Marangoni Effects

Even if a bubble remains quite spherical, it can experience forces due to gradients in the surface tension, S, over the surface that modify the surface boundary conditions and therefore the translational velocity. These are called Marangoni effects. The gradients in the surface tension can be caused by a number of different factors. For example, gradients in the temperature, solvent concentration, or electric potential can create gradients in the surface tension. The *thermocapillary* effects due to temperature gradients have been explored by a number of investigators (for example, Young, Goldstein, and Block 1959) because of their importance in several technological contexts. For most of the range of temperatures, the surface tension decreases linearly with temperature, reaching zero at the critical point. Consequently, the controlling thermophysical property, dS/dT, is readily identified and more or less constant for any given fluid. Some typical data for dS/dT is presented in table 1 and reveals a remarkably uniform value for this quantity for a wide range of liquids.

Surface tension gradients affect free surface flows because a gradient, dS/ds, in a direction, s, tangential to a surface clearly requires that a shear stress act in the negative s direction in order that the surface be in equilibrium. Such a shear stress would then modify the boundary conditions (for example, the Hadamard-Rybczynski conditions used in section (Nec)), thus altering the flow and the forces acting on the bubble.

As an example of the Marangoni effect, we will examine the steady motion of a spherical bubble in a viscous fluid when there exists a gradient of the temperature (or other controlling physical property), dT/dx_1, in the direction of motion). We must first determine whether the temperature (or other controlling property) is affected by the flow. It is illustrative to consider two special cases from a spectrum of possibilities. The first and simplest special case, that is not so relevant to the thermocapillary phenomenon, is to assume that $T = (dT/dx_1)x_1$ throughout the flow field so that, on the surface of the bubble,

$$\left(\frac{1}{R}\frac{dS}{d\theta}\right)_{r=R} = -\sin\theta\left(\frac{dS}{dT}\right)\left(\frac{dT}{dx_1}\right) \quad \text{(Nfd1)}$$

Much more realistic is the assumption that thermal conduction dominates the heat transfer ($\nabla^2 T = 0$) and that there is no heat transfer through the surface of the bubble. Then it follows from the solution of Laplace's equation for the conductive heat transfer problem that

$$\left(\frac{1}{R}\frac{dS}{d\theta}\right)_{r=R} = -\frac{3}{2}\sin\theta\left(\frac{dS}{dT}\right)\left(\frac{dT}{dx_1}\right) \quad \text{(Nfd2)}$$

The latter is the solution presented by Young, Goldstein, and Block (1959), but it differs from equation (Nfd1) only in terms of the effective value of dS/dT. Here we shall employ equation (Nfd2) since we focus on thermocapillarity, but other possibilities such as equation (Nfd1) should be borne in mind.

For simplicity we will continue to assume that the bubble remains spherical. This assumption implies that the surface tension differences are small compared with the absolute level of S and that the stresses normal to the surface are entirely dominated by the surface tension.

With these assumptions the tangential stress boundary condition for the spherical bubble becomes

$$\rho_L\nu_L\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)_{r=R} + \frac{1}{R}\left(\frac{dS}{d\theta}\right)_{r=R} = 0 \quad \text{(Nfd3)}$$

Table 1: Values of the temperature gradient of the surface tension, $-dS/dT$, for pure liquid/vapor interfaces (in $kg/s^2\ K$).

Water	2.02×10^{-4}	Methane	1.84×10^{-4}
Hydrogen	1.59×10^{-4}	Butane	1.06×10^{-4}
Helium-4	1.02×10^{-4}	Carbon Dioxide	1.84×10^{-4}
Nitrogen	1.92×10^{-4}	Ammonia	1.85×10^{-4}
Oxygen	1.92×10^{-4}	Toluene	0.93×10^{-4}
Sodium	0.90×10^{-4}	Freon-12	1.18×10^{-4}
Mercury	3.85×10^{-4}	Uranium Dioxide	1.11×10^{-4}

and this should replace the Hadamard-Rybczynski condition of zero shear stress that was used in section (Nec). Applying the boundary condition given by equations (Nfd3) and (Nfd2) (as well as the usual kinematic condition, $(u_r)_{r=R} = 0$) to the low Reynolds number solution given by equations (Nec1), (Nec2), and (Nec3) leads to

$$A = -\frac{R^4}{4\rho_L \nu_L}\frac{dS}{dx_1} \quad ; \quad B = \frac{WR}{2} + \frac{R^2}{4\rho_L \nu_L}\frac{dS}{dx_1} \tag{Nfd4}$$

and consequently, from equation (Nec4), the force acting on the bubble becomes

$$F_1 = -4\pi\rho_L \nu_L W R - 2\pi R^2 \frac{dS}{dx_1} \tag{Nfd5}$$

In addition to the normal Hadamard-Rybczynski drag (first term), we can identify a Marangoni force, $2\pi R^2(dS/dx_1)$, acting on the bubble in the direction of *decreasing* surface tension. Thus, for example, the presence of a uniform temperature gradient, dT/dx_1, would lead to an additional force on the bubble of magnitude $2\pi R^2(-dS/dT)(dT/dx_1)$ in the direction of the warmer fluid since the surface tension decreases with temperature. Such thermocapillary effects have been observed and measured by Young, Goldstein, and Block (1959) and others.

Finally, we should comment on a related effect caused by surface contaminants that increase the surface tension. When a bubble is moving through liquid under the action, say, of gravity, convection may cause contaminants to accumulate on the downstream side of the bubble. This will create a positive $dS/d\theta$ gradient that, in turn, will generate an effective shear stress acting in a direction opposite to the flow. Consequently, the contaminants tend to immobilize the surface. This will cause the flow and the drag to change from the Hadamard-Rybczynski solution to the Stokes solution for zero tangential velocity. The effect is more pronounced for smaller bubbles since, for a given surface tension difference, the Marangoni force becomes larger relative to the buoyancy force as the bubble size decreases. Experimentally, this means that surface contamination usually results in Stokes drag for spherical bubbles smaller than a certain size and in Hadamard-Rybczynski drag for spherical bubbles larger than that size. Such a transition is observed in experiments measuring the rise velocity of bubbles and can be see in the data of Haberman and Morton (1953) included in section (Nfc). Harper, Moore, and Pearson (1967) have analyzed the more complex hydrodynamic case of higher Reynolds numbers.