885) for water waves and by Mach (Courant & Friedrichs 1948; Krehl & van der Geest 1991) for shocks in gases. The phase shift sign in such case is the same as the sign in the overtaking collisions discussed by Zabusky & Kruskal (1965) in their seminal paper where they also introduced the soliton concept. Phase shifts and the formation of bound states have been numerically observed. Starting with, for example, an initial condition of two nearby ‘solitary’ pulses, the system evolves according to equation (5.1) to a wave train with unequally spaced maxima. All maxima have the same value, and hence the same velocity dictated by the energy balance (5.2) in the steady state.

(ii) *Experiments*

Both mass absorption and desorption, and heat transfer experiments have been carried out with Bénard layers (Weidman *et al.* 1992; Linde *et al.* 1993*a*, *b*, 1997; Wierschem 1997). As a matter of fact, with the theory sketched in the previous subsection I unearthed some 25-year-old experiments by H. Linde, who at about the same time of the numerical discovery of the soliton (Zabusky & Krustal 1965) made its experimental finding (including the collision kinematics of solitons) in surface tension gradient-driven flows.

For the case of heat transfer (liquid depths from 0.3 to 0.8 cm) liquid octane was poured in a square or cylindrical vessel, and in an annular channel (1.5 and 2.0 cm inner and outer radii, respectively). The bottom was cooled by air or water at 20 °C and the quartz cover, placed at 0.3 cm above the liquid, was heated, establishing a temperature gradient in the liquid layer. For values of this gradient ranging from 10 to 200 K cm^{-1}, solitary waves and periodic wave trains have been observed showing behaviour in head-on and oblique collisions similar to results from mass transfer experiments.

For mass transfer the following set-up was devised. In a vessel A, either a cylindrical container or an annular channel was filled with liquid (liquid depth 1.8 cm). Two vessels B_1 and B_2 were also filled with another liquid. With pentane in B_1 and B_2 either xylene, nonane, trichloroethylene or benzene were used as an absorbing liquid in A, while with toluene as an absorbing liquid in A either hexane, pentane, acetone or diethylether were used in B_1 and B_2. In all cases the results were qualitatively the same. A glass cover, C, was placed on top of the vessels B_1 and then when the vessel C was full of hexane vapor, say, it was placed on top of A thus allowing the absorption of hexane by the toluene liquid in A. The adsorption and subsequent absorption processes were rather strong, creating Marangoni stresses high enough to trigger and sustain instability. During the whole duration of the experiment, hexane vapor was also allowed to diffuse from the two vessels B_2 to A.

Observation and recording with a CCD camera was made by shadowgraph from the top with pointlike illumination from the bottom up (work is in progress with more sophisticated means). For instance, with cylindrical or annular cylindrical containers, rather violent chaotic motions occurred at first along the surface in A with waves moving in practically all directions, but finally after about one minute, when most of the vapor in C has been absorbed, a dramatic self-organization led to regular wave motion. Long-time-lasting synchronically colliding counter-rotating periodic wave trains have been observed for about 50–200 s, while the single (periodic) wave train with either clockwise or counter-clockwise rotation remained up to 450 s. As the Marangoni stresses decay the number of crests in each train increases with corresponding wavelength decrease. Subsequently, a single set of either clockwise or counter-clockwise (periodic) rotating waves remains until finally when the constraint fades away all convective motions disappear. Typical mean wave velocities at the outer wall of the annular channel before and after collision are, respectively, 2.7 and 1.7 cm s^{-1} (corresponding to angular speeds of 71.4 and 45.7° s^{-1}, respectively). Thus the mean wave velocity right after collision is about 64% (with less than 2% error) the mean wave speed measured before collision. About 0.2 s after collision the original wave speed is recovered. The phase shift shows the same sign as in the case of head-on collisions of 'solitary' waves in rectangular vessels. Reflections at walls also illustrate the solitonic/shock behaviour of the waves which occur with and without the formation of a (phase locked, third wave) Mach stem according to the angle of incidence. I have sketched just some of our findings. The phenomena observed are complex and only recently have there been clear-cut distinction between mostly surface waves (Marangoni–Bénard problem) and (mostly) internal waves (Rayleigh–Marangoni problems), all of them are triggered and sustained by the Marangoni effect, as heuristically discussed in § 5 *a*. Further details about the experiments can be found in Weidman *et al.* (1992), Linde *et al.* (1993*a*, *b*, 1997) and Wierschem (1997).

This paper summarizes work done in the past few years in my laboratory at the Instituto Pluridiciplinar in Madrid. It is the result of fruitful collaborative research with Michèle Adler, J. Bragard, C. I. Christov, A. de Ryck, H. Linde, A. A. Nepomnyashchy, A. Ye. Rednikov, M. Santiago-Rosanne, V. Starov and A. Wierschem. The research was supported by various grants: DGICYT PB93-0081, EU Network ERBCHRX-CT96-0107, EU Network ERBFMRX-CT96-0010, and Fundación BBV (Programa Cátedra, University of Cambridge).

References

Barton, K. D. & Subramanian, R. S. 1989 *J. Coll. Interf. Sci.* **133**, 211.

Borgas, M. S. & Grotberg, J. B. 1988 *J. Fluid Mech.* **193**, 151.

Bragard, J. & Velarde, M. G. 1997 *J. Non-Equilib. Thermodyn.* **19**, 95.

Bragard, J. & Velarde, M. G. 1998 *J. Fluid Mech.* (In the press.)

Bragard, J., Pontes, J. & Velarde, M. G. 1996 *Int. J. Bifur. Chaos* **6**, 1665.

Bratukhin, Yu. K., Evdokimova, O. A. & Pschenichnikov, A. F. 1979 *Izv. Akad. Nauk USSR* (*Mech. Liquids Gases*) **5**, 55–57. (In Russian.)

Bratukhin, Yu. K., Briskman, V. A., Zuev, A. L., Pschenichnikov, A. F. & Rivkind, V. Ya. 1982 In *Hydrodynamics and heat-mass transfer in weightlessness*, pp. 98–109. Moscow: Nauka. (In Russian.)

Braun, B., Ikier, Ch., Klein, H. & Woermann, D. 1994 In *Rocket experiments in fluid science and materials sciences*, vol. 4, p. 119. Paris: ESA.

Christov, C. I. & Velarde, M. G. 1995 *Physica* D **86**, 323.

Chu, X.-L. & Velarde, M. G. 1988 *Physico Chem. Hydrodyn.* **10**, 727.

Chu, X.-L. & Velarde, M. G. 1991 *Phys. Rev.* A **43**, 1094.

Courant, R. & Friedrichs, K. O. 1948 *Supersonic flow and shock waves.* New York: Interscience.

Davis, S. H. 1987 *A. Rev. Fluid Mech.* **19**, 403.

Edwards, D. A., Brenner, H. & Wasan, D. T. 1991 *Interfacial transport processes and rheology* Boston, MA: Butterworth-Heineman.

Garazo, A. N. & Velarde, M. G. 1991 *Phys. Fluids* A **3**, 2295.

García-Ybarra, P. L. & Velarde, M. G. 1987 *Phys. Fluids* **30**, 1649.

Gaver, D. P. & Grotberg, J. B. 1990 *J. Fluid Mech.* **213**, 127.

Gaver, D. P. & Grotberg, J. B. 1992 *J. Fluid Mech.* **235**, 399.

Happel, J. & Brenner, H. 1965 *Low Reynolds number hydrodynamics.* Englewood Cliffs, NJ: Prentice-Hall.

Hardy, S. C. 1979 *J. Coll. Interf. Sci.* **69**, 157.

Koschmieder, E. L. 1993 *Bénard cells and Taylor vortices.* Cambridge University Press.

Krehl, P. & van der Geest, M. 1991 *Shock Waves* **1**, 3.

Levchenko, E. B. & Chernyakov, A. L. 1981 *Sov. Phys. JETP* **54**, 102.

Levich, B. G. 1965 *Physicohemical hydrodynamics.* Englewood Cliffs, NJ: Prentice-Hall.

Levich, B. G. & Krylov, V. S. 1969 *A. Rev. Fluid Mech.* **1**, 293.

Linde, H., Chu, X.-L. & Velarde, M. G. 1993*a* *Phys. Fluids* A **5**, 1068.

Linde, H., Chu, X.-L., Velarde, M. G. & Waldhelm, W. 1993*b* *Phys. Fluids* A **5**, 3162.

Linde, H., Velarde, M. G., Wierschem, A., Waldhelm, W., Loeschcke, K. & Rednikov, A. Ye. 1997 *J. Coll. Interf. Sci.* **188**, 16.

Lucassen, J. 1968 *Trans. Faraday Soc.* **64**, 2221.

Manneville, P. 1990 *Dissipative structures and weak turbulence.* San Diego, CA: Academic.

Merritt, R. M. & Subramanian, R. S. 1988 *J. Coll. Interf. Sci.* **125**, 333.

Nekorkin, V. I. & Velarde, M. G. 1994 *Int. J. Bifur. Chaos* **4**, 1135.

Nepomnyashchy, A. A. & Velarde, M. G. 1994 *Phys. Fluids* **6**, 187.

Normand, Ch., Pomeau, Y. & Velarde, M. G. 1977 *Rev. Mod. Phys.* **49**, 581, and references therein.

Ostrach, S. 1982 *A. Rev. Fluid Mech.* **14**, 313.

Pearson, J. R. J. 1958 *Fluid Mech.* **4**, 489.

Proudman, I. & Pearson, J. R. A. 1957 *J. Fluid Mech.* **2**, 237.

Rednikov, A. Ye., Ryazantsev, Yu. S. & Velarde, M. G. 1994*a* *Phys. Fluids* **6**, 451.

Rednikov, A. Ye., Ryazantsev, Yu. S. & Velarde, M. G. 1994*b* *J. Coll. Interf. Sci.* **164**, 168.

Rednikov, A. Ye., Ryazantsev, Yu. S. & Velarde, M. G. 1994*c* *Int. J. Heat. Mass Transf.* **37**, supp. 1, 361.

Rednikov, A. Ye., Ryazantsev, Yu. S. & Velarde, M. G. 1994*d* *J. Non-Equilib. Thermodyn.* **19**, 95.

Rednikov, A. Ye., Ryazantsev, Yu. S. & Velarde, M. G. 1994*e* *Phys. Scripta* T **55**, 115.

Rednikov, A. Ye., Kurdyumov, V. N., Ryazantsev, Yu. S. & Velarde, M. G. 1995*a* *Phys. Fluids* **7**, 2670.

Rednikov, A. Ye., Velarde, M. G., Ryazantsev, Yu. S., Nepomnyashchy A. A. & Kurdyumov, V. N. 1995*b* *Acta Appl. Math.* **39**, 457.

Rednikov, A. Ye., Colinet, P., Velarde, M. G. & Legros, J. C. 1998*a* Oscillatory themocapillary instability in a liquid layer with deformable open surface: capillary-gravity waves, longitudinal waves and mode-mixing. *J. Fluid Mech.* (Submitted).

Rednikov, A. Ye., Colinet, P., Velarde, M. G. & Legros, J. C. 1998*b* Rayleigh–Marangoni oscillatory instability in a liquid layer heated from above: coupling between internal and surface waves. *J. Fluid Mech.* (Submitted).

Russell, J. S. 1885 *The wave of translation in the oceans of water, air and ether.* London: Trübner & Co.

Santiago-Rosanne, M., Adler, M. & Velarde, M. G. 1997 *J. Coll. Interf. Sci.* **191**, 65.

Scriven, L. E. & Sternling, C. V. 1960 *Nature* **187**, 186.

Starov, V., Ryck, A. de & Velarde, M. G. 1997 *J. Coll. Interf. Sci.* **190**, 104.

Subramanian, R. S. 1981 *AIChE. Jl* **27**, 646.

Subramanian, R. S. 1992 In *Transport processes in bubbles, drops and particles* (ed. R. P. Chhabra & D. de Kee). New York: Hemisphere.

Taylor, T. D. & Acrivos, A. 1964 *J. Fluid. Mech.* **18**, 466.

Velarde, M. G. & Normand, C. 1980 *Sci. Am.* **243**, 92.

Velarde, M. G., Chu, X.-L. & Garazo, A. N. 1991 *Phys. Scripta* T **35**, 71.

Velarde, M. G., Nekorkin, V. I. & Maksimov, A. 1995 *Int. J. Bifur. Chaos* **5**, 831.

Velarde, M. G., Rednikov, A. Ye. & Ryazantsev, Yu. S. 1996 *J. Phys.* C **8**, 9233.

Weidman, P. D., Linde, H. & Velarde, M. G. 1992 *Phys. Fluids* A **4**, 921.

Wierschem, A. 1997 Ph.D. dissertation, Humboldt Universitat, Berlin.

Wozniak, G., Siekmann, J. & Srulijes, J. 1988 *Z. Flugwiss. Weltraumforsch.* **12**, 137.

Young, N. O., Goldstein J. S. & Block, M. J. 1959 *J. Fluid Mech.* **6**, 350.

Zabusky, N. J. & Kruskal, M. D. 1965 *Phys. Rev. Lett.* **15**, 57.

Discussion

S. K. Wilson (*Department of Mathematics, University of Strathclyde, Glasgow, UK*). As an applied mathematician working on the theoretical investigation of

Marangoni phenomena it has been very interesting to see some new situations in materials processing in which Marangoni effects are important. However, researchers in materials processing should be aware that work on similar phenomena is ongoing in other areas. These include crystal growing (about which we have heard something at this Meeting), the coating industry (see, for example, the paper by Wilson (1993)) and biological applications (see, for example, the recent review article by Grotberg (1994)). In all these cases I'm sure both parties would benefit from collaboration between workers in apparently very different subject areas.

J. R. Helliwell (*Department of Chemistry, University of Manchester, Manchester, UK*). Marangoni convection driven fluid flow is one type of convection effect (Helliwell 1988; Chayen *et al.* 1996). In any 'real' experiment, such as one to produce a high quality protein crystal (a type of materials processing, certainly), there are a variety of effects which can defeat the reaching of the ideal situation, which I define here as growing a protein crystal that does not move in the fluid due to sedimentation (on Earth), or due to g-jitter in orbit, and where also the mother liquor is not subject to (turbulent) fluid flow. A real situation then is a superposition of perturbation effects away from an ideal and each of which may induce some sort of defect. Neverthless, the choice of particular crystallization geometry, e.g. avoiding vapour diffusion (i.e. liquid–vapour interface) can avoid Marangoni effects. However, in a linear liquid–liquid diffusion geometry other effects due to g-jitter are more difficult to eliminate and, except perhaps in the case of an uncrewed orbiting platform, may always prevent the ideal conditions every truly being realized. I am interested to hear from other areas of 'materials processing' the relative importance for Marangoni over other convection or g-jitter driven effects. Perhaps cases like crystal growth from a liquid bridge, of initially molten material, simply cannot avoid Marangoni convection? By contrast, in protein crystal growth it seems that Marangoni convection can be avoided rather simply by avoidance of liquid vapour droplet geometry. The exploration of the ultimate protein crystal quality obtainable relates to the exceptionally fine X-ray brilliance available from the new generation of SR X-ray sources and harnessing their full technical capability. In addition, the overall motivation for such studies in protein crystallography is to better understand the factors that can lead to a poor quality crystal or indeed no crystal at all (or at best a 'microcrystal').

Additional references

Chayen, N. E., Boggon, T. J., Cassetta, A., Deacon, A., Gleichmann, T., Habash, J., Harrop, S. J., Helliwell, J. R., Nieh, Y. P., Peterson, M. R. and 9 others 1996 Trends and challenges in experimental macromolecular crystallography. *Q. Rev. Biophys.*, **29**, 227–278.

Grotberg, J. B. 1994 Pulmonary flow and transport phenomena. *A. Rev. Fluid Mech.* **26**, 529–571.

Helliwell, J. R. 1988 Protein crystal perfection and the nature of radiation damage. *J. Cryst. Growth* **90**, 259–272.

Wilson, S. K. 1993 The levelling of paint films. *IMA J. Appl. Math.* **50**, 149–166.