6 Fluid mechanics of bubbles and drops

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The literature on the motion of bubbles and drops, due to the action of interfacial tension gradients which arise from temperature variation along the interface, is reviewed, highlighting recent work. First, theoretical developments are considered. These include asymptotic analyses of the motion of an isolated drop or bubble when convective transport effects are either very small or very large as well as a variety of numerical solutions of the problem. Also, theoretical work on drops interacting with other drops or with neighboring surfaces is mentioned very briefly. This is followed by a discussion of results from ground-based and reduced gravity experiments. Experiments on thermocapillary migration on the ground have been restricted to conditions wherein convective transport effects play only a small role. The only ground-based experiments in which such effects are large involve drops that are held stationary under the combined influence of gravity and thermocapillarity. Experiments were initiated under reduced gravity conditions in the late seventies, and gathered momentum in the last two decades of the twentieth century due to the availability of long periods of reduced gravity conditions aboard the United States space shuttle. We conclude this review with comments about future prospects for this field, pointing out the importance of conducting experiments under low gravity conditions.

6.1 INTRODUCTION

Bubbles and drops are encountered in our day-to-day life. They also appear in a variety of engineering and materials processing applications. The word *bubble* represents an object that contains a gas or vapour and the word *drop* is used to designate an object that contains liquid. In this review, we shall frequently use the term *drop* to refer to both types of objects. In some cases, it is desirable to have a collection of bubbles in a material as in polymer foams. In other situations, such as when growing a crystal, we wish to produce a material that is free of such inclusions. Stable suspensions of drops are necessary for producing a composite material by cooling a liquid containing more than one component through a miscibility gap into a solid. On the other hand, after contacting one liquid dispersed as drops with another to exchange some component between them, it is necessary to settle out the drops and separate the two phases in mass transfer applications.

On Earth, gravity is always present and when the density of a dispersed phase differs from that of the continuous phase, the dispersed phase material will sink if it is more dense than the continuous phase or rise if it is less dense. We depend on this motion induced by gravity for a variety of applications. In experiments carried out aboard a space vehicle such as an orbiting space laboratory or an outer space probe, gravitational effects on particles, bubbles, or drops suspended in a fluid are so small as to be virtually unimportant in this respect. This is the motivation for studying the motion of these objects due to forces other than gravity. One can think of a few mechanisms independent of gravity that will cause a drop or a rigid particle suspended in a liquid to move. For instance, under suitable conditions, an electric or magnetic field can be used to induce the motion of an object. The most common mechanism that has been used is, however, the application of a temperature gradient in the continuous phase. This is because, it is easy to produce temperature variations in a liquid and such gradients also occur naturally in many materials processing applications because of the use of heating or cooling as an integral part of the process. The subject of this review is the motion of drops in a temperature gradient. The occurrence of this motion depends critically on the presence of a mobile interface between the drop and the surrounding fluid. Therefore the same mechanism does not operate on rigid particles, which also will move in a temperature gradient due to thermophoresis. The motion of rigid particles in reduced gravity is an important subject in its own right; however, we shall not consider that topic in the present review. Also, we shall not discuss the effects of electric and magnetic fields, and the motion within a stationary suspended drop that is caused perhaps by oscillations or rotation of the drop. Some experiments in reduced gravity have indeed been performed on rotating and/or oscillating drops and a brief discussion can be found in Wang (1992).

In this chapter, the continuous phase always is considered to be a liquid. There will be no sharp interface between two gases in the absence of an intervening liquid film. With such a film, a bubble containing gas can be present in another gas. A familiar example is a soap bubble. Little fundamental research has been carried out on the motion of bubbles of this type or that of liquid drops in a gas in reduced gravity. Therefore, we confine our review to the motion of a drop or bubble in a liquid.

A drop moves in a liquid under the action of a temperature gradient because of the variation of its interfacial tension σ with temperature T. It is typical of most fluids that the interfacial tension decreases with increase in temperature so that the coefficient σ_T is negative. Its magnitude lies usually in the range $0.01 - 0.1 mN/(m \bullet K)$. The change in interfacial tension over the drop surface causes a shear stress to be exerted on the neighboring fluids on either side of the interface, typically from the warm pole toward the cold pole. This is called a *thermocapillary* stress, because, it arises from a temperature gradient at the interface. The resulting fluid motion induces a hydrodynamic force on the drop whose sense is to cause the drop to move toward warmer fluid, in the direction of the applied temperature gradient. Once the drop starts moving, it encounters resistance to this motion from the fluid, and it is possible to imagine steady motion when the hydrodynamic force on the drop is exactly zero. In practice, drops rarely move at steady state because the physical properties of the fluids vary with temperature. The most important property in this respect is the viscosity. One can usually expect the drop to continue to accelerate as it moves into warmer fluid because of the reduction in viscosity with temperature. In the less common instance where the interfacial tension increases with increase in temperature, a drop, when released from a state of rest, would initially accelerate toward cooler fluid but will ultimately decelerate as it encounters more viscous liquid. This type of situation does not arise in pure liquids, but is encountered sometimes in the case of mixtures.

The literature on thermocapillary migration up to about 1989 is reviewed in Wozniak *et al.* (1988) and Subramanian (1992). Also, a summary of research carried out in one of our laboratories (RSS) has been provided by Subramanian (1995). Therefore, our principal goal in this contribution is to highlight recent work which has not been discussed in detail in the above reviews and present our thoughts regarding the direction of future research in this field. After briefly discussing the relevant dimensionless groups, we consider theoretical developments in a historical context, and then the experiments. The reader interested in the mathematical aspects of the problems, such as the detailed governing equations, boundary conditions, and techniques used for solution, may wish to consult the monograph by Subramanian and Balasubramaniam (2001).

6.2 IMPORTANT DIMENSIONLESS GROUPS

The most important entity that is measured in thermocapillary migration experiments is the trajectory of the drop. This permits one to infer its velocity at a given instant in time. Of course, from visual records of the migration process on video or motion picture film, the size and shape of the drop can be obtained. Other items of interest are the velocity and temperature fields in the two phases. Theoretical models attempt to provide predictions of some or all of these quantities, subject to idealized assumptions. When the governing equations and boundary conditions are non-dimensionalized, three important dimensionless groups emerge. They are the Reynolds, Marangoni, and Capillary numbers, represented by the symbols Re, Ma, and Ca respectively. Definitions based on the properties of the continuous phase follow:

$$\mathrm{Re} = \frac{Rv_0}{\nu} \tag{6.1}$$

$$\mathrm{Ma} = \frac{Rv_0}{\kappa} \tag{6.2}$$

$$\mathrm{Ca} = \frac{\mu v_0}{\sigma} \tag{6.3}$$

Here, R is the radius of the drop, ν is the kinematic viscosity of the continuous phase, κ is its thermal diffusivity, and μ is its dynamic viscosity. The symbol σ refers to the interfacial tension between the drop and the continuous phase. The reference velocity, v_0, obtained by balancing the thermocapillary stress at the interface with a typical viscous stress, is defined as:

$$v_0 = \frac{|\sigma_T||\nabla T_\infty|R}{\mu} \tag{6.4}$$

where, σ_T is the rate of change of interfacial tension with temperature, and ∇T_∞ is the temperature gradient imposed in the continuous phase fluid. The ratios of the dynamic viscosities, thermal conductivities, thermal diffusivities, and the densities of the two phases are additional parameters in the problem that one must include in modelling the process. Therefore, in the general problem, there are seven independent dimensionless parameters. When inertial effects are important, the Reynolds number and the

Weber number, We = CaRe = $\rho R v_0^2/\sigma$, influence deformation. Here, ρ is a reference density usually taken to be that of the continuous phase. The Marangoni number plays the role of a Péclet number, reflecting the relative importance of convective transport of energy when compared with conduction. It is the product of the Reynolds number and the Prandtl number (Pr = ν/κ).

Clearly, one can define similar groups in the drop phase and it is possible to consider situations wherein convective transport can be important in one phase and not the other. Usually, the physical property ratios involved are such that large values of either the Reynolds number or the Marangoni number in one phase imply similarly large values of the corresponding group in the other phase. Exceptions arise when one considers fluid pairs with a large contrast in kinematic viscosity or thermal diffusivity, but the above statement is correct in most common systems.

6.3 THEORETICAL DEVELOPMENTS

The first study that focussed specifically on thermocapillary movement of bubbles was that of Young *et al.* (1959) who performed experiments on air bubbles in a column of silicone oil suspended between the anvils of a micrometer. The authors used a downward temperature gradient to cause the bubbles to almost come to a standstill, and measured the radius of a bubble that is nearly stationary in a given temperature gradient. Young *et al.* also constructed the first theoretical description of the motion of a drop under the combined influence of gravity and thermocapillarity. They solved the governing conservation equations in the linear limit when convective transport of energy and momentum are negligible, namely when Re $\to$ 0, and Ma $\to$ 0. In this limit, the contribution to the steady velocity of a drop from gravity, predicted by Hadamard (1911) and Rybczyński (1911), and that from thermocapillarity are additive. We use the symbol V_{YGB} to designate the magnitude of this thermocapillary contribution to the quasi-steady velocity of a drop. The velocity can be considered only quasi-steady since physical properties such as viscosity and density depend upon temperature. Since the drop continues to move into warmer fluid, these properties will change continuously and true steady state cannot be obtained. Therefore, one assumes that the time taken for the fields to achieve steady representations corresponding to the local conditions around the drop is small compared to the time taken for the drop to move into a region in which the properties are appreciably different. Note that the problem does not arise in isothermal situations involving purely gravitational settling, where steady motion can be conveniently realized. The result for V_{YGB} is

$$V_{\mathrm{YGB}} = \frac{2v_0}{(2+3\alpha)(2+\beta)} \tag{6.5}$$

where, $\alpha = \mu'/\mu$ is the ratio of the dynamic viscosity of the drop phase to that of the continuous phase and $\beta = k'/k$ is a similar ratio of thermal conductivities. In the limit of negligible convective transport, the scaled velocity is independent of the density ratio and the thermal diffusivity ratio mentioned earlier in the list of parameters. It can be established that when the solution of Young *et al.* is applicable, the drop takes on a spherical shape regardless of the value of the Capillary number. We note that this result for the shape in the limit Re $\to$ 0 and Ma $\to$ 0 holds only when the applied temperature gradient is uniform. If a spherical shape is assumed, the migration velocity can be calculated from equation (6.5) even when the applied temperature gradient is not uniform. In doing so, the value of the undisturbed temperature gradient evaluated at the location of the centre of the drop must be used for calculating v_0 from equation (6.4). A similar result can be written for the steady migration velocity of a drop due to axisymmetric absorption of incident radiation as shown by Oliver and DeWitt (1988). In this case, one replaces the applied temperature gradient in the definition of the reference velocity with $\frac{1}{4k}\int_0^\pi q(\theta)\sin 2\theta d\theta$, where, θ is the polar angle measured from the forward stagnation streamline, and $q(\theta)$ stands for the distribution of the radiant heat flux that is absorbed.

Bratukhin (1975) used an asymptotic expansion in the Reynolds number to obtain a result that he presumed to be valid for small non-zero values of Re. Bratukhin did not specify the shape of the drop except to require departures from the spherical shape to be small. He found that the correction to the result for the migration velocity given in equation (6.5) was zero at $O(\mathrm{Re})$, but was able to use his solution to calculate small deformations from the spherical shape. Later, Thompson *et al.* (1980) extended Bratukhin's solution to the next higher order in Re; however, the solution for the temperature field at the second order fails to satisfy the boundary condition at infinity. This is a well-known problem in fluid mechanics dating back to Whitehead's attempt to improve Stokes's solution for flow past a rigid sphere. The difficulty with a simple perturbation scheme is that the terms representing convective transport of momentum (and energy in the present problem) are presumed uniformly small everywhere in space when compared to the molecular transport terms. In the unbounded domain associated with the problem, as recognized by Oseen (1910), the convective terms become comparable in importance to the molecular transport terms at a distance that is of the order of the ratio R/Re. Proudman and Pearson (1957) showed how the method of matched asymptotic expansions can be used to overcome the difficulty. The method consists of constructing a second asymptotic expansion in the Reynolds number while keeping a new radial coordinate $\chi = \mathrm{Re}\frac{r}{R}$ fixed. The expansion that is valid near the sphere, called the inner expansion, is then matched with that valid far from the sphere, called the outer expansion, in an overlap domain since both expansions represent the same function. Subsequently, Acrivos and Taylor (1962) solved the heat transfer analog of this problem for a rigid sphere. By using this method of matched asymptotic expansions, it is possible to overcome the difficulty encountered in the solution procedure used by Bratukhin and Thompson *et al.* Subramanian (1981; 1983) pointed this out and developed an analytical solution in the case of highly viscous fluids, setting the Reynolds number to zero, and writing a perturbation expansion in the Marangoni number. He found that the correction to the result given in equation (6.5) at $O(\mathrm{Ma})$ is zero, and that the first non-zero correction appears at $O(\mathrm{Ma}^2)$. This result was subsequently extended by Merritt (1988) to $O(\mathrm{Ma}^4)$. Crespo *et al.* (1998) performed a similar perturbation expansion in the Marangoni number for the case of a gas bubble when the Reynolds number is large. These authors found that the first correction to the result in equation (6.5) in that problem also occurs at $O(\mathrm{Ma}^2)$. To date, the corresponding asymptotic problem including inertial effects and deformation has not been solved.

Crespo and Manuel (1983) and, independently, Balasubramaniam and Chai (1987), discovered that the solution for the velocity field in purely thermocapillary motion given by Young *et al.* which is a potential flow in the continuous phase and Hill's spherical vortex in the drop phase, is an exact solution at all values of the Reynolds number, provided the temperature field is that given by the solution of Laplace's equation. The latter implies that convective transport of energy must be ignored so that the solution applies for fluids of relatively small values of the Prandtl number, Pr. The shape is no longer spherical, however, and Balasubramaniam and Chai obtained a result for small inertial corrections to the spherical shape. Subsequently, Haj-Hariri *et al.* (1990) constructed the solution of this problem in invariant form and calculated the correction to the migration velocity caused by the shape deformation.

In the limit when convective transport of momentum and energy are negligible, the unsteady motion of a drop can be analysed using Laplace transforms. This was done by Dill and Balasubramaniam (1992) who provided predictions including asymptotic trends in limiting situations. A similar analysis was published by Galindo *et al.* (1994) who also included a gravitational contribution to the motion in their development for completeness.

Perturbation solutions for accommodating small amounts of convective momentum or energy transport are clearly not sufficient because they only permit predictions to be made for relatively small values of Re and Ma, respectively. Therefore, efforts began in the eighties to obtain solutions by numerical means. In the limit of a gas bubble, only the transport problems in the continuous phase need to be solved and therefore this was the first type of problem to be addressed. Shankar and Subramanian (1988) considered the Stokes motion of a gas bubble for $0 < \mathrm{Ma} \leqslant 200$ and obtained a solution of the energy equation by the method of finite differences. For the velocity field, they used an analytical solution of Stokes's equation. The authors identified an interesting flow structure that arises in thermocapillary migration problems which involves a separated reverse flow wake behind the moving bubble, and discussed the physical reason for the appearance of this structure. Subsequently, Merritt and Subramanian (1992) used the same finite difference technique to obtain a numerical solution in the case when a bubble moves under the combined action of buoyancy and thermocapillarity. The solution is reported only for Marangoni number in the range 0–5, but results are given for a wide range of values of a group that characterizes the relative importance of buoyancy when compared with thermocapillarity. It is the only reported solution as of this writing, in which the role of the gravitational force is accommodated and convective transport effects are considered. Returning now to purely thermocapillary motion, Szymczyk and Siekmann (1988) and Balasubramaniam and Lavery (1989) solved both the momentum and the energy equations in the gas bubble case using finite differences. Szymczyk and Siekmann reported results for $0 < \mathrm{Re} \leqslant 100$ for Prandtl numbers in the range 0.01–10 and for $0 < \mathrm{Re} \leqslant 50$ for $\mathrm{Pr} = 100$. Balasubramaniam and Lavery permitted the Reynolds number to vary from 0.1 to 2 000 and the Prandtl number to vary from 0.01 to 1 000; however, pairs of values of these groups were chosen such that the product of the two, namely, the Marangoni number, was constrained to the range 0–1 000. In all these studies, the bubble was assumed to be spherical and therefore the normal stress balance, which could not be satisfied, was not used. The authors scaled the migration velocity of the bubble with v_0 so that the scaled velocity v_∞ would be 1/2 in the limit $\mathrm{Re} \to 0$ and $\mathrm{Ma} \to 0$. They found that this scaled velocity decreased with increasing values of Ma for fixed Re and that it increased gently with increasing Re for fixed Ma. Balasubramaniam and Lavery (1989) also noted the appearance of a separated reverse flow wake behind the bubble when fluid inertial effects were included, similar to that found by Shankar and Subramanian (1988) who neglected inertia. More recently, Balasubramaniam (1995) and Crespo *et al.* (1998) have reported numerical solutions of the thermocapillary migration problem for a gas bubble, assuming potential flow to prevail in the continuous phase. Results from these calculations are in agreement with those from Balasubramaniam and Lavery when Ma $\rightarrow 0$ and an asymptotic result in the limit Ma $\rightarrow \infty$ that is mentioned later. We note that Treuner *et al.* (1996) performed calculations in the gas bubble limit, similar to those of Balasubramaniam and Lavery (1989), up to a Marangoni number of 2 500. Chen and Lee (1992) permitted the bubble to deform from the spherical shape, and showed that a small deformation can lead to a large decrease in the quasi-steady migration velocity. Unsteady thermocapillary motion of a bubble was first treated by Oliver and DeWitt (1994) who solved the problem assuming negligible inertia. They showed that steady state can be expected when a bubble has moved a distance approximately equal to 1–5 radii, at values of the Marangoni number up to 200. This is logical because this is the order of the time required to reach steady state in the thermal boundary layer at the bubble surface. Later, Welch (1998) numerically solved the transient problem, accommodating both inertia and deformation of the bubble shape. Welch demonstrated that a true steady state solution is not possible because of the continuous increase in the deformation of a bubble as it moves into warmer fluid, caused by the corresponding decrease in surface tension.

In recent years, numerical work has been performed in the case of migrating liquid drops. In some cases deformation of the shape from a sphere has been accommodated, which makes the computations more involved. The list of articles includes Ehmann *et al.* (1992), Nas (1995), Haj-Hariri *et al.* (1997), and most recently, Ma *et al.* (1999). Ehmann *et al.* were the first to make computations for spherical liquid drops. Ma *et al.* solved this problem numerically by extending the code developed by Balasubramaniam and Lavery (1989) for a gas bubble. The most important observation made by Ma *et al.* is that the scaled velocity of a liquid drop initially decreases in magnitude with increasing values of the Marangoni number, but that beyond a value of Ma that lies somewhere in the range 50–200 depending upon the parameters, the scaled velocity increases with further increase in Ma. We shall see shortly that this remarkable result is consistent with an asymptotic prediction by Balasubramaniam and Subramanian (2000). Nas and Haj-Hariri *et al.* accounted for the possibility of shape deformation. As demonstrated by Chen and Lee (1992) and Welch (1998) in the case of a gas bubble, the authors found that a slight deformation of shape has a substantial effect on the migration velocity of a liquid drop. Most of Nas's computations are for 2D drops which are deformed infinite cylinders moving with a velocity perpendicular to their axes. There are some qualitative differences in the predictions between the 2D case considered by Nas and the 3D case treated by Haj-Hariri *et al.* for reasons which are not entirely clear at this time.

Numerical solutions cannot easily handle the asymptotic situation where the parameters become very large. If the Reynolds number in the continuous phase is large, it can be established that the flow in the continuous phase is described by potential flow almost everywhere. There is a momentum boundary layer next to the surface of the bubble in which the tangential stress adjusts to the correct value at the interface, but the velocity change due to the presence of this boundary layer is small. If the Marangoni number in the continuous phase is large, the situation is more complicated. This problem for a gas bubble was analysed in detail by Balasubramaniam and Subramanian (1996). Over most of the continuous phase, heat transfer is dominated by convection, with conduction being of negligible consequence. The solution obtained by ignoring conduction is, however, unable to satisfy the boundary condition of negligible heat flux at the bubble surface and a thermal boundary layer is formed over the bubble surface in which conduction is as important as convective transport. Furthermore, the temperature itself undergoes substantial change in this boundary layer because the field obtained ignoring conduction is singular on the bubble surface, being proportional to $\log(r-R)$ where r is a radial coordinate measured from the centre of the bubble. There are additional complications because the temperature field both outside and within the thermal boundary layer becomes singular as the rear stagnation point is approached, once again in a logarithmic dependence on the angle measured from the rear stagnation streamline. This wake singularity is relieved by a solution that accommodates conduction in the angular direction at leading order. Balasubramaniam and Subramanian obtained solutions in the limit $\mathrm{Ma} \to \infty$ in two cases. For $\mathrm{Re} \to \infty$ they confirmed the earlier result of Crespo and Jimenez-Fernandez (1992a), namely, $v_\infty = \frac{1}{3} - \frac{1}{8}\log 3 \approx 0.1960$. But for $\mathrm{Re} \to 0$, they found $v_\infty = 0.1538$ in contrast to the value obtained by Crespo and Jimenez-Fernandez (1992b). The authors went on to provide an improved result in the case $\mathrm{Re} \to \infty$, namely:

$$v_\infty = \frac{1}{3} - \frac{1}{8}\log 3 + \frac{1}{\sqrt{\mathrm{Ma}}}[0.06845\log(\mathrm{Ma}) + 0.6578] \tag{6.6}$$

Balasubramaniam and Subramanian (2000) analysed the motion of a drop in the case when both the Reynolds number and the Marangoni number are large. The flow in the continuous phase is described by a potential flow velocity field while that within the drop is Hill's spherical vortex. The transport of thermal energy is dominated by convection in both fluids over most of the domain. Conduction is important only in thin thermal boundary layers in each fluid adjacent to the interface. These boundary layers ensure continuity of temperature and heat flux at the interface. In this asymptotic limit, the authors found that the migration velocity, scaled by v_0, is proportional to the Marangoni number. As noted earlier, this is consistent with the numerical finding of Ma *et al.* (1999). This remarkable result, which implies that the physical velocity is proportional to $|\sigma_\mathrm{T}|^2 \, |\nabla T_\infty|^2 \, R^3$, is very different from the corresponding asymptotic result obtained by Balasubramaniam and Subramanian (1996) in the gas bubble limit. As noted earlier, the asymptotic migration velocity of a gas bubble is proportional to $|\sigma_\mathrm{T}||\nabla T_\infty| \, R$. The striking contrast between the two results arises from the fact that in the gas bubble problem, the thermal conductivity of a gas bubble is assumed to be zero. The drop makes a demand for energy to increase its temperature at a constant rate as it moves into warmer fluid at a constant velocity. This energy must be supplied from the continuous phase to the contents of the drop. Within the drop, heat flows by conduction across recirculating streamlines when viewed from the perspective of the drop. Since conduction is weak, the temperature gradient required to supply this heat is relatively large, leading to relatively low temperatures in the vicinity of the drop and within it. The scaled temperature is predicted to be smaller by a factor of Ma in the thermal boundary layers near the drop surface when compared with the values far from the drop. It is smaller by another factor of Ma in the core of the drop when compared with the values that prevail in the thermal boundary layers.

Recently, Balasubramaniam (1998) has analysed the motion of a gas bubble in the limit $\mathrm{Ma} \to \infty$ in a liquid in which the viscosity varies linearly with temperature. The analysis applies for large values of the Reynolds number, so that potential flow can be assumed in the liquid. Balasubramaniam permitted a buoyant contribution to the motion as well as a thermocapillary contribution. He concluded that in purely thermocapillary migration, the decrease in viscosity with temperature leads to a reduction in the scaled velocity of the bubble when compared with the value that would be calculated using an average viscosity at the temperature corresponding to the current location of the bubble. The physical reason is that in any given plane perpendicular to the direction of motion, the liquid near the bubble is cooler than that far away from it. Thus, if one uses an average temperature based on the temperature field far from the bubble, one under-estimates the viscosity of the liquid.

It is known that surfactants, which adsorb on the interface between the drop and the continuous phase, can affect the motion of a drop. In gravitational settling, the effect is to reduce the mobility of the interface and it is possible for sufficiently small drops to move as though their surface is rigid, as noted by Bond (1927) and Bond and Newton (1928). Surfactants have a larger impact on thermocapillary migration than on gravitational settling because the entire driving force for thermocapillary motion resides at the interface. When a drop moves, surfactant adsorbed at the interface is swept to the rear of the drop. This leads to a concentration gradient of surfactant which causes the interfacial tension to decrease as one moves from the front to the rear of the drop. In thermocapillary migration, this opposes the interfacial tension gradient that arises from the temperature difference. Theoretical developments for low Reynolds number motion were developed by Kim and Subramanian (1989a,b) who used an idealized linear equation of state for the surfactant. When the presence of an insoluble surfactant is accommodated, a new dimensionless group, which can be termed the Elasticity number E, is introduced in the analysis. It is defined as $E = \mathcal{R}T_0\Gamma/(\mu v_0)$, where, $\mathcal{R}$ is the gas constant, T_0 represents a reference temperature at the interface, and Γ stands for a reference concentration of the surfactant on the interface. The Elasticity number provides a measure of the relative role of the surfactant in lowering the interfacial tension, when compared with that of the varying temperature in altering the interfacial tension. Also, a dimensionless gas constant $\Lambda = \mathcal{R}\Gamma/(-\sigma_T)$ multiplies the product of the scaled interfacial temperature and the scaled surfactant concentration on the interface in an additive contribution to the scaled interfacial tension. When the surfactant concentration at the interface is relatively small, the contribution from this non-linear term can be neglected. Kim and Subramanian considered the case when surfactant forms a stagnant cap (1989a) and a more general situation where surfactant is present over the entire surface (1989b). Using a perturbation scheme, Nadim and Borhan (1989) obtained the solution permitting the shape of the drop to be slightly deformed from a sphere in the situation when the dependence of the interfacial tension on the surfactant concentration is relatively weak. Shortly thereafter, Nadim *et al.* (1990) calculated the correction to the migration velocity due to the shape distortion, using a technique similar to that employed by Haj-Hariri *et al.* (1990) for calculating a similar correction due to small inertial effects. Recently, Chen and Stebe (1997) have analysed the thermocapillary motion of a drop in the presence of surfactants using more realistic models of surfactant adsorption permitting the possibility of monolayer saturation and non-ideal surfactant interactions. They find that the Langmuir framework, which accommodates monolayer saturation effects, leads to less retardation of drop motion by a surfactant, when compared with the predictions from a linear model. This is because the linear model permits adsorbed surfactant concentration to increase without limit, whereas the Langmuir framework places a maximum limit on the concentration. The authors also use the Frumkin framework, which takes interactions among surfactant molecules into account in addition, to show that cohesion of the molecules increases surface concentration gradients, leading to strong retardation effects from the surfactant. Repulsion among the surfactant molecules has the opposite effect. Chen and Stebe point out that when the adsorption and desorption occur rapidly when compared with surface convective transport, the interface can be remobilized. Physically, this means that surfactant can be distributed nearly uniformly over the surface so as to make the interfacial tension gradient arising from the surfactant concentration gradient negligible. This is accomplished by using elevated bulk concentrations of the surfactant or by the addition of appropriate amounts of a remobilizing surfactant. We note that reverse flow structures in the wake similar to those found by Shankar and Subramanian (1988) are reported by Chen and Stebe (1997), and they occur due to the same reason. Other interesting flow structures arise when a drop moves under the combined action of gravity and thermocapillarity. Details can be found in Merritt *et al.* (1993).

It is evident that considerable progress has been made in developing theoretical predictions in the case of an isolated drop. Theoretical advances also have been made in the context of interactions between a pair of drops or a drop and a boundary and more recently on the thermocapillary motion of a collection of drops. Virtually all of the theoretical work has been restricted to the limit $\mathrm{Re} \to 0$ and $\mathrm{Ma} \to 0$ so that a linear problem can be posed and solved. Most of the available results are restricted to spherical drops. This is implied in the discussion of the literature here, and we explicitly point out when shape deformation is accommodated by the authors. In the case of two drops or a drop and a plane boundary, axisymmetric solutions of Laplace's and Stokes's equation in bispherical coordinates obtained by Jeffery (1912) and Stimson and Jeffery (1926), respectively, were specialized in the gas bubble limit by Meyyappan *et al.* (1981; 1983). A more general solution applicable to asymmetric situations, provided by O'Neill (1964), was used by Meyyappan and Subramanian (1987) in analysing the case of a gas bubble moving in an arbitrary direction with respect to a plane surface. A solution for two drops obtained using the method of reflections is given by Anderson (1985) who also calculated a result for a suspension of equal-sized drops. Results for a liquid drop moving normal to a plane surface are given by Barton and Subramanian (1990) and Chen and Keh (1990); Barton and Subramanian (1991) subsequently conducted experiments which confirmed the correctness of their predictions for the migration velocity. Recently, Chen (1999a,b) has provided approximate solutions of problems involving the thermocapillary motion of a drop near a surface by the method of reflections. The case of a deformable liquid drop moving normal to a plane surface was solved numerically by Ascoli and Leal (1990). Morton *et al.* (1990) analysed the thermocapillary motion of a compound drop which implies a droplet present within a drop. The drop migrates in the applied temperature gradient, and the droplet moves within the drop. The authors considered both the concentric configuration and a more general eccentric configuration, but restricted the analysis to axisymmetric fields. Borhan *et al.* (1992) analysed the axisymmetric motion of a concentric compound drop accommodating the influence of surfactants, and also obtained corrections to the spherical shapes of both the drop and the droplet, for small values of the Capillary number. Keh and Chen (1990) obtained results for interactions between a pair of drops immersed in a continuous phase. The case of three bubbles or drops aligned in a chain was solved by Keh and Chen (1992; 1993) and Wei and Subramanian (1993) who used the solution for a single sphere given in Lamb (1932) and satisfied the boundary conditions on selected collocation rings. Nas (1995) solved model problems involving a collection of several drops using a full numerical solution of the governing equations, and accommodating shape deformation. The motion of a collection of bubbles of identical size was analysed by Acrivos *et al.* (1990); subsequently the treatment was extended to a bidisperse collection by Wang *et al.* (1994). The collision and subsequent coalescence of drops undergoing thermocapillary migration leads to an evolution of the size distribution with time. This subject is discussed in Satrape (1992), Zhang and Davis (1992), and Zhang *et al.* (1993). When a drop and a surface are very close, or when two drops are very close to each other, lubrication theory can be used to make predictions as shown by Loewenberg and Davis (1993a,b). In a variation on the theme, Golovin (1995) analysed the motion of a rigid sphere and a gas bubble, which arises because of a temperature difference between the rigid sphere, assumed to be at a fixed temperature, and the continuous phase, which is isothermal in the undisturbed state. The resulting temperature gradient in the fluid causes thermocapillary migration of the bubble, and a drift of the rigid sphere in the resulting flow. A similar analysis is presented by Leshansky *et al.* (1997) for the case of a rigid sphere placed near a fluid interface. In a recent article, Lavrenteva *et al.* (1999) have treated the influence of unsteady and convective transport effects on the Stokes motion of a pair of drops that is driven by interfacial tension gradients. These gradients arise as a result of non-uniform transport of a surfactant between the drops and the continuous phase, in which the concentration of surfactant is uniform in the undisturbed state. This is the only article at the time of this writing in which both the unsteady and convective transport effects are treated in a problem involving interacting drops. We also note that Balasubramaniam and Subramanian (1999) have analysed the axisymmetric motion of two bubbles in a temperature gradient when convective transport effects are asymptotically large, both in the momentum transport and in the energy transport problem. Subject to the assumptions made by the authors, the leading bubble is unaffected, whereas the trailing bubble moves less rapidly than it otherwise would. While this particular analysis was motivated by our experiments in reduced gravity, it will be seen from subsequent sections that experiments have generally lagged behind theory in the area of interactions among drops.

6.4 EXPERIMENTS ON THE GROUND

The first experiments on the thermocapillary motion of bubbles were performed by Young *et al.* (1959) as mentioned in the introduction to the previous section. Young *et al.* held bubbles nearly stationary in a downward temperature gradient. From their theory, they predicted that the temperature gradient needed to hold a bubble still would be proportional to its radius, and independent of the viscosity of the liquid. In spite of the uncertainties associated with their measurements, they indeed verified these predictions. Interestingly, it can be shown that it would be difficult to hold a gas bubble still in a liquid by applying a downward temperature gradient. While a bubble, which neither dissolves nor grows, can be placed at a certain location where the forces on it are balanced, slight departures from that location can cause it to move away. Whether the bubble actually does so will depend upon the physical properties of the liquid and the magnitude of the applied temperature gradient. Dissolution or growth that invariably occurs because the liquid can be saturated with the gas at only one temperature, also would make it impossible to hold a bubble still. In the experiments of Young *et al.* the bubbles moved so slowly that the authors considered them practically stationary. Hardy (1979) refined the experiment, using a single bubble at a time, and found the bubbles to move up and down in the cell in a cyclic fashion. From the turning points where the bubble changed direction, assuming the prediction made by Young *et al.* to be correct, he evaluated the coefficient σ_T for a silicone oil and found it to be in good agreement with the value he measured using the pendant drop technique. The linear scaling of the migration velocity with the radius was verified in the case of gas bubbles by Merritt and Subramanian (1988) who performed experiments on air bubbles moving under the combined influence of buoyancy and a downward temperature gradient in silicone oils. Later, the linear dependence of the migration velocity upon the radius as well as that on the applied temperature gradient was confirmed by Barton and Subramanian (1989) who observed the motion of ethylsalicylate drops in diethylene glycol in an upward temperature gradient. These authors found, however, that the values of the coefficient, σ_T, evaluated from the migration experiments, were lower than the values obtained from static Du Noüy Ring measurements made by others. We also note that Morick and Woermann (1993) reported experimental results on the motion of gas bubbles in a vertical temperature gradient which are consistent with the earlier observations made by Hardy and Merritt and Subramanian.

Very little has been done experimentally on the role of surfactants in influencing thermocapillary migration. Young *et al.* (1959), in their original experiments, demonstrated the important role of surfactants by showing that they could not make bubbles move downward in *n*-hexadecane by using a downward temperature gradient when trace amounts of a silicone oil, which is a surfactant in that liquid, were added. Following their example, Barton and Subramanian (1989) demonstrated the role of thermocapillarity in their experiments by deliberately adding a surfactant, Triton X-100, to both phases to suppress the thermocapillary contribution. Nallani and Subramanian (1993) reported that methanol drops moved in a silicone oil at velocities lower than those predicted by assuming an uncontaminated interface, and fitted their data to the stagnant surfactant cap model given in Kim and Subramanian (1989a).

Work on the ground on moving drops has been mostly confined to the linear limit when Re and Ma are both negligible. This has been for two reasons. One is that the superposition principle permits us to extract the purely thermocapillary contribution to the velocity of a drop under these conditions. As an example, Merritt and Subramanian (1989) inferred that, in Stokes flow, the thermocapillary interaction with a boundary is much weaker than the interaction that occurs when motion is driven by gravity. They were able to decouple the two contributions because the experiments were performed in the linear limit. The other reason for using small values of Re and Ma is to minimize interference from gravitational effects. To obtain Reynolds and Marangoni numbers that are not small, one must use relatively large bubbles and drops and apply a sufficiently large temperature gradient. The relative importance of the gravitational force on a drop increases with the size of the drop. When a downward temperature gradient is used, due to the resulting unstable density stratification, the maximum temperature gradient that can be employed is limited by the onset of cellular convection in the continuous phase. Even when an upward temperature gradient is employed, which leads to stable stratification, increasing the temperature gradient leads to problems. This is because of the resulting increased temperature contrast between the experimental test cell and the surroundings. This increases horizontal temperature gradients, and therefore, horizontal density variations, leading to more buoyant convection in the test cell.

Much of the work on the ground on relatively large drops has been conducted on liquid pairs of nearly matched densities in which a drop can be held motionless under the action of a temperature gradient. Therefore, the gravitational and thermocapillary effects on the drop are balanced. It is possible to achieve substantial values of the Reynolds and Marangoni numbers on the ground in this case. In the experiments, an upward temperature gradient is applied and a drop is inserted into the continuous phase. The liquids are chosen such that the coefficient of thermal expansion of the continuous phase is larger than that of the drop phase. At some temperature, the drop phase has exactly the same density as that of the continuous phase. At larger temperatures, the drop phase is more dense. Drops migrate above the level of matched densities and find a stationary location. At this location, the net downward force due to gravity, which is the weight of the drop minus the buoyant force, is precisely balanced by the upward hydrodynamic force exerted on the drop due to the motion induced by the interfacial tension gradient. This equilibrium is stable to small vertical disturbances. While the drop itself is stationary, there is considerable motion, especially in the vicinity of the interface. These types of experiments have been performed by Wozniak (1986), Hähnel *et al.* (1989), Rashidnia and Balasubramaniam (1991), Chen *et al.* (1997), and most recently Ma (1998), using a variety of immiscible pairs of fluids. All the studies report information on the ultimate stationary location of the drop relative to the matched density level, for drops of various sizes and for different applied temperature gradients. In addition, Wozniak obtained interferometry images which permitted him to describe the temperature field around the drop. Rashidnia and Balasubramaniam used tracer particles to follow the motion. Using this technique, they inferred the magnitudes of the velocity at the interface and clearly demonstrated the role of thermocapillarity in driving the observed motion in both fluids. Chen *et al.* used the same system as Hähnel *et al.* but studied the role of an added surface-active chemical which reduced the distance at which the drop was located above the neutral density point, depending upon its concentration. As discussed in Section 6.3, a gradient in surfactant concentration on the interface, which arises from interfacial motion, leads to an interfacial tension gradient which opposes that caused by temperature variation. This is the reason for the observations reported by Chen *et al.* Ma 1998 made a comparison of his observations on two pairs of fluids with a solution of the governing conservation equations and boundary conditions obtained by numerical means, and presented the results in a suitable dimensionless form. He reported reasonable agreement between his observations and predictions.

In the only available study on interactions between a pair of bubbles moving under the combined action of gravity and thermocapillarity, Wei and Subramanian (1994) demonstrated that the predictions from the method of reflections were sufficient to describe their observed results. It was possible to superpose predictions for motion driven by a body force with those for purely thermocapillary motion because the Reynolds and Marangoni numbers were negligibly small, making the theoretical problems linear. The authors also commented that a large bubble moving downward in a vertical temperature gradient can cause a neighbouring small bubble to move upward. If the large bubble were not present, the small bubble would move downward in the same temperature gradient. This interesting reversal of direction of the small bubble is due to the upward thermocapillary flow generated by the large bubble in its vicinity. Wei and Subramanian (1995) subsequently provided a detailed discussion of flow structures that arise when two bubbles move under the combined action of buoyancy and thermocapillarity.

Finally, we note that when a drop immersed in a liquid or surrounded by a gas is allowed to approach a solid or fluid surface, the application of a temperature difference between the drop and the surface can prevent the drop from spreading over the surface. This is a consequence of the presence of a thin film of fluid between the drop and the surface, which is entrained by thermocapillary flow in the drop. This topic is considered in detail by Castagnolo and Monti (2001) in Chapter 4. The authors discuss both experimental work and theoretical models.

6.5 EXPERIMENTS IN REDUCED GRAVITY

After the appearance of the initial article by Young *et al.* very little was published on thermocapillary migration for approximately 15 years. The literature on the subject began to grow in the seventies and eighties mainly because of the impetus provided by the space programme. Research was conducted on the ground as much as possible, but suffered from interference caused by gravitational effects. Therefore, experiments in reduced gravity were initiated beginning in the late seventies in the NASA sounding rocket program named SPAR which provided about 5 min of reduced gravity conditions. The first experiments were performed by Papazian and Wilcox (1978) who correctly surmised that thermocapillary motion can be an important mechanism for managing bubbles in crystal growth in reduced gravity. They proceeded to study the behaviour of bubbles at a solidification interface in carbon tetrabromide aboard a sounding rocket flight. Unfortunately, the bubbles did not move in the temperature gradient and the authors advanced some possible explanations. The most likely cause would have been the presence of some surface-active contaminant which adsorbed on the interface. In later experiments conducted aboard similar sounding rocket flights, Wilcox and coworkers (Smith *et al.* 1982; Meyyappan *et al.* 1982) indeed observed the motion of gas bubbles in the direction of a temperature gradient in a sodium borate melt.

Thompson (1979) conducted a systematic study of the motion of bubbles of nitrogen in different liquids in the drop tower at NASA Lewis Research Centre (now Glenn Research Centre), and the results are reported in Thompson *et al.* (1980). The reduced gravity experiment time was approximately 5 s. Thermocapillary migration could not be observed in water, likely because of surfactant contamination effects. Migration velocities in ethylene glycol were consistent with the predictions of Young *et al.* given in equation (6.5), even up to a Reynolds number of 5.66 and Marangoni numbers as large as 713. This is a puzzling observation. However, bubbles in ethanol and a silicone oil were observed to move at smaller velocities than those given in equation (6.5). Given the conditions of Thompson's experiments, one must conclude that the non-linearity of the temperature profile, coupled with the initial transients, must have had significant impact on the measured velocities of the bubbles.

Langbein and Heide (1984) performed experiments on sounding rockets using a binary liquid mixture of cyclohexane and methanol in which drops were observed to move in the direction of the temperature gradient. Shortly thereafter, experiments were conducted aboard the D-1 mission of the NASA space shuttle by Siekmann and colleagues, and the results are reported in Nähle *et al.* (1987) and Szymczyk *et al.* (1987). The authors injected a collection of air bubbles into a silicone oil in one cell, and a collection of water drops into the same silicone oil in a second cell. A temperature gradient was applied to the silicone oil and it evolved with time during the experiment. The water drops did not move while the air bubbles moved in the direction of the applied temperature gradient. The experimental data on the velocity of air bubbles up to a value of $\mathrm{Ma} = 288$ were presented in Szymczyk *et al.* and shown to be consistent with predictions from a numerical solution of the governing equations.

Aboard the same D-1 mission of the space shuttle, another experiment on thermocapillary migration was carried out by Neuhaus and Feuerbacher (1987). These authors used three similar silicone oils as the continuous phase. Air bubbles in AK100 silicone oil moved at velocities consistent with the predictions of Young *et al.* whereas, bubbles moved at velocities smaller than those predicted in silicone oil AS100, and did not move at all in silicone oil AP100. No information is available on the Reynolds or Marangoni numbers corresponding to these experiments. Based on results from additional ground-based experiments on gravitational rise, the authors suggest that one must account for dissipation processes at the interface through an interfacial dilational viscosity, but it is not clear why this particular hypothesis is put forward.

Wozniak (1991) conducted experiments aboard sounding rockets on drops of paraffin oil moving in a solution of ethanol and water, the same pair on which he had conducted studies on the ground earlier. Approximately 7 min of reduced gravity time was available. The drops ranged in radius from 0.7 to 2.4 mm and a temperature gradient of 0.8–0.9 K/mm was used. The maximum Reynolds and Marangoni numbers in the continuous phase were approximately 25 and 588, respectively. Predictions were made from a numerical solution of the governing equations. Wozniak found that the measured velocities were only a fraction of the predicted values, and ranged from approximately 3.6–31.7% of the predicted values with the worst agreement being displayed for the smallest drop. He attributes the discrepancy to possible interactions with the boundaries and to the influence of surface-active contaminants even though every effort was made to work with very pure liquids. Braun *et al.* (1993) performed experiments aboard a sounding rocket that provided approximately 5.5 min of experiment time in reduced gravity conditions using a mixture of 2-butoxyethanol and water, which exhibits an inverted miscibility gap. Drops of a mean diameter of 11 μm, rich in 2-butoxyethanol, were observed to move toward cooler fluid in a temperature gradient. This direction of movement was consistent with the sign of the coefficient, σ_T, which is reported to be positive for this system; that is, the interfacial tension increases with increasing temperature. The Marangoni numbers ranged from 10^{-5} to 10^{-6} and the Reynolds numbers were even smaller. The migration velocities were found to be consistent with predictions from equation (6.5). Experiments in another system, which exhibits a positive value of σ_T over a certain range of temperatures, were carried out aboard the space shuttle in 1994 and 1996 by Viviani and Golia (1998). The authors used a solution of *n*-heptanol in water which exhibits a surface tension minimum around 40 °C, according to measurements made by Pétré *et al.* (1983). Air bubbles injected into this solution were observed to move from a region near the hot wall toward cooler regions in the test cell. The bubbles came to rest at a location where the temperature was estimated to be approximately 8–10 °C, near the cold wall which was held at 5 °C. The temperature estimate was based on an assumed linear temperature distribution between the hot and cold walls. As noted, the static measurements reveal a minimum in surface tension to occur in the neighbourhood of 40 °C in this aqueous solution. This implies a positive value of σ_T at temperatures larger than approximately 40 °C, and a negative value of σ_T at lower temperatures. Therefore, the bubbles should have moved from the hot wall toward cooler regions until this temperature was reached and should have stopped at that location. They continued to move, however, into cooler regions in a direction opposite to that which would have been predicted from theory for an isolated bubble. The observation remains unexplained. Since the temperatures in the liquid were not measured directly, but inferred from an assumed linear distribution, there is some question about the actual temperature prevailing in the region where the bubbles came to rest, but the discrepancy is unlikely to be so large as to explain the observation.

Recently, Treuner *et al.* (1996) conducted thermocapillary migration experiments in the drop tower in Bremen, Germany, which provides approximately 4.7 seconds of low gravity conditions. Bubbles of air, varying from 0.5 mm to 2 mm in diameter, were found to move in a temperature gradient in three liquids, *n*-octane, *n*-decane, and *n*-tetradecane. Much of the data are in the transient regime and Treuner *et al.* provide several plots of data on the velocities of the bubbles as well as an interferometry image that displays refractive index distributions around the moving bubbles. The observed velocities were consistent with those predicted from a numerical solution. As a bubble moved into warmer fluid, however, the Marangoni number for the bubble changed with time, as did the scaled velocity of the bubble. This variation of the scaled velocity of an individual bubble with the Marangoni number was quite often in a direction opposite to that predicted by a quasi-steady numerical solution.

We conclude this section with a brief discussion of our own results from reduced gravity experiments conducted aboard the NASA space shuttle Columbia in two series, the first in summer 1994, and the second in summer 1996. The experiments in 1994 were included in the International Microgravity Laboratory-2 (IML-2) mission and those in 1996 were part of the Life and Microgravity Spacelab (LMS) mission. We have described the apparatus, procedure, and results in detail in Balasubramaniam *et al.* (1996) and Hadland *et al.* (1999), and only a summary is provided here.

The apparatus, known as the Bubble, Drop, Particle Unit (BDPU), was designed and built under the auspices of the European Space Agency (ESA), and made available for our use through a cooperative arrangement with NASA. The BDPU consisted of a facility that provided power, optical diagnostics and illumination, imaging facilities including a video camera and a motion picture camera, and other support services such as heating and cooling. Different test cells could be inserted into the BDPU facility by the astronauts when needed. We used two identical test cells that were filled with a silicone oil. One test cell permitted the injection of air bubbles, while the second test cell was equipped to inject drops of Fluorinert FC-75. The cells were of rectangular cross-section, 60 mm long and 45×45 mm square in cross-section. The continuous phase used in the IML-2 mission was a DC-200 silicone oil of nominal viscosity 50 cs, whereas, that used in the LMS mission was a silicone oil of nominal viscosity 10 cs. During injection or extraction of a bubble or drop, the test cell was connected to mechanical systems that ensured the compensation of the volume of the bubble or drop. In each experiment, a steady and uniform temperature gradient was established at first over a period of 2 h. Then bubbles and drops of the desired size were injected, and their traverses were captured on videotape. Images in selected runs were recorded on motion picture film. The bubbles and drops ranged in radius from approximately 0.5 mm to 8 mm. It was found that the bubbles and drops traversed the cell sufficiently rapidly for size change to be negligible. In evaluating the velocity of an object from the video or cine film, data on position vs. time near the middle of the cell, away from the end walls, were used in order to minimize the effects of interaction with these boundaries.

In our flight experiments, the Marangoni number in the continuous phase ranged from 5.4 to 5 780 in the case of air bubbles, and from 2.5 to 3 700 for the migration of Fluorinert drops. The corresponding Reynolds number ranges were 0.0096–87.2 for bubble runs, and 0.0045–49.1 in the case of drops. The Prandtl number for the silicone oil used in the IML-2 experiments ranged from 371–567 while the range was 59.4–92.9 in the LMS experiments. The Reynolds and Marangoni numbers were not varied independently because, the Prandtl numbers of the fluids did not change by much from one run to another. Therefore, the Reynolds and Marangoni numbers virtually tracked each other. In Figure 6.1, the scaled velocity of air bubbles, from the IML-2 and the LMS experiments, is displayed against the Marangoni number. The velocity is scaled with the value it would have if convective transport of momentum and energy played a negligible role, namely, V_{YGB}. In calculating the values of V_{YGB} and v_0, the local value of the viscosity at the instantaneous location of the bubble was used.

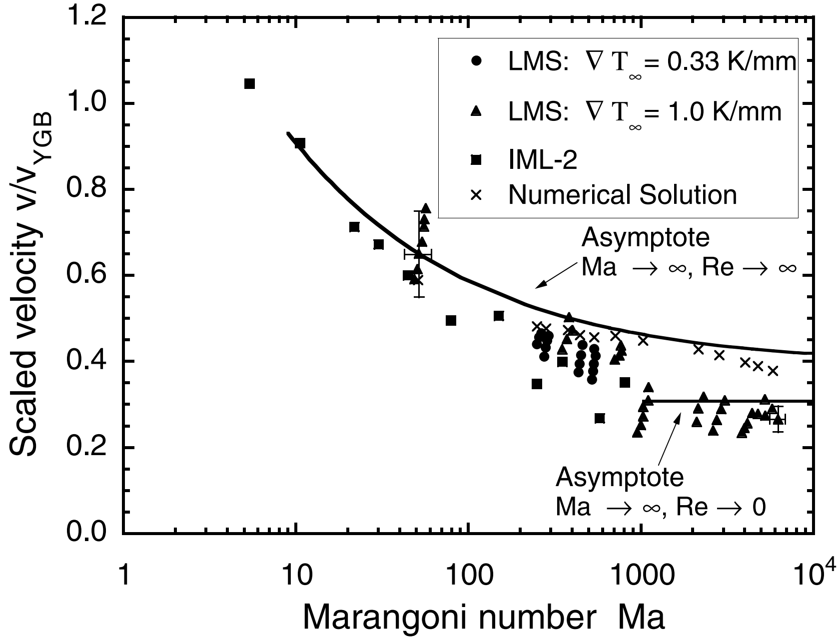

Figure 6.1 Scaled velocity of air bubbles migrating in a DC-200 silicone oil, plotted against the Marangoni number; data from the LMS and IML-2 experiments aboard the space shuttle are shown, along with predictions from a numerical solution and two asymptotic solutions; reproduced from Hadland *et al.* (1999). Thermocapillary migration of bubbles and drops at moderate to large Marangoni number and moderate Reynolds number in reduced gravity. *Experiments in Fluids* **26**, 240–248, with permission from Springer-Verlag GmbH & Co. KG.

During the course of an experiment, as a bubble moved into warmer liquid, it accelerated. Therefore, the value of the scaled velocity, as well as that of the Marangoni number, changed during the traverse. In the LMS runs, we have displayed this variation by using a set of data points for each bubble. These data were obtained for approximately 10 mm of traverse in the middle region of the cell between the hot and cold walls. In the IML-2 experiments, only a single data point was obtained for each bubble. In Figure 6.1, a numerical solution of the governing equations obtained by Ma (1998) is included for comparison, along with the asymptotic results in the limit $Ma \to \infty$ for $Re \to 0$ and for $Re \to \infty$. The former is just a constant equal to 0.3076 and the latter is calculated from equation (6.6). It is evident from the figure that the results from the flight experiments are generally consistent with the numerical predictions. Also, even though the Prandtl number of the silicone oil in the IML-2 experiments was approximately six times larger than that in the LMS experiments, the scaled velocities are not very sensitive to the variation in the Prandtl number. This is because the Prandtl number is large in both series of experiments. The results appear to be approaching the asymptotic prediction for small Reynolds number as the Marangoni number becomes large. It is interesting that the prediction for large Reynolds number does remarkably well when compared with the experimentally observed

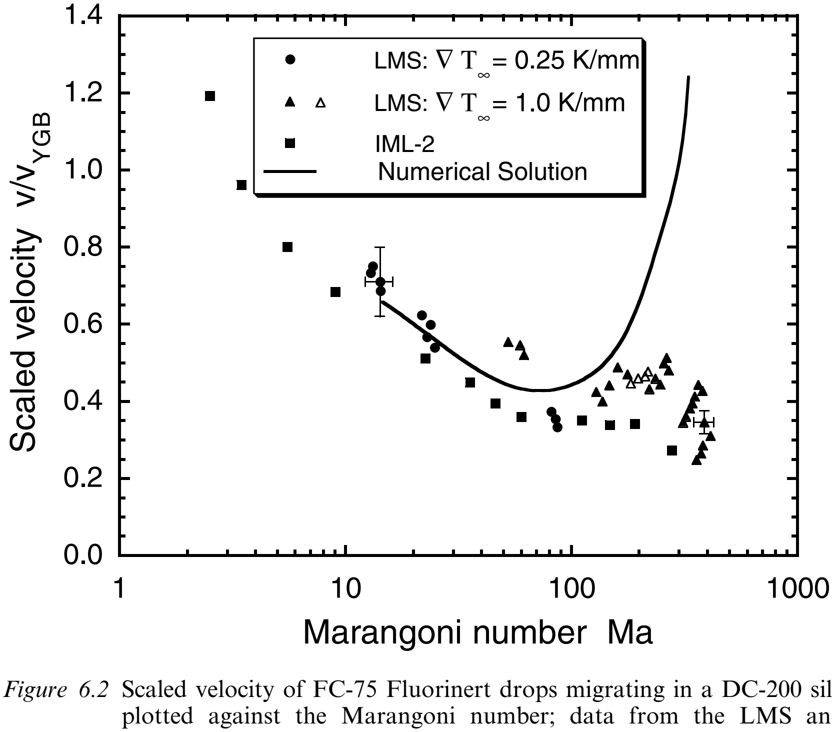

Figure 6.2 Scaled velocity of FC-75 Fluorinert drops migrating in a DC-200 silicone oil, plotted against the Marangoni number; data from the LMS and IML-2 experiments aboard the space shuttle are shown, along with predictions from a numerical solution; reproduced from Hadland *et al.* (1999). Thermocapillary migration of bubbles and drops at moderate to large Marangoni number and moderate Reynolds number in reduced gravity. *Experiments in Fluids* **26**, 240–248, with permission from Springer-Verlag GmbH & Co. KG.

velocities. We suspect that if the next term in the expansion for large Ma can be calculated in the limit Re $\rightarrow 0$, that prediction would do well when compared with the data. Finally, it is worth noting the trend of the scaled velocity vs. Marangoni number for a given bubble during its traverse, which is opposite to that expected from the quasi-steady predictions. This is consistent with the observations reported by Treuner *et al.* (1996) from their drop tower experiments.

The results for Fluorinert FC-75 drops smaller than approximately 2.5 mm in radius are plotted in Figure 6.2 along with a numerical solution obtained by Ma (1998). Again, data are displayed from both the IML-2 and the LMS experiments. The LMS data for each drop consist of a set of points corresponding to a traverse of approximately 10 mm in the middle of the cell, just as in the case of air bubbles. In the IML-2 runs, only a single data point was obtained for each drop. The data are consistent with the numerical prediction up to about Ma $= 90$. Beyond that value of Ma, the scaled velocities continue to decrease with increasing values of the Marangoni number, while the theoretical prediction is for them to increase. The experimental data for relatively large drops, not included in Figure 6.2, fell in the range of values of Ma from 1 300 to 3 700. They showed a lack of sensitivity of the scaled migration velocity to change in the value of Ma in this range. It was concluded, however, that these data corresponded to a regime where the velocity of the drop was quite far from steady state. So, no meaningful comparison with the quasi-steady solution could be attempted for the data on these large drops. We also found that even the largest drops displayed no measurable deformation from a spherical shape. The largest bubbles, of radius larger than 6 mm, for which the Weber number exceeded unity, were slightly deformed, becoming oblate spheroids. These conclusions are based on a view of the objects from a single direction.

6.6 FUTURE PROSPECTS

In this section, we highlight some of the gaps in our knowledge about thermocapillary migration identifying potential experiments in reduced gravity as well as areas of advancement in theoretical research. The most interesting experimental problems are those involving two or more bubbles or drops. Very little has been done on this subject in reduced gravity. In our IML-2 flight experiments, we had an opportunity to study the axisymmetric interaction between a pair of drops. Several pairs of drops were formed in which the leading drop was smaller than the trailing drop. We noted that the leading small drop moves virtually as though it is isolated, but that the trailing large drop is drastically slowed by the interaction with the leading drop. We attributed this to the effect of the thermal wake left by the leading drop in which the temperature gradient is weakened. This fluid wraps around the interface of the trailing drop and therefore reduces the driving force for its motion. As noted earlier, Balasubramaniam and Subramanian (1999) have recently analysed the motion of two gas bubbles of negligible viscosity and thermal conductivity, in the limit Re $\rightarrow \infty$ and Ma $\rightarrow \infty$, and predicted precisely such an effect. However, the analysis is not directly applicable to the experiments because, the Reynolds number in the experiments was relatively small, and they were conducted using liquid drops whose conductivity cannot be considered negligible. In the LMS flight, we observed the same phenomenon in some runs, but noticed even more interesting physical behaviour in others. Often, we found that a large trailing bubble or drop would move away from the axis of the cell. Its velocity toward the hot wall would increase, and in some cases, the trailing drop would pass the smaller leading drop. A likely cause of this is an instability of the motion of the trailing drop in the wake left by the leading drop. If a natural disturbance leads to a slight displacement of the trailing drop from the centreline of the cell along which it was injected, this instability would result in its moving further away from the centreline. When the trailing drop has moved a sufficient distance away from the axis, the interaction with the thermal wake of the leading drop would be weak. The hydrodynamic interaction with the leading drop is likely to be weak as well, so long as the separation distance is at least three times the radius of the leading drop. Being uninfluenced by the leading drop, the trailing drop would move more rapidly, as though it were isolated. Since the velocity of isolated drops increases with their size, the trailing drop can pass the leading drop when there is sufficient time during the traverse to do it. Unfortunately, this phenomenon could not be explored systematically in the LMS experiments, and it will need to be studied in detail in a future flight experiment.

Another interesting observation we made in a very small number of runs involved a chain of drops. These were typically introduced into the cell by accident, usually during the first attempt to inject a drop. These drops executed a 3D trajectory through the cell. Unfortunately, only one view could be captured on video. In this view, the trajectory of each drop across the cell appears as an undulating pattern, not quite sinusoidal, but qualitatively similar. Also, these spatial oscillations in position take the drop away from the axis. Interferometry images recorded from an orthogonal direction reveal a similar pattern, even though making precise measurements from this view is not possible. Therefore, we are led to conjecture that the drops did not proceed in a straight path along the axis of the cell, but rather followed a spiral path. This phenomenon remains unexplained and unexplored at this time.

We note that no experiments have been carried out on a well-characterized collection of drops moving in a continuous phase under the influence of a temperature gradient. Predictions have been made for monodisperse and bidisperse collections of this type by Acrivos and co-workers, but these remain to be tested. Also, predictions have been made by Zhang *et al.* (1993) regarding the evolution of the size distribution of a cloud of drops undergoing thermocapillary migration. These authors consider pairwise interactions in a dilute suspension and predict how the size distribution changes with time as the drops grow by coalescence. It would be interesting to perform controlled experiments in which the size distribution is measured experimentally *in situ*, perhaps by optical techniques.

The ground-based experiments of Merritt and Subramanian (1989), and later Barton and Subramanian (1991), have established the correctness of the predictions from the low Reynolds number theory for the motion of a drop normal to a plane surface. No experimental data have been reported for motion parallel to a plane surface, or in the more general case of motion in an arbitrary direction with respect to the surface. It would be useful to perform experiments on drops moving near boundaries to gauge the effects of the boundaries on thermocapillary migration when convective transport of momentum and energy are not negligible. In this case, the problem is inherently unsteady. Therefore, theoretical predictions, while straightforward to make in principle, are difficult to obtain because of the need for numerical solution of the governing equations. Of course, the experiments would have to be done in reduced gravity because, the problems are non-linear and the gravitational contribution in ground-based experiments cannot be simply decoupled.

Eventhough a number of experiments have been performed in reduced gravity on isolated bubbles and drops, much work remains to be done in this area. Recall that the prediction for large values of Ma in the case of drops is that the scaled velocity should increase with increasing values of the Marangoni number. In physical terms, for a fixed set of property ratios, this implies that the physical velocity must be proportional to the cube of the radius of the drop and the square of the applied temperature gradient. In contrast, for a gas bubble of negligible thermal conductivity, the prediction at large values of the Marangoni number is for the velocity to depend on the first power of the radius and the applied temperature gradient, the same as the prediction at negligible values of Ma. The theoretical result for drops is so remarkable that experiments should be performed to verify it. The main difficulty here is in achieving quasi-steady conditions within the drop. One needs to use a drop of sufficiently large thermal diffusivity that conduction across streamlines within the drop can be expected to occur rapidly. This was not possible in the IML-2 and LMS flight experiments because the thermal diffusivity of Fluorinert FC-75 was too small. A liquid metal is a good choice for the drop phase in such experiments.

In certain applications, such as in metallurgy, drops will change size rapidly during the course of their migration. Dill (1991) constructed a theoretical description of the motion of an isolated drop that changes size in the case when the Reynolds and Marangoni numbers are negligibly small. He defined a dimensionless parameter that contrasts the rate of size change with the typical velocities resulting from thermocapillary motion. For small values of this parameter, he predicted that the size change should have no effect on the migration velocity because it merely produces an additive potential flow that is radially directed. This is consistent with the experimental observations of Merritt and Subramanian (1988). No predictions are available, however, for situations where the assumptions of Dill's analysis are relaxed. It would be useful to perform thermocapillary migration experiments on drops and bubbles that dissolve or grow at rapid rates under reduced gravity conditions. Such observations would be extremely useful in extending the present theoretical descriptions to accommodate mass transfer situations.

Earlier, we noted the limited nature of the available experimental results involving the role of added surfactants on thermocapillary migration. The fluids used for studying thermocapillary migration were carefully selected to avoid contamination by trace impurities that act as surface-active agents. This is the primary reason for the choice of silicone oils as the continuous phase in numerous studies since contaminants in these liquids appear to stay in bulk solution instead of adsorbing at the air–silicone oil interface. The second reason is that silicone oils in a given family are available in a wide range of viscosities, while the other physical properties remain virtually constant. If thermocapillary migration is to be used as a practical tool in applications in the reduced gravity environment, a variety of liquids must be used as the continuous and dispersed phases and some contamination by surfactants is inevitable. Therefore, studies of the role of surfactants in influencing thermocapillary migration must be performed in reduced gravity. For this purpose, a well-characterized surfactant should be used so that the physical parameters associated with surfactant adsorption, desorption, and transport in the bulk as well as on the interface, would be known. Then, thermocapillary migration experiments can be performed, in which the concentration of this surfactant in each phase is varied systematically, and the results used to validate and improve the theoretical descriptions.

Temperature gradients naturally arise at the surface of a translating drop in an otherwise isothermal fluid. The physical basis of this phenomenon, first analysed by Harper *et al.* (1967), is as follows. Elements of area of the interface are growing in the forward half of the drop surface as they move toward the equatorial region. The internal energy that is needed is provided by the neighbouring fluid which is cooled as a consequence. The reverse occurs in the rear half. The resulting interfacial tension gradient leads to a thermocapillary stress that opposes the motion of the drop. Harper *et al.* were interested in establishing whether this phenomenon could explain the fact that small drops and bubbles translating through a second fluid, encounter more resistance than that predicted by theory. They concluded that the effect was too small in common fluids, and that the explanation provided by Frumkin and Levich (1947), based on the adsorption of surface active contaminants, is the correct one. The phenomenon analysed by Harper *et al.* is indeed important in certain fluids. This was recognized by Torres and Herbolzheimer (1993), who pointed out that this effect can lead to macroscopic temperature gradients when a swarm of bubbles rises in an otherwise isothermal liquid. The same phenomenon will reduce the thermocapillary migration velocity of a drop, as noted by these authors. Its relative importance is characterized by a dimensionless group $E_s = -(e_s - \sigma)\sigma_T/(\mu k)$, where e_s stands for the interfacial internal energy per unit area. When this group is of the order unity or larger, the effect is predicted to be important. Examples of fluids in which E_s is sufficiently large for the effect to be pronounced, cited by Torres and Herbolzheimer (1993), are cyclopentanone, dimethylphenyl carbinol, abietic acid, and even water at elevated temperatures, as well as liquid nitric oxide, methane, and carbon dioxide. No results from thermocapillary migration experiments in these fluids have been reported that confirm the predictions of even the linear theory, which applies when convective transport effects are negligible. Experiments should be performed on gas bubbles migrating in these fluids under the action of a temperature gradient, both on the ground, and in reduced gravity in the long run.

It is possible for a drop, initially stationary in isothermal surroundings, to move due to the action of a uniform source of heat within the drop, or uniform generation of heat at the surface of the drop due to chemical reaction, as first pointed out by Ryazantsev (1985). Normally, the source of energy would lead to a uniform temperature on the surface of the drop, which can be different from that of the undisturbed continuous phase, resulting in no motion. However, a disturbance that causes a slight movement of the drop will lead to a temperature variation on the surface of the drop, because of non-uniform heat transport between the drop and the surrounding fluid arising from the action of the convective transport terms. Under the right conditions, the drop will continue to move in the same direction due to the action of the thermocapillary stress, sustaining the motion indefinitely. Since the appearance of the original work by Ryazantsev (1985), a variety of situations have been analysed. Examples can be found in Golovin *et al.* (1986), and Rednikov *et al.* (1994a). A review is provided by Rednikov *et al.* (1994b). No experiments have been reported in which these predictions have been tested. It would be appropriate to perform such experiments under low gravity conditions so that interference from gravitational effects can be minimized.

We conclude by noting that the achievement of true quasi-steady conditions may very well be impossible for large values of the Reynolds and Marangoni numbers if the viscosity (or any other relevant physical property, for that matter) varies strongly with temperature. Therefore, experimental measurements must be evaluated against predictions made from a consideration of the fully transient problem accommodating the dependence of physical properties on temperature. Such predictions have yet to be made. This is the most important theoretical problem that needs to be addressed for an isolated drop. Of course, a variety of problems involving size change, interaction of drops with each other and with boundaries, and the behaviour of a collection of drops, remain to be solved under conditions when the Reynolds and Marangoni numbers assume that which are not negligible.

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NOMENCLATURE

Ca	Capillary number
e_s	internal energy of the interface per unit area
E	Elasticity number
E_s	dimensionless group representing the relative importance of temperature gradients naturally arising on the interface due to drop motion
k	thermal conductivity of the continuous phase
k'	thermal conductivity of the drop phase
Ma	Marangoni number
Pr	Prandtl number
q	radiant heat flux absorbed by a drop surface
r	radial coordinate
R	radius of the drop
$\mathcal{R}$	universal gas constant
Re	Reynolds number
T	temperature
T_0	reference temperature on the interface
v_0	reference velocity
v_∞	physical migration velocity scaled by the reference velocity
V_{YGB}	velocity predicted by Young *et al.*
We	Weber number
$\alpha = \frac{\mu'}{\mu}$	ratio of the dynamic viscosity of the drop phase to that of the continuous phase
$\beta = \frac{k'}{k}$	ratio of the thermal conductivity of the drop phase to that of the continuous phase
Γ	reference concentration of surfactant on the interface
θ	polar angle measured from the forward stagnation streamline
κ	thermal diffusivity of the continuous phase
Λ	dimensionless gas constant

μ	dynamic viscosity of the continuous phase
μ'	dynamic viscosity of the drop phase
ν	kinematic viscosity of the continuous phase
ρ	density of the continuous phase
σ	interfacial tension between the drop phase and the continuous phase
σ_T	rate of change of interfacial tension with temperature
χ	scaled radial coordinate in an outer expansion of the velocity field
∇T_∞	applied temperature gradient

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