LECTURE 4: Marangoni flows

Marangoni flows are those driven by surface tension gradients. In general, surface tension σ depends on both the temperature and chemical composition at the interface; consequently, Marangoni flows may be generated by gradients in either temperature or chemical concentration at an interface.

In lecture 2, we derived the tangential stress balance at a free surface:

$$\mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} \;=\; -\,\mathbf{t} \cdot \nabla\sigma \quad , \tag{1}$$

where $\mathbf{n}$ is the unit outward normal to the surface, and $\mathbf{t}$ is any unit tangent vector. The tangential component of the hydrodynamic stress at the surface must balance the tangential stress associated with gradients in σ. Such Marangoni stresses may result from gradients in temperature or chemical composition at the interface. For a static system, since $\mathbf{n} \cdot \mathbf{T} \cdot \mathbf{t} = 0$, the tangential stress balance equation indicates that: $0 = \nabla\sigma$. This leads us to the following important conclusion:

There cannot be a static system in the presence of surface tension gradients. While pressure jumps can sustain normal stress jumps across a fluid interface, they do not contribute to the tangential stress jump. Consequently, tangential surface stresses can only be balanced by viscous stresses associated with fluid motion.

4.1 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 glass of any but the weakest wines following the establishment of a thin layer of wine on the walls of the wine glass.

The tears or legs of wine are taken by sommeliers to be an indicator of the quality of wine. An illustration of the tears of wine phenomenon is presented in Figure 1 (see also http://www-math.mit.edu/ bush/tears.html). 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 alcohol is completely evaporated.

4.2 Surfactants

Surfactants are molecules that have an affinity for interfaces; common examples include soap and oil. Owing to their molecular structure (often a hydrophylic head and hydrophobic tail), 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

Figure 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.

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 concentration is achieved, beyond which σ remains constant.

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

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

where $\mathbf{u}_s$ is the surface velocity, ∇_s is the surface gradient operator and D_s is the surface diffusivity of the surfactant. 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 (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, $J = 0$, and many surfactants have sufficiently small D_s that surface diffusivity may be safely neglected.

The principal dynamical influence of surfactants is to impart an effective elasticity to the interface. 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

Figure 2: 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.

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 responsible for the ‘footprints of whales’ (see Figure 2). In the wake of whales, even in turbulent roiling seas, one seas 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 serves as a surfactant that suppresses capillary waves.

4.3 The soap boat

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 length in a direction tangent to the surface, we see that the total surface tension force acting on the body is:

$$F_c = \int_C \sigma \, \mathbf{s} \, d\ell \quad , \tag{3}$$

where $\mathbf{s}$ is the unit vector tangent to the free surface and normal to C, and $d\ell$ is an incremental 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.

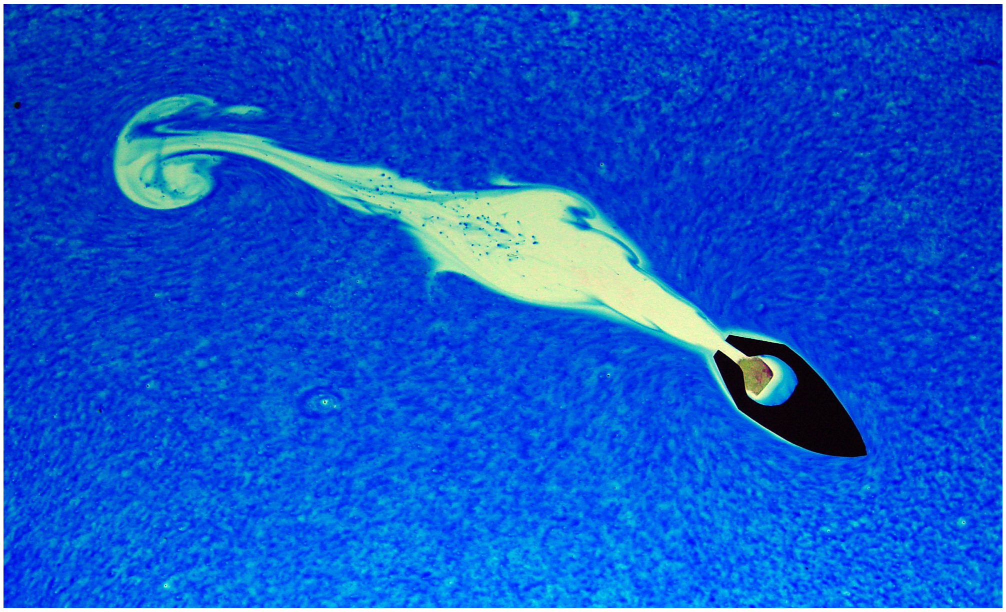

Figure 3: The soap boat. A floating body (length 2.5cm) contains a small volume of soap, which serves as its fuel in propelling it across the free surface.The soap exits the rear of the boat, decreasing the local surface tension. The resulting fore-to-aft surface tension gradient propels the boat forward. The water surface is covered with Thymol blue, which parts owing to the presence of soap, which is visible as a white streak.

The 'soap boat' may be simply generated by coating one end of a toothpick with soap, which acts to reduce surface tension (see Figure 3). 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.

4.4 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 generaly 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.