

THE MARANGONI EFFECTS

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Cause of, and Resistance to, Surface Movements

WITH the name of the Italian physicist Carlo Marangoni of Pavia and Florence (1840–1925) have been associated two distinct although related surface effects. The first of these is movement in a fluid interface. The motion is caused by local variations of interfacial tension that are caused in turn by differences in composition or temperature. The second is the conjugate of the first: it is the departure from equilibrium tension that is produced by extension or contraction of an interface, that is, by dilational deformation. Both effects were correctly explained in a qualitative way nearly a hundred years ago. A wealth of information about them was reported by Marangoni and his contemporaries, among whom were some of the foremost scientists of the nineteenth century—Plateau, Gibbs, and Rayleigh.

Certain aspects of surface spreading and dynamic surface tension have continued to receive attention in the physical chemistry of fluid interfaces, especially as that subject pertains to foams and emulsions. However, little effort has been directed toward quantitative understanding of these effects as they affect the dynamic behaviour of fluid interfaces. To-day there is heightened interest in this goal, because of the growing number of diverse, practically important situations in which their influence is being recognized. For example, it is now known that local variations of surface tension may set into intricate motion an entire liquid film such as a drying coat of paint. Again, it is now appreciated that the difference between dynamic and equilibrium behaviour of interfaces is responsible for the paradoxical motion under buoyancy of small bubbles and drops in various liquids.

Surface Movements

"On Certain Curious Motions Observable at the Surfaces of Wine and other Alcoholic Liquors", published in 1855 by the British engineer and physicist James Thomson¹, contains the first correct explanation of the spreading of a drop of alcohol on the surface of water, the well-known tears of strong wine, and related phenomena. Thomson rightly inferred that the same sort of surface-tension-driven flows were responsible for the "numerous motions of extremely wonderful characters in fluids undergoing evaporation" that Varley had observed earlier with the aid of a microscope². Similar microscopic studies of convection patterns in evaporating drops were made independently by Weber³.

Numerous fascinating experiments with surface movements were reported afterwards^{4–7}; but Thom-

son's paper went unnoticed until van der Mensbrugghe's definitive memoir appeared in 1869 in a now obscure Belgian journal⁸. Van der Mensbrugghe reviewed all the earlier work, including the literature on the camphor dance dating back to 1686, and established that all the varied instances of surface movement were caused by local differences of interfacial tension. When Marangoni contested the priority of van der Mensbrugghe's finding⁹, Thomson's paper again went unmentioned, and it is probably for this reason that the effect has come to bear Marangoni's name (cf. ref. 10).

The classic qualitative studies have been continued by more recent investigators: Marcelin devised surface engines¹¹, Loewenthal was fascinated by tears of strong wine¹², the Langmuirs discovered that surface movements enhance the rate of evaporation¹³, and Jebsen-Marwedel found that surface-tension-driven flows critically affect mixing and wall erosion in glass-melting furnaces^{14,15}. Photographs of tears of strong wine have recently appeared¹⁶. There have been discussions of the role of such flows in crystal growth^{17,18}, motion of protoplasm^{19–21}, transport of bacteria²¹, surface fractionation²², absorption and distillation²³, foam stability^{24,25} and other phenomena^{26,27}. Mention should be made of the thermodynamic theories of spreading of surface films²⁸.

The cellular convection patterns induced by surface tension that Varley² and others^{3,19} saw were later the subject of Bénard's beautiful experiments^{29,30}. Bénard's work inspired the Rayleigh–Jeffreys theory of convection currents induced by density variations in liquids heated from below. However, this theory is at variance with Bénard's experiments in several respects. From the new experiments of Block³¹ and theoretical analysis of Pearson³² it is now known that surface tension rather than density variations produced Bénard's cells. Meanwhile the Rayleigh–Jeffreys theory has been confirmed by other experiments to which it properly applies³³. It is interesting that Sutherland was led to postulate density-induced convection currents in order to explain the surprisingly rapid attainment of equilibrium tension at certain newly formed gas-liquid interfaces³⁴. Surface-tension-driven flows seem no less likely an explanation.

The periodic twitching of an air bubble in water, toward which a fine jet of alcohol is directed, seems to have been first described by Quincke³⁵, who showed that surface-tension-driven flow is responsible. Recently rediscovered in slightly different guise by Lewis and Pratt³⁶, the phenomenon has attracted great interest in the field of liquid-liquid extraction. A semi-quantitative theoretical analysis was made by Haydon and Davies^{36,37}. Similar phenomena occur at all sorts of fluid interfaces across which material diffuses^{38,39}. Notable is the extensive investigation by Wei⁴⁰. This spontaneous agitation of the interface between two unequilibrated fluids, which has come to

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be known as 'interfacial turbulence', has not yet been taken into account in the classic theories of interphase mass transfer. In order to arrive at an adequate theory, it will be necessary to know precisely the conditions which give rise to interfacial turbulence as well as the details of the flows. We have considered the preliminary problem from the point of view of the theory of hydrodynamic stability, arriving at a partial understanding of the factors that determine 'Marangoni instability'—the onset of interfacial agitation driven by local variations of interfacial tension⁴¹.

Our analysis shows how it is that some systems are stable with solute transfer in one direction across the interface yet unstable with transfer in the opposite direction (cf. ref. 42). It indicates the importance of solute diffusivity in the two phases, the viscosities of the fluids, the dependence of interfacial tension on composition, and other parameters. In at least some circumstances the phenomenon known as spontaneous emulsification seems to originate in interfacial-tension-driven flows⁴³.

Surface Elasticity and Viscosity

The resistance of a fluid interface to deformation was first noted by the blind Belgian physicist Joseph Plateau, famous for his researches on capillary action, especially the equilibrium configurations of liquid masses under the influence of surface tension (see his great treatise⁴⁴). The different rates of damping of an oscillating compass needle suspended on one hand in the surface and on the other in the bulk of various liquids led Plateau to infer the existence of a 'superficial viscosity' peculiar to a liquid surface but analogous to the ordinary viscosity of fluids in bulk^{44,45}. In so far as his needle subjected the surface to shear, Plateau's inference was substantially correct: since his time, measurements of shear viscosity and elasticity of surface films have become commonplace^{28,46-51}. However, if surfaces of pure liquids have a peculiar resistance to shear, present experimental techniques are not sufficiently sensitive to detect it.

What Plateau did not appreciate is that virtually every liquid surface is contaminated with insoluble material to some degree, and that there exists an equilibrium between material dissolved in the bulk and adsorbed on the surface of solutions. Thus the advancing needle tended to concentrate contamination and adsorbed material ahead and to dilute them behind it. This produced a difference in surface tension on either side of the needle, the difference being of the proper sense to damp the motion.

Marangoni⁵² first clearly recognized this effect in the experiments of Plateau, who remained unconvinced⁵³⁻⁵⁵. It remained for Gibbs to give it a completely satisfactory explanation⁵⁶; hence the name, 'Plateau-Marangoni-Gibbs effect'⁵⁷. There is a lucid and definitive paper on the subject by Lord Rayleigh⁵⁸, who made other valuable contributions to the understanding of surface movements and the resistance thereto⁵⁹⁻⁶¹. The part played by the 'Plateau-Marangoni-Gibbs effect' in stabilizing free films and foams has long been recognized in a general way, often under the name 'Gibbs elasticity' (for example, ref. 25). But the 'profound analysis of the act of thinning of a film' called for by Derjaguin and Titijevskaya⁵⁷ has not yet appeared. The mathematics of such an analysis is formidable, owing to the

complicated velocity and concentration fields involved.

As Birkhoff observed in connexion with the 'rising-bubble paradox', the mechanics of real fluid interfaces is far less simple than the classical hydrodynamic treatments would suggest⁶². The paradox is that the motion under buoyancy of small bubbles and drops through a liquid is usually much closer to the behaviour of rigid spheres than to that expected for fluid spheres capable of internal circulation. But in systems cleansed of interfacially active material, the paradoxical behaviour does not occur, except with the smallest of bubbles and drops^{63,64}. The seeming exception may be due to the extreme difficulty of eliminating the last traces of interfacial contamination^{6,46,56,58,66}. If circulation of the bubble or drop is retarded or arrested, there must exist a force not contained in classical hydrodynamics which opposes the viscous traction exerted on its surface by the surrounding liquid; and because the viscous traction tends to expand the surface phase over the leading hemisphere and contract it behind, the 'Plateau-Marangoni-Gibbs effect' is sufficient to account for the existence of this force. The first to recognize this was Boussinesq⁶⁷, who showed that any viscous-like resistance to dilational deformation of the surface, whatever its origin, causes fluid spheres to move more slowly than expected from classical treatments, in which the possibility had been overlooked. Modern mathematical analyses have shown how the kinetics of adsorption of soluble surface-active materials can account for a 'dilational surface viscosity'^{68,69}. The Marangoni effect mentioned above may also enter; for with mass transfer between the dispersed and continuous fluids, as occurs in liquid-liquid extraction and related operations, there may be a sufficiently high concentration—hence also interfacial tension—gradient in the proper direction along the interface to arrest or even reverse the internal circulation. The entire situation of drop circulation and the effects of surface-active materials was recently discussed by Linton and Sutherland⁷⁰.

The role of shear viscosity and elasticity of surface phases and of the 'Plateau-Marangoni-Gibbs effect' in other free boundary flows has been considered by at least a few hydrodynamicists after Aitken's discussion of the calming action of oil on capillary waves on the surface of water⁷¹. Specific reference should be made to the writings of Lamb⁷², Levich (as cited by Fedosov⁶⁹), and especially Oldroyd⁷³, whose theoretical work on the effect of surface properties in the rheological behaviour of emulsions is partly confirmed by the recent experiments of Nawab and Mason on the viscosity of dilute emulsions containing surfactants⁷⁴.

The resistance of fluid interfaces to deformation is manifest, though not yet completely understood, in the stagnation of portions of interfaces in certain liquid-liquid extraction^{35,41,75} gas absorption⁷⁶, and vacuum distillation experiments^{65,66}.

Quantitative understanding of the dynamic behaviour of fluid interfaces requires that their mechanics be described mathematically. The earliest attempts at this seem to have been made by Tait, who considered the effect of flexural-rigidity of a surface on ripples in a viscous fluid⁷⁷, and by Basset, who examined certain consequences of interfacial behaviour that allows slip between two phases in contact⁷⁸. The most useful description for approximating the behaviour of real interfaces is that begun

by Boussinesq, who set up the two-dimensional analogue of the three-dimensional Newtonian fluid⁴⁷. In this model the mechanics of the interface is completely characterized by its static (equilibrium) tension and two coefficients governing its behaviour in flow: the surface shear viscosity and the dilational surface viscosity.

It was this model that Boussinesq appealed to in his explanation of the rising-bubble paradox. Only recently was it used in treating another free boundary flow, by Oldroyd as mentioned above. Surface-active materials inhibit the transition of falling liquid films from smooth to wavy flow⁷⁹. In a new analysis of this transition regarded as a hydrodynamic stability question, Barr-David and one of us have suggested how to account for this influence of surfactants: we adopted Boussinesq's model in formulating boundary conditions at the free surface of the film⁸⁰. In order to account for a similar inhibitory influence of surface-active materials on interfacial turbulence, the same thing was done in our analysis of Marangoni instability⁴¹.

In the original equations of Boussinesq and in their alternative statement as in Oldroyd's equation (4)⁷³, the model interface is constrained to shape and total extent both constant in time. While this restriction is reasonable for free boundaries in steady flows, or when the interfacial tension is sufficiently high, it is violated in many real situations. Consequently we have generalized Boussinesq's equations so as to describe the dynamics of a Newtonian fluid interface undergoing continuous change in shape and extent⁸¹. The analysis leads to the interfacial boundary conditions on non-steady flows with free boundaries. Also tabulated are boundary conditions for the relatively simple cases of planar, cylindrical, and spherical surfaces. The work of Oldroyd suggests the possibility of further extensions to describe interfaces displaying all types of linear visco-elastic behaviour, many of which have, in fact, been observed in the laboratory^{17,25,28,50}.

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