

10. Marangoni Flows II

10.1 Tears of Wine

The first Marangoni flow considered was the tears of wine phenomenon (*Thomson 1885*), which actually predates Marangoni's first published work on the subject by a decade. The tears of wine phenomenon is readily observed in a wine glass following the establishment of a thin layer of wine on the walls of the glass.

An illustration of the tears of wine phenomenon is shown in Fig. 10.1. Evaporation of alcohol occurs everywhere along the free surface. The alcohol concentration in the thin layer is thus reduced relative to that in the bulk owing to the enhanced surface area to volume ratio. As surface tension decreases with alcohol concentration, the surface tension is higher in the thin film than the bulk; the associated Marangoni stress drives upflow throughout the thin film. The wine climbs until reaching the top of the film, where it accumulates in a band of fluid that thickens until eventually becoming gravitationally unstable and releasing the tears of wine. The tears or "legs" roll back to replenish the bulk reservoir, but with fluid that is depleted in alcohol.

The flow relies on the transfer of chemical potential energy to kinetic and ultimately gravitational potential energy. The process continues until the fuel for the process, the alcohol is completely depleted. For certain liquors (e.g. port), the climbing film, a Marangoni shear layer, goes unstable to streamwise vortices and an associated radial corrugation - the "tear ducts of wine" (*Hosoi & Bush, JFM 2001*). When the descending tears reach the bath, they appear to recoil in response to the abrupt change in σ . The tears or legs of wine are taken by sommeliers to be an indicator of the quality of wine.

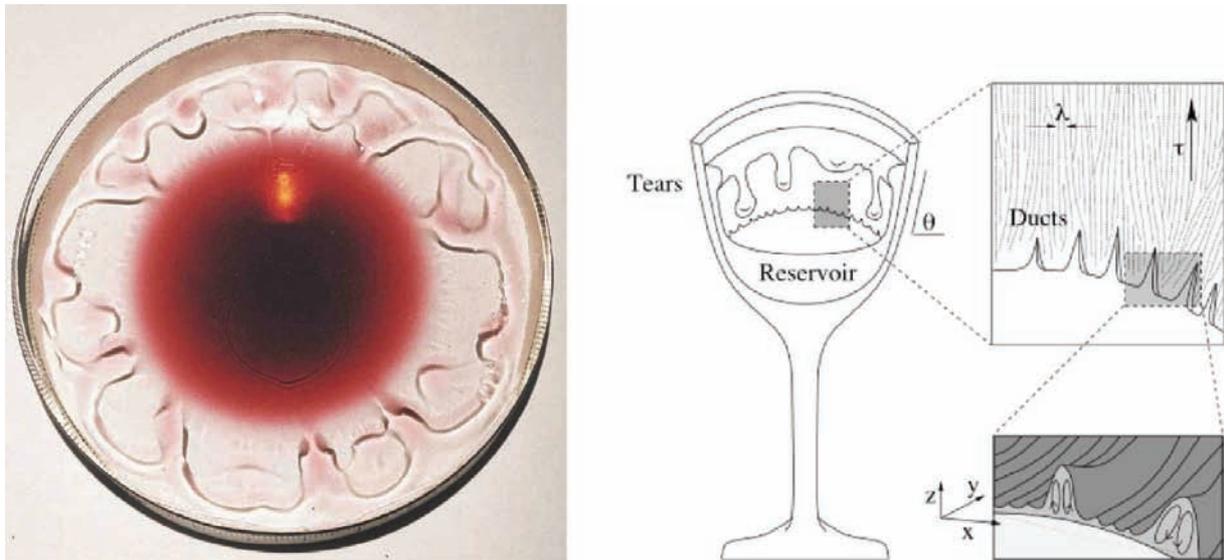


Figure 10.1: The tears of wine. Fluid is drawn from the bulk up the thin film adjoining the walls of the glass by Marangoni stresses induced by evaporation of alcohol from the free surface.

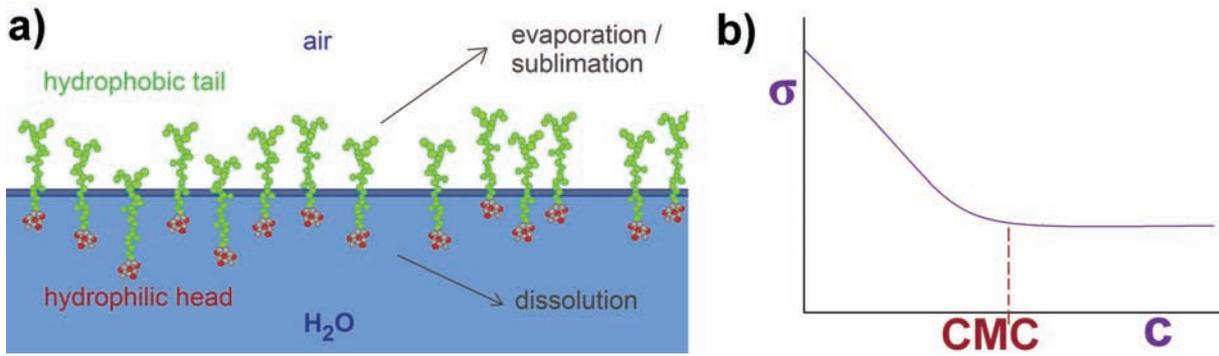


Figure 10.2: a) A typical molecular structure of surfactants. b) The typical dependence of σ on surfactant concentration c .

10.2 Surfactants

Surfactants are molecules that have an affinity for interfaces; common examples include soap and oil. Owing to their molecular structure (e.g. a hydrophilic head and hydrophobic tail, Fig. 10.2a), they find it energetically favourable to reside at the free surface. Their presence reduces the surface tension; consequently, gradients in surfactant concentration Γ result in surface tension gradients. Surfactants thus generate a special class of Marangoni flows. There are many different types of surfactants, some of which are insoluble (and so remain on the surface), others of which are soluble in the suspending fluid and so diffuse into the bulk. For a wide range of common surfactants, surface tension is a monotonically decreasing function of Γ until a critical micell concentration (CMC) is achieved, beyond CMC there is no further dependence of σ on Γ (Fig. 10.2b).

Surfactant properties:

- **Diffusivity** prescribes the rate of diffusion, D_s (bulk diffusivity D_b), of a surfactant along an interface
- **Solubility** prescribes the ease with which surfactant passes from the surface to the bulk. An insoluble surfactant cannot dissolve into the bulk, must remain on the surface.
- **Volatility** prescribes the ease with which surfactant sublimates.

Theoretical Approach: because of the dependence of σ on the surfactant concentration, and the appearance of σ in the boundary conditions, N-S equations must be augmented by an equation governing the evolution of Γ . In the bulk,

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D_b \nabla^2 c \quad (10.1)$$

The concentration of surfactant Γ on a free surface evolves according to

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{u}_s) + \Gamma (\nabla_s \cdot \mathbf{n}) (\mathbf{u} \cdot \mathbf{n}) = J(\Gamma, C_s) + D_s \nabla_s^2 \Gamma \quad (10.2)$$

where \mathbf{u}_s is the surface velocity, ∇_s is the surface gradient operator and D_s is the surface diffusivity of the surfactant (Stone 1999). J is a surfactant source term associated with adsorption onto or desorption from the surface, and depends on both the surface surfactant concentration Γ and the concentration in the bulk C_s . Tracing the evolution of a contaminated free surface requires the use of Navier-Stokes equations, relevant boundary conditions and the surfactant evolution equation (10.2). The dependence of surface tension on surfactant concentration, $\sigma(\Gamma)$, requires the coupling of the flow field and surfactant field. In certain special cases, the system may be made more tractable. For example, for insoluble surfactants, $J = 0$. Many surfactants have sufficiently small D_s that surface diffusivity may be safely neglected.



Figure 10.3: The footprint of a whale, caused by the whales sweeping biomaterial to the sea surface. The biomaterial acts as a surfactant in locally suppressing the capillary waves evident elsewhere on the sea surface. Observed in the wake of a whale on a Whale Watch from Boston Harbour.

Special case: expansion of a spherical surfactant-laden bubble.

$\frac{\partial \Gamma}{\partial t} + \Gamma (\nabla \cdot \mathbf{n}) u_r = 0$. Here $\nabla \cdot \mathbf{n} = 2/R$, $u_r = \frac{dR}{dt}$ so $\frac{d\Gamma}{dt} + \Gamma \frac{2}{R} \frac{dR}{dt} = 0 \Rightarrow \frac{d\Gamma}{\Gamma} = -2 \frac{dR}{R}$ $4\pi R^2 \Gamma = \text{const.}$, so the surfactant is conserved.

Marangoni Elasticity The principal dynamical influence of surfactants is to impart an effective elasticity to the interface. One can think of a clean interface as a “slippery trampoline” that resists deformation through generation of normal curvature pressures. However, such a surface cannot generate traction on the interface. However, a surface-laden interface, like a trampoline, resists surface deformation as does a clean interface, but can also support tangential stresses via Marangoni elasticity. Specifically, the presence of surfactants will serve not only to alter the normal stress balance (through the reduction of σ), but also the tangential stress balance through the generation of Marangoni stresses.

The presence of surfactants will act to suppress any fluid motion characterized by non-zero surface divergence. For example, consider a fluid motion characterized by a radially divergent surface motion. The presence of surfactants results in the redistribution of surfactants: Γ is reduced near the point of divergence. The resulting Marangoni stresses act to suppress the surface motion, resisting it through an effective surface elasticity. Similarly, if the flow is characterized by a radial convergence, the resulting accumulation of surfactant in the region of convergence will result in Marangoni stresses that serve to resist it. It is this effective elasticity that gives soap films their longevity: the divergent motions that would cause a pure liquid film to rupture are suppressed by the surfactant layer on the soap film surface.

The ability of surfactant to suppress flows with non-zero surface divergence is evident throughout the natural world. It was first remarked upon by Pliny the Elder, who rationalized that the absence of capillary waves in the wake of ships is due to the ships stirring up surfactant. This phenomenon was also widely known to spear-fishermen, who poured oil on the water to increase their ability to see their prey, and by sailors, who would do similarly in an attempt to calm troubled seas. Finally, the suppression of capillary waves by surfactant is at least partially responsible for the ‘footprints of whales’ (see Fig. 10.3). In the wake of whales, even in turbulent roiling seas, one sees patches on the sea surface (of characteristic width 5-10m) that are perfectly flat. These are generally acknowledged to result from the whales sweeping biomaterial to the surface with their tails, this biomaterial serving as a surfactant that suppresses capillary waves.

Surfactants and a murder mystery. From *Nature*, 22, 1880:

*“In the autumn of 1878 a man committed a terrible crime in Somerset, which was for some time involved in deep mystery. His wife, a handsome and decent mulatto woman, disappeared suddenly and entirely from sight, after going home from church on Sunday, October 20. Suspicion immediately fell upon the husband, a clever young fellow of about thirty, but no trace of the missing woman was left behind, and there seemed a strong probability that the crime would remain undetected. On Sunday, however, October 27, a week after the woman had disappeared, some Somerville boatmen looking out towards the sea, as is their custom, were struck by observing in the Long Bay Channel, the surface of which was ruffled by a slight breeze, a **streak of calm such as, to use their own illustration, a cask of oil usually diffuses around it when in the water.** The feverish anxiety about the missing woman suggested some strange connection between this singular calm and the mode of her disappearance. Two or three days after - why not sooner I cannot tell you - her brother and three other men went out to the spot where it was observed, and from which it had not disappeared since Sunday, and with a series of fish-hooks ranged along a long line dragged the bottom of the channel, but at first without success. Shifting the position of the boat, they dragged a little further to windward, and presently the line was caught. With water glasses the men discovered that it had caught in a skeleton which was held down by some heavy weight. They pulled on the line; something suddenly gave way, and up came the skeleton of the trunk, pelvis, and legs of a human body, from which almost every vestige of flesh had disappeared, but which, from the minute fragments remaining, and the terrible stench, had evidently not lain long in the water. The husband was a fisherman, and Long Bay Channel was a favourite fishing ground, and he calculated, truly enough, that the fish would very soon destroy all means of identification; but it never entered into his head that as they did so their ravages, combined with the process of decomposition, **set free the matter which was to write the traces of his crime on the surface of the water.** The case seems to be an exceedingly interesting one; the calm is not mentioned in any book on medical jurisprudence that I have, and the doctors seem not to have had experience of such an occurrence. A diver went down and found a stone with a rope attached, by which the body had been held down, and also portions of the scalp and of the skin of the sole of the foot, and of clothing, by means of which the body was identified. The husband was found guilty and executed.”*

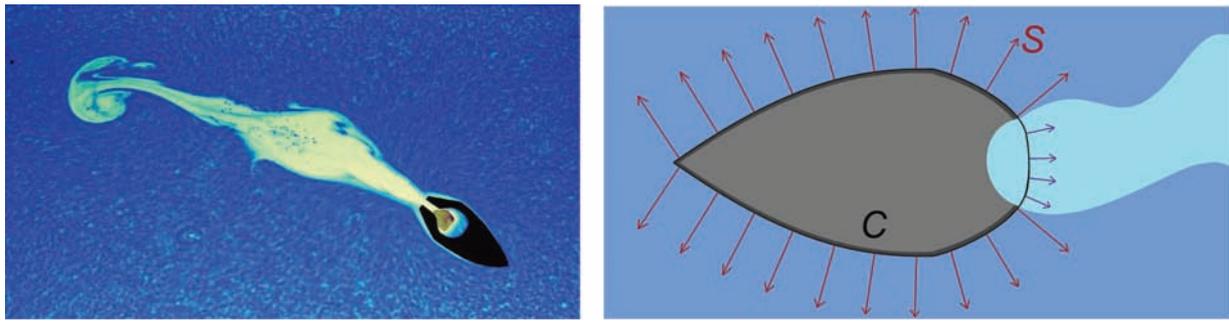


Figure 10.4: The soap boat. A floating body (length 2.5cm) contains a small volume of soap, which serves as its fuel in propelling it across the free surface. The soap exits the rear of the boat, decreasing the local surface tension. The resulting fore-to-aft surface tension gradient propels the boat forward. The water surface is covered with Thymol blue, which parts owing to the presence of soap, which is thus visible as a white streak.

10.3 Surfactant-induced Marangoni flows

1. Marangoni propulsion

Consider a floating body with perimeter C in contact with the free surface, which we assume for the sake of simplicity to be flat. Recalling that σ may be thought of as a force per unit length in a direction tangent to the surface, we see that the total surface tension force acting on the body is:

$$F_c = \int_C \sigma \mathbf{s} dl \quad (10.3)$$

where \mathbf{s} is the unit vector tangent to the free surface and normal to C , and dl is an increment of arc length along C . If σ is everywhere constant, then this line integral vanishes identically by the divergence theorem. However, if $\sigma = \sigma(\mathbf{x})$, then it may result in a net propulsive force. The ‘soap boat’ may be simply generated by coating one end of a toothpick with soap, which acts to reduce surface tension (see *right*). The concomitant gradient in surface tension results in a net propulsive force that drives the boat away from the soap. We note that an analogous Marangoni propulsion technique arises in the natural world: certain water-walking insects eject surfactant and use the resulting surface tension gradients as an emergency mechanism for avoiding predation. Moreover, when a pine needle falls into a lake or pond, it is propelled across the surface in an analogous fashion owing to the influence of the resin at its base decreasing the local surface tension.

2. Soap film stability

Pinching a film increases the surface area, decreases Γ and so increases σ . Fluid is thus drawn in and the film is stabilized by the Marangoni elasticity.

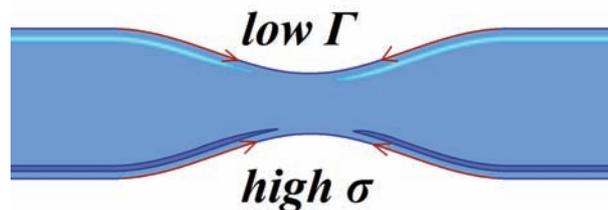


Figure 10.5: Fluid is drawn to a pinched area of a soap film through induced Marangoni stresses.

3. Vertical Soap Film

- Vertical force balance: $\rho gh(z) = \frac{d\sigma}{dz}$. The weight of a soap film is supported by Marangoni stress.
- Internal dynamics: note that film is dynamic (as are all Marangoni flows), if it were static, its max height would be ℓ_c . It is constantly drying due to the influence of gravity.
- On the surface: $\frac{d\sigma}{dz} \sim \mu \frac{du}{dx}$ balance of Marangoni and viscous stresses.
- Inside: $\rho g \sim \mu \frac{d^2u}{dx^2}$ Gravity-viscous.

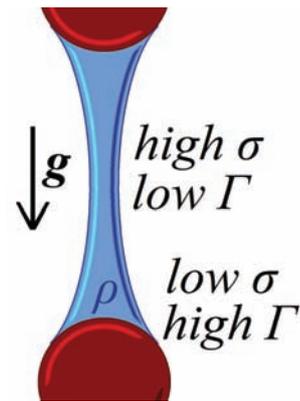


Figure 10.6: The weight of a vertical soap film is supported by Marangoni stresses on its surface.

10.4 Bubble motion

Theoretical predictions for the rise speed of small drops or bubbles do not adequately describe observations. Specifically, air bubbles rise at low Reynolds number at rates appropriate for rigid spheres with equivalent buoyancy in all but the most carefully cleaned fluids. This discrepancy may be rationalized through consideration of the influence of surfactants on the surface dynamics. The flow generated by a clean spherical bubble of radius a rising at low $Re = Ua/\nu$ is intuitively obvious. The interior flow is toroidal, while the surface motion is characterized by divergence and convergence at, respectively, the leading and trailing surfaces. The presence of surface contamination changes the flow qualitatively.

The effective surface elasticity imparted by the surfactants acts to suppress the surface motion. Surfactant is generally swept to the trailing edge of the bubble, where it accumulates, giving rise to a local decrease in surface tension. The resulting fore-to-aft surface tension gradient results in a Marangoni stress that resists surface motion, and so rigidifies the bubble surface. The air bubble thus moves as if its surface were stagnant, and it is thus that its rise speed is commensurate with that predicted for a rigid sphere: the no-slip boundary condition is more appropriate than the free-slip. Finally, we note that the characteristic Marangoni stress $\Delta\sigma/a$ is most pronounced for small bubbles. It is thus that the influence of surfactants is greatest on small bubbles.

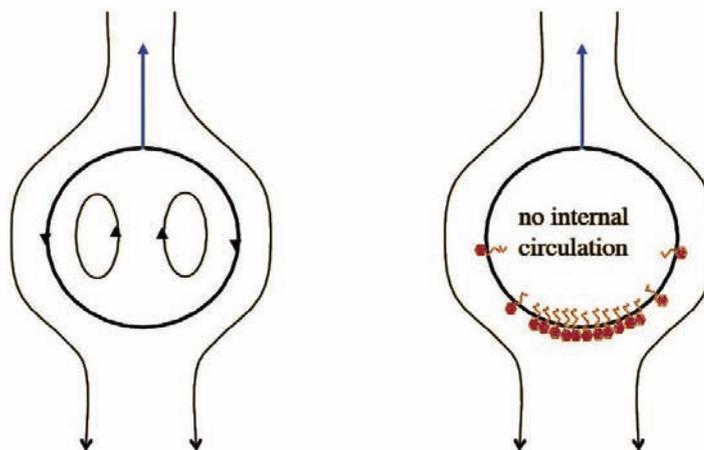


Figure 10.7: A rising drop or bubble (*left*) is marked by internal circulation in a clean system that is absent in a contaminated, surfactant-laden fluid (*right*). Surfactant sticks to the surface, and the induced Marangoni stress rigidifies the drop surface.

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