

Page : 67 Renumbr the second Eq. (2.10) as (2.11)

- " 71 For  $v'_\alpha$  (lines 11, 12, 13, 15, 31) and  $u_\alpha$  (4.21) read  $v'_\beta$
- " 72  $\lambda$ . -15 For  $v'_\alpha$  read  $v'_\beta$   
 $\lambda$ . -10 For  $R^k$  read  $R^{-k}$
- " 74  $\lambda$ . 8 Between  $sl=0$  and  $ml=0$  insert ,
- " 78  $\lambda$ . 2 below (2.48) For  $\chi = 0.1$  read  $\chi = 1.1$
- " 81 ~~For~~ Eq. (2.55) Insert factor  $p$  in second term.
- " 90 Last line of (3.6) For  $\sum_{n=3}^\infty$  read  $\sum_{n=2}^\infty$
- " 91  $\lambda$ . -4 Before Tyrolier et al. (1971) insert Savic (1953) and
- " 92  $\lambda$ . -3 For theorems read theorem
- " 95 Eq. (3.17)  $\lambda$ .2 For  $c$  read  $C$
- " 103 Eq. (4.5) For . at end read , if temperature changes are negligible.  
line below (4.5) delete and if temperature changes are negligible.
- " 104  $\lambda$ . 3 to 6 Delete sentence Physically ..... separation.
- " 105 Eq. (4.11) For  $\partial c_1/\partial t$  read  $Dc_1/Dt$
- " 109 Eq. 4.29 Should read  $D_e = \frac{(z^+ + z^-) D^+ D^-}{z^+ D^+ + z^- D^-}$
- " 111  $\lambda$ . below (4.35) For at read of
- " 111  $\lambda$ . -4 For  $\sum_n P_n(u)$  read  $\sum_n P_n(u)$
- " 115  $\lambda$ . 7 For  $\sin^4 \theta$  read  $\sin^2 \theta$
- " 122  $\lambda$ .15 Delete , for bubbles

## The Motion of Bubbles and Drops Through Liquids

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### I. Introduction

Chemical engineers, metallurgists, geologists, brewers, and cooks all try to understand processes in which bubbles or drops move through liquids. Until recent years there was not much theoretical analysis to help them, but satisfactory theories now exist for a number of important special cases. The

work is interesting mathematically, and also throws light on the physical chemistry of interfaces between moving fluids.

Because interfacial phenomena affect the motion in a number of different ways, there are many cases to consider. We begin in Section II with the simplest. This is a bubble rising in a Newtonian liquid, far enough from boundaries (including other bubbles) to be treated as if isolated. We assume that the viscosity and density of the internal gas are negligible, and that the surface rheology reduces to the single parameter of a constant uniform surface tension. Section III is concerned with drops whose interior viscosity and density are taken into account, but which satisfy the other conditions of Section II.

The most restrictive condition is constancy of the surface tension, for it requires exceptionally pure fluids. Experiments seldom agree with the predictions of Sections II and III for small bubbles or drops unless great care is taken to remove impurities. These adsorb at the surface and lower the surface tension. The flow of the fluid then carries the impurities around the surface, setting up inequalities of concentration and hence of surface tension, which oppose the motion. So much surface-active material may be adsorbed that it forms a layer with a measurable surface elasticity or surface viscosity of its own. If a soluble surfactant diffuses across the interface, it can induce instability of the motion (interfacial turbulence). Only for surfactants so dilute that the motion is stable, and the surface tension and its gradient are the only significant mechanical properties of the interface, do quantitative theories exist. We take the surface tension to depend linearly on the concentrations in the bulk fluids which are proportional to each other, and we assume that the viscosities and the bulk and surface diffusion coefficients are constant. Section IV contains an account of the motion of drops and bubbles in these ideal solutions of surfactants. This is a first step towards a complete theory in rather the same way that the theory of ideal gases is a useful first approximation to the behavior of real gases.

The rheology of nonideal solutions and non-Newtonian liquids lies outside the scope of this review, as do interfacial turbulence, the mutual influences of two or more bubbles or drops, wall effects, and chemical reactions. Information on these topics can be obtained from Brodkey (1967) and Lane and Green (1956) for fluid dynamics, from Adam (1968) and Defay *et al.* (1966) for physical chemistry and thermodynamics of surfaces, and J. T. Davies and Rideal (1963) and Levich (1962) for both physical chemistry and fluid dynamics.

Because moving drops and bubbles are studied by such a wide variety of scientists and engineers, it is useful to indicate where bibliographical information can be found. *Chemical Abstracts* and *Physics Abstracts* are

the best general sources of information about current literature, the former in particular having a very broad coverage. *Applied Mechanics Reviews* often has short critical articles on work in the field. Several of the bibliographical reviews published in *Industrial and Engineering Chemistry* were helpful in the preparation of this work (Gal-Or *et al.*, 1969; Gill *et al.*, 1969, 1970; Gomezplata and Regan, 1968; Regan and Gomezplata, 1970; Shedlovsky, 1968; Stabel and Ferrell, 1968; Tavlirides *et al.*, 1970); this journal has now ceased publication and been replaced by *Chemical Technology*. Finally, Gouse (1966) has published an index to over 5000 papers on two-phase gas-liquid flow, up to 1965.

## II. A Bubble with Constant Surface Tension Rising Under Gravity

### A. DIMENSIONAL ANALYSIS

Consider a bubble of gas in an unbounded pure liquid whose surface tension against the gas is  $\sigma$ . We shall assume that  $\sigma$  does not vary around the surface. The bubble will rise steadily if its motion is stable to random small disturbances, and if the time taken to approach very close to the terminal velocity is much less than the time required for the bubble's size to change by a significant fraction of itself. Changes in size may be due to evaporation or condensation, to changes in ambient pressure, or to gases moving in or out of solution (as in a glass of beer). This field of "bubble dynamics" has been reviewed by Plesset (1964), one of the chief contributors to it. Its name is unfortunate, because the theory of rising bubbles of constant size is hardly "bubble statics"!

Suppose that the motion is steady, with a bubble of the same constant volume as a sphere of diameter  $d$  (the "equivalent sphere"), rising at speed  $U$  in a liquid of density  $\rho$  and dynamic viscosity  $\eta = \rho\nu$ . Let  $\rho$  and  $\eta$  be much greater than the density and viscosity of the gas. Then  $U$  must be determined by  $d = 2a, \rho, \eta$  or  $\nu, \sigma$ , and  $g$ , the acceleration due to gravity. To make our calculations independent of particular units of measurement and particular fluids, we seek dimensionless products of the above parameters. A number are in common use, but Schmidt (1933) showed that only one can be formed from the given physical properties of the liquid, namely

$$M = g\eta^4/\rho\sigma^3. \quad (2.1)$$

In different liquids  $M$  takes values over a very wide range: in highly viscous oils it can exceed  $10^5$ , and in liquid metals it can be less than  $10^{-13}$ . Other dimensionless parameters must depend on  $U$  or  $d$  or both, and they

include the Reynolds number  $R$ , drag coefficient  $C_D$ , Weber number  $W$ , Froude number  $F$ , Eötvös number  $E$ , and Bond number  $B$ , defined by the equations

$$R = Ud/\nu = Ud\rho/\eta, \quad (2.2)$$

$$C_D = \frac{\text{force on bubble}}{\frac{1}{2}\rho U^2 \cdot \pi a^2} = \frac{\frac{4}{3}\pi \rho g a^3}{\frac{1}{2}\pi \rho U^2 a^2} = \frac{4gd}{3U^2}, \quad (2.3)$$

$$W = \rho U^2 d/\sigma = (4MR^4/3C_D)^{1/3}, \quad (2.4)$$

$$F = U^2/gd = 4/3C_D, \quad (2.5)$$

$$E = B^2 = g^2 d^2 \rho/\sigma = \frac{4}{3}WC_D. \quad (2.6)$$

The reader is warned that some authors use  $a$  in the above definitions in place of  $d$ , and others use the bubble's equatorial or polar diameter.

Any independent pair of these dimensionless numbers must determine all the rest in steady flow. It is convenient to choose  $M$ , which specifies the fluid, and  $R$  which determines the mechanics. Our basic problem is then to calculate the flow pattern and hence  $C_D$  as functions of  $R$  and  $M$  from the equations of motion.

## B. SUMMARY OF EXPERIMENTAL RESULTS

Haberman and Morton (1953, 1956) and Peebles and Garber (1953) carried out experiments and collected those of previous workers to give graphs of  $C_D$  against  $R$  for bubbles in a variety of pure liquids. Selected results are shown as solid curves in Fig. 1. (The curve N9 with  $M = 1.17 \times 10^{-9}$  is for Bryn's (1933) ethyl alcohol solution in water—Haberman and Morton miscalculated  $M$  as  $1.17 \times 10^{-8}$ .) Also in Fig. 1

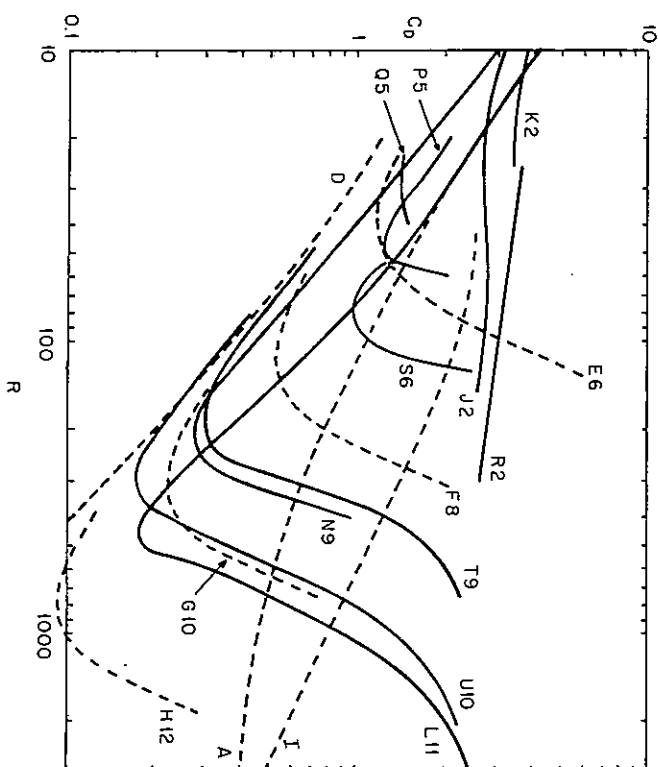
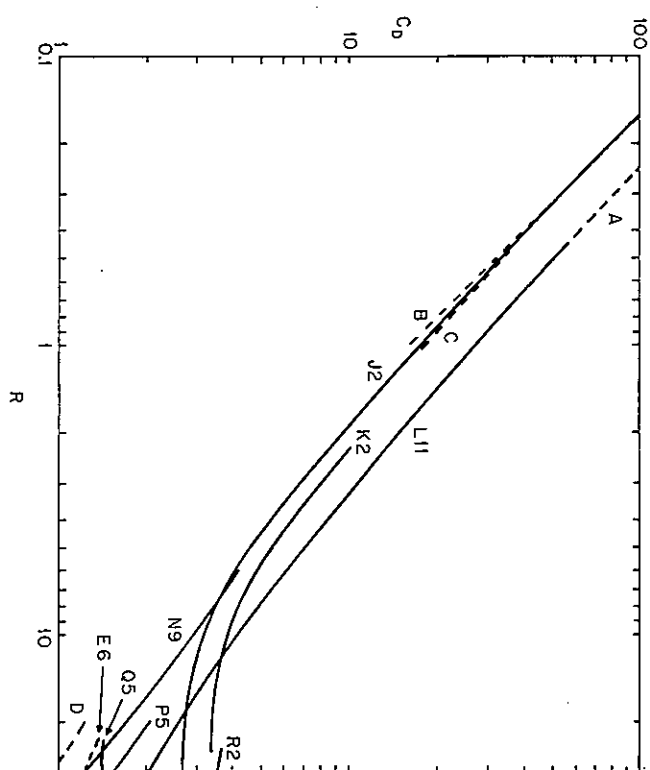


Fig. 1. Drag coefficient  $C_D$  plotted against Reynolds number  $R$  for rising bubbles. Experimental curves are drawn solid, theoretical curves dotted. Each curve bears an identifying letter, as in the list following, and also (where relevant) the nearest integer to  $-\log_{10} M$ . A. Rigid spheres (Perry *et al.*, 1963). B. Tangentially free spheres,  $R \ll 1$  (Rybczynski, 1911; Hadamard, 1911). C. Tangentially free spheres,  $R \ll 1$ , second approximation (Taylor and Acrivos, 1964). D. Tangentially free spheres,  $R \gg 1$  (Moore, 1963). E, F, G, H. Tangentially free spheroids (Moore, 1965),  $M$  respectively  $10^{-6}$ ,  $10^{-8}$ ,  $10^{-10}$ ,  $10^{-12}$ . I. Spherical caps (Parlange, 1969). J.  $M = 1.45 \times 10^{-2}$  (Haberman and Morton, 1953). K.  $M = 1.87 \times 10^{-2}$  (Kojima *et al.*, 1968). L.  $M = 2.5 \times 10^{-11}$  (Haberman and Morton, 1953). N.  $M = 1.17 \times 10^{-9}$  (Haberman and Morton, 1953). P.  $M = 6.55 \times 10^{-9}$  (Peebles and Garber, 1953). Q.  $M = 2.08 \times 10^{-5}$  (Peebles and Garber, 1953). R.  $M = 2.93 \times 10^{-2}$  (Angelino, 1966). S.  $M = 3.22 \times 10^{-7}$  (Peebles and Garber, 1953). T.  $M = 2.41 \times 10^{-9}$  (Haberman and Morton, 1953). U.  $M = 8.9 \times 10^{-11}$  (Haberman and Morton, 1953).

are the experimental results of Angelino (1966) for  $M = 2.93 \times 10^{-2}$  and Kojima *et al.* (1968) for  $M = 1.87 \times 10^{-2}$ . The dotted curves show  $C_D(R)$  for rigid spheres (Perry *et al.*, 1963; Pruppacher *et al.*, 1970) and the theories due to Rybczynski (1911), Hadamard (1911), Taylor and Acrivos (1964), Moore (1963, 1965), and Parlange (1969), which are discussed below. For low values of  $M$  (of order  $10^{-8}$  or less) many more results are available but those in Fig. 1 suffice to indicate the general character of all of them. We have used parts only of two of Peebles and Garber's graphs, in a range of  $M$  where Haberman and Morton had no liquids, because all their experiments were done in a tube only one inch in diameter. The velocity of the bubbles is appreciably less than that in an "infinite" liquid wherever the equivalent spherical diameter  $d$  is greater than about one-fifth of the diameter of the tube. It will be seen that Haberman and Morton's (and Angelino's and Kojima's) graphs tend, at their right-hand ends, towards a fairly constant value of  $C_D \approx 2.6$ , while Peebles and Garber's values of  $C_D$  tend to become proportional to  $R$ , because  $U$  becomes constant. Many other workers have experimented with bubbles, but the present author has been unable to find any more results with  $M > 10^{-6}$ , over the range of Reynolds number between 10 and 100, in tubes of sufficiently large diameter.

It is clear that the main features of the experimental graphs are as follows:

1. For each liquid with  $M < 10^{-2}$ ,  $C_D$  has a minimum value  $C_{Dm}$  which decreases, at a value  $R_m$  of  $R$  which increases, as  $M$  decreases.
2. For values of  $R$  less than  $R_m$ ,  $C_D$  rises steadily as  $R$  falls, being close to Levich's (1962) asymptotic value of  $48/R$  if  $R \gg 1$ , or to Rybczynski's (1911) and Hadamard's (1911)  $16/R$  if  $R \ll 1$ . Water is a conspicuous exception (curve L11 in Fig. 1) for which  $C_D$  is much closer to the value for rigid spheres, as it is in liquids known to be impure. The reason for the anomalous behavior of water is thought (Levich, 1962) to be the presence of trace impurities; see Section IV. In this range of  $R$  ( $< R_m$ ) the drag coefficient is not much affected by the value of  $M$ .
3. If  $R > R_m$ ,  $C_D$  first increases rapidly with  $R$  and then levels off at a value of about 2.6, provided that the minimum ( $C_{Dm}$ ) was lower than that value.
4. If  $M > 10^{-2}$  approximately, the minimum of  $C_D$  is very shallow or absent. The  $C_D(R)$  curves then tend to the Hadamard-Rybczynski asymptote for small  $R$ , but level off in the region  $2.6 < C_D < 3$ . More experimental results are desirable for  $R > 10$  and  $M > 10^{-6}$ ; there seems to be a change in the character of the curves between  $M = 10^{-5}$  and  $M = 10^{-2}$ , but no transitional cases are available.

The bubbles rise steadily, and their motion is stable, provided that they are not too large. Hartunian and Sears (1957) collated previous results and also experimented on a number of fluids. Their results are shown in Fig. 2, in which the Weber number  $W$  (as defined in Eq. 2.4) is plotted against  $R$  for marginally unstable bubbles. The relevant values of  $M \times 10^{12}$  are also plotted, as are curves of the dependence of  $W$  on  $R$  as bubble size varies, for some typical values of  $M$ . (As Hartunian and Sears did not tabulate  $M$ , values have been found from their references or from the other data in their Table 1. In the process it was discovered that the Bond numbers in that table are all the reciprocals of the values defined by the authors, except for their liquids 13 and 15, for which the table gives ten times the true values.)

For pure liquids, marginal instability occurs at a value of  $W$  near 3, provided that  $M$  is low enough (less than  $10^{-9}$ ) for this to occur when

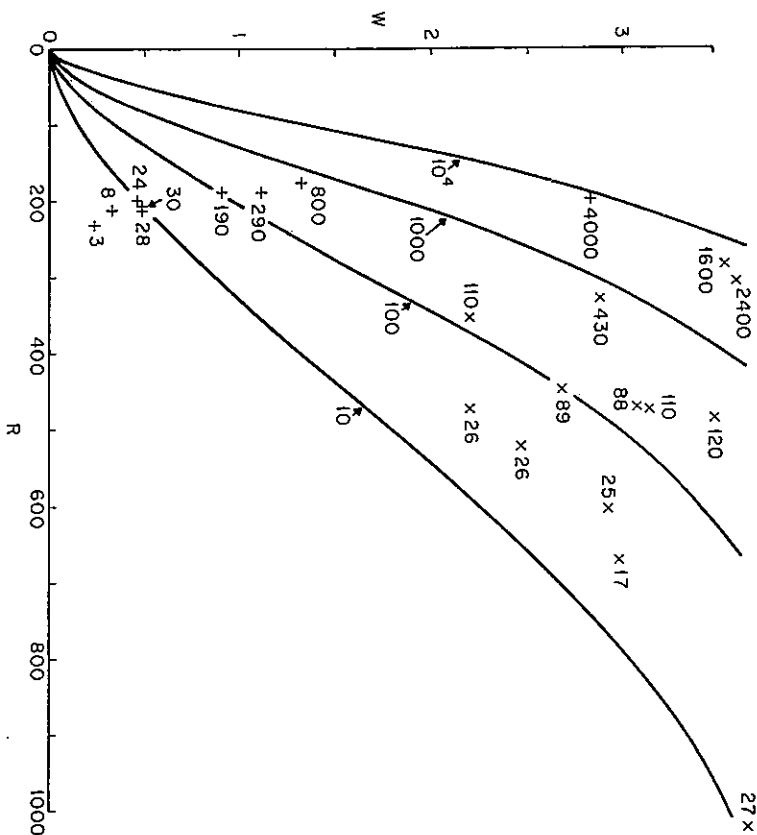


Fig. 2. Critical stability plot, in the  $(R, W)$  plane: the curves (based on Fig. 1) show  $W(R)$  for four hypothetical liquids with  $M = 10^{-9}$ ,  $10^{-9}$ ,  $10^{-10}$ ,  $10^{-11}$ . The plotted points indicate marginally unstable bubbles according to Hartunian and Sears (1957),  $\times$  for pure liquids,  $+$  for contaminated liquids. The associated numbers are values of  $10^{12}M$ .

$R > 200$ . If  $M < 10^{-8}$  and the liquid is impure, instability occurs at  $R \approx 200$ , which requires that  $W < 3$ . Bubbles are therefore less stable in an impure liquid than in the same liquid pure. No experiments were reported with  $M > 10^{-8}$  in which the motion became unstable; in Haberman and Morton's (1953) oil with  $M = 1.45 \times 10^{-2}$  bubbles were still stable at  $R = 175$ ,  $W = 180$ , and Angelino (1966) found no sign of instability up to  $R = 300$ ,  $W = 494$  in a mixture of glycols with  $M = 2.93 \times 10^{-2}$ . When steady vertical motion is unstable, the bubbles rise either in a helical path or in a plane zigzag (see Section II, D).

The other chief property of rising bubbles besides drag and stability is their shape. Sufficiently small bubbles are always spherical, but as  $W$  increases towards order unity the bubbles distort, first to oblate spheroids (flattened ellipsoids of revolution) with their short axes of symmetry vertical and their longer equatorial axes horizontal, and ultimately to a spherical cap shape, convex upwards, as  $C_D$  becomes constant. Prolate spheroids (rugby football-shaped) are not observed in Newtonian liquids except momentarily during some types of oscillation. We must now turn to the theories which have been advanced to explain this diverse collection of phenomena, taking them in order from left to right across Fig. 1, and then considering Fig. 2.

### C. THEORY FOR A SPHERICAL BUBBLE

#### 1. Low Reynolds Number

If the Reynolds number  $R$  is very small, viscous stresses which are of order  $\eta U/d$  in the neighborhood of the bubble must dominate inertial ones of order  $R\eta U/d$ , and so the total force exerted by the liquid on the bubble is of order (stress  $\times$  area) or  $\eta U d$ . In steady flow this balances the gravitational upthrust of order  $\rho g d^3$ , and so  $U$  is of order  $gd^2/\nu$ , and  $C_D = 4gd/(3U^2) \propto d^{-3} \propto R^{-1}$ . The constant of proportionality depends on the shape of the bubble and the surface conditions. We discuss only shapes close to a sphere; highly distorted bubbles can exist at low Reynolds numbers if  $M$  is large enough, but no theory appears to have been published to describe them. The only experiments seem to be those of Pan and Acrivos (1968) and Jones (1965); the undersides of their bubbles became flattened and eventually concave as  $R$  increased.

Let us define  $\psi$  to be the Stokes (axisymmetric) stream function given in spherical polar coordinates by

$$u_r = -\frac{1}{r^2} \frac{\partial \psi}{\sin \theta \partial \theta}, \quad u_\theta = \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r}, \quad (2.7)$$

where  $r$  measures distance from the center of mass of the bubble, making  $r = a$  on the surface if it is a sphere,  $\theta$  is the polar angle measured from the upstream direction, and  $(u_r, u_\theta)$  are the corresponding velocity components. Then  $\psi \sim \frac{1}{2} U r^2 \sin^2 \theta$  at large distances from the bubble, and we may write the well-known dynamical equation governing Stokes flow as

$$D^4 \psi = 0, \quad (2.8)$$

where, with  $\cos \theta$  denoted by  $\mu$ ,

$$D^2 = \frac{\partial^2}{\partial r^2} + \frac{1 - \mu^2}{r^2} \frac{\partial^2}{\partial \mu^2}. \quad (2.9)$$

This equation is known to give a good approximation to the real flow for small  $R$  provided that  $r \ll a/R$  (see, for example, Happel and Brenner, 1965).

The general solution of (2.8) with the correct limiting form for  $r \gg a$  is given by

$$\frac{\psi}{U a^2} = \left( \frac{r^2}{a^2} - \alpha_2 \frac{r}{a} + \beta_2 \frac{a}{r} \right) \mathcal{J}_2(\mu) - \sum_{n=3}^{\infty} \left( \alpha_n \frac{a^{n-3}}{r^{n-3}} - \beta_n \frac{a^{n-1}}{r^{n-1}} \right) \mathcal{J}_n(\mu), \quad (2.10)$$

where  $\mathcal{J}_n(\mu)$  is defined in terms of the Legendre polynomial  $P_{n-1}(\mu)$  for  $n = 2, 3, 4, \dots$  by

$$\mathcal{J}_n(\mu) = \int_{\mu}^1 P_{n-1}(x) dx = \frac{1 - \mu^2}{n(n-1)} \frac{dP_{n-1}(\mu)}{d\mu}. \quad (2.11)$$

For sufficiently high surface tension (or low  $M$ ) the bubble may be assumed with very little error to be a sphere, on the surface of which we may put  $\psi = 0$ , so that  $\beta_2 = \alpha_2 - 1$  and  $\beta_n = \alpha_n$  for  $n \geq 3$  in (2.10). Then the drag coefficient may be calculated by integrating the streamwise component of stress over the surface of the sphere, or by finding the momentum flux at a distance (Happel and Brenner, 1965), as

$$C_D = 16\alpha_2/R. \quad (2.12)$$

To render the solution unique and find  $\alpha_2$  we need another surface condition. If, for example, the sphere were rigid, making  $u_\theta = 0$  at  $r = a$ , the use of (2.7) and (2.8) would immediately give Stokes's results  $\alpha_n = \beta_n = 0$  for  $n \geq 3$ ,  $\alpha_2 = 3/2$ , and  $C_D = 24/R$ . In our case of constant surface tension the surface shear stress component  $p_{r\theta}$  vanishes (see Levich, 1962; Landau and Lifshitz, 1959), and because

$$p_{r\theta} = \frac{\eta a}{\sin \theta} \frac{\partial}{\partial r} \left( \frac{1}{r^2} \frac{\partial \psi}{\partial r} \right)$$

on the surface, where  $u_r = 0$ , we have for all  $\mu$  in  $-1 \leq \mu \leq 1$ ,

$$p_0 = \frac{\eta U}{a \sin \theta} [6(\alpha_2 - 1)\mathcal{F}_2(\mu) + \sum_{n=3}^{\infty} (4n - 2)\alpha_n \mathcal{F}_n(\mu)], \quad (2.13)$$

which leads to the Rybczynski-Hadamard results  $\alpha_n = \beta_n = 0$  for  $n \geq 3$ ,  $\alpha_2 = 1$ ,  $C_D = 16/R$ , and  $u_\theta = \frac{1}{2}U \sin \theta$  at  $r = a$ .

The method used above is exactly similar for free and rigid surfaces, only the boundary conditions and therefore the numerical values being different. The same is true for higher approximations in  $R$ : one uses matched Stokes and Oseen asymptotic expansions in  $r \ll Ra$ ,  $r \gg a$  respectively, in the manner pioneered by Lagerstrom and Cole (1955) and Proudman and Pearson (1957). Taylor and Acrivos (1964) carried the work through, for drops as well as bubbles, with tangentially stress-free surfaces. They found higher approximations to the drag, the next for a bubble being  $C_D = (16/R) + 2$ , and showed how to determine the first-order perturbations of shape from a sphere. If the surface of the bubble is at

$$r = a[1 + \xi(\mu)], \quad \max |\xi| \ll 1, \quad (2.14)$$

the conditions that  $a$  be the radius of the equivalent sphere and that the origin be the center of mass are, to first order,

$$\int_{-1}^1 \xi(\mu) d\mu = \int_{-1}^1 \mu \xi(\mu) d\mu = 0. \quad (2.15)$$

We also require that the difference between the normal components of stress just inside and just outside the surface be the surface tension times the sum of the principal curvatures. Using this condition, Taylor and Acrivos found for a gas bubble that

$$\xi = -\frac{5}{48}WP_2(\mu) = \frac{5}{48}W(1 - 3\cos^2 \theta), \quad (2.16)$$

to the first order (we recall that  $W = \rho U^2 a / \sigma$ ). The bubble is thus an oblate spheroid with its short axis vertical, the ratio  $\chi$  of longest to shortest diameter being given by

$$\chi = 1 + \frac{5}{32}W. \quad (2.17)$$

We shall not here pursue higher approximations to the shape or the drag: Taylor and Acrivos give some, which predict flattened undersides of rising bubbles, but their neglected terms are less important only if  $W \ll 1$ ,  $R \ll 1$ , and  $\rho\nu^2/a\sigma \ll 1$ , i.e.  $R \ll M$ . The last inequality is frequently too restrictive: it would be helpful to have also the next approximation for  $W \ll 1$ ,  $R \ll 1$  and  $R \gg M$ . Pan and Acrivos (1968) have, however, published some experimental results in an oil with  $M = 171$  which agreed with the theory for  $R \ll M$ .

The surprising point about Eq. (2.17) is that  $\chi - 1$  is proportional to  $W$ , a ratio of inertial to surface tension stress. One would have expected  $\eta U / \sigma$  instead, because viscous stresses dominate inertial ones in determining the motion, but it happens that terms of order  $\eta U / \sigma$  cancel in the derivation of (2.16). They must, of course, for a shape symmetrical about the equatorial plane, like the spheroid of Eq. (2.16): reversing  $U$  would not alter the shape, and so the distortion must be an even function of  $U$ . As a result, a spherical bubble is an exact solution in Stokes flow with inertial terms neglected. We observe finally that  $\chi - 1$  is a rapidly increasing function of  $R$ : if  $C_D = 16/R$ ,  $W = (32/5)(\chi - 1) = (MR^5/12)^{1/2}$ , by Eq. (2.4).

## 2. High Reynolds Numbers

For  $R \gg 1$ , the theories of motion past solid spheres and tangentially stress-free bubbles are quite different. It is easy to see why this must be so. In either case vorticity must be generated at the surface because irrotational flow does not satisfy all the boundary conditions. The vorticity remains within a boundary layer of thickness  $\delta = O(aR^{-1/2})$ , for it is convected around the surface in a time  $t$  of order  $a/U$ , during which viscosity can diffuse it away to a distance  $\delta$  if  $\delta^2 = O(\nu t) = O(a^2/R)$ . But for a solid sphere the fluid velocity must change by  $O(U)$  across the layer, because it vanishes on the surface, whereas for a gas bubble the normal derivative of velocity must change by  $O(U/a)$  in order that the shear stress be zero. That implies that the velocity itself changes by  $O(U\delta/a) = O(UR^{-1/2}) = O(U)$ , as was first pointed out by Levich (1949).

In the boundary layer on the bubble, therefore, the fluid velocity is only slightly perturbed from that of the irrotational flow, and velocity derivatives are of the same order as in the irrotational flow. Then the viscous dissipation integral has the same value as in the irrotational flow, to the first order, because the total volume of the boundary layer, of order  $a^2\delta$ , is much less than the volume, of order  $a^3$ , of the region in which the velocity derivatives are of order  $U/a$ . The volume of the wake is not small, but the velocity derivatives in it are, and it contributes to the dissipation only in higher order terms (Moore, 1963). By evaluating the dissipation in irrotational flow past a sphere, Levich (1949) obtained

$$C_D = 48/R, \quad (2.18)$$

as a first approximation to the drag coefficient of a bubble at high  $R$ , as did Ackeret (1952) and Chan and Prince (1965) later but independently. The bubble must be spherical if the surface tension pressure, of order  $\sigma/a$ , is much greater than the dynamic pressure of order  $\rho U^2$ , i.e. if  $W \ll 1$ .

Further developments have been remarkable for the number of errors perpetrated: most writers on this subject seem to have made at least one in published work. Let us begin by considering the velocity distribution in the boundary layer, assuming the bubble to be spherical and using the same spherical polar coordinate system as at low Reynolds numbers. Let the  $\theta$  velocity component  $u_\theta = \bar{u}_\theta + u'_\theta$ , where  $\bar{u}_\theta$  denotes the velocity of the irrotational flow past the sphere and  $u'_\theta$  the perturbation due to viscosity. Then

$$\bar{u}_\theta = U \sin \theta \left( 1 + \frac{a^3}{2r^3} \right), \quad (2.19)$$

as is well known. To find  $u'_\theta$  it is convenient to start by defining a "circulation density"  $\Omega$  in terms of the azimuthal vorticity component  $\omega$

$$\Omega = \frac{\omega}{r \sin \theta} = \frac{D^2 \psi}{r^2 \sin^2 \theta} = \frac{1}{r^2 \sin^2 \theta} \left[ \frac{\partial^2 \psi}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \theta} \right) \right]. \quad (2.20)$$

The reason for the name "circulation density" (for which I am indebted to Prof. J. E. Ffowcs Williams) is that  $\Omega$  is  $2\pi$  times the circulation round an infinitesimal vortex tube, divided by the volume of the tube.

The form of the vorticity equation in terms of  $\Omega$ , for time-dependent axially symmetric flow in general orthogonal curvilinear coordinates  $(\alpha, \beta, \gamma)$  is frequently useful, and does not appear in the usual reference books. If  $(\alpha, \beta, \gamma)$  are a right-handed set of coordinates in which  $\gamma$  is the azimuthal angle, and the element of distance  $ds$  is given by

$$(ds)^2 = h_1^2 (d\alpha)^2 + h_2^2 (d\beta)^2 + m^2 (d\gamma)^2, \quad (2.21)$$

where  $m$  is distance from the axis of symmetry, and the velocity components  $u_\alpha, u_\beta$  are given by

$$u_\alpha = -\frac{1}{mh_2} \frac{\partial \psi}{\partial \beta}, \quad u_\beta = \frac{1}{mh_1} \frac{\partial \psi}{\partial \alpha}, \quad (2.22)$$

then the vorticity equation can be written as

$$\frac{\partial \Omega}{\partial t} + \frac{1}{mh_1 h_2} \frac{\partial(\psi, \Omega)}{\partial(\alpha, \beta)} = \nu (\nabla^2 \Omega + \frac{2}{m} \nabla m \cdot \nabla \Omega), \quad (2.23)$$

after a simple transformation from the form given by Goldstein (1938), where the circulation density  $\Omega$  is given by

$$\Omega = \frac{1}{m^2} D^2 \psi = \frac{1}{mh_1 h_2} \left[ \frac{\partial}{\partial \alpha} \left( \frac{h_2}{mh_1} \frac{\partial \psi}{\partial \alpha} \right) + \frac{\partial}{\partial \beta} \left( \frac{h_1}{mh_2} \frac{\partial \psi}{\partial \beta} \right) \right]. \quad (2.24)$$

In our thin small-perturbation boundary layer in steady flow, with  $\alpha, \beta$  respectively the stream function  $\bar{\psi}$  and velocity potential  $\bar{\phi}$  of the irrotational first approximation, and  $\bar{v}$  the speed of the fluid in that approximation,  $h_1 = 1/(m\bar{v})$ ,  $h_2 = 1/\bar{v}$ . To a sufficient approximation (2.23) is then

$$\frac{1}{m^2} \frac{\partial \Omega}{\partial \bar{\phi}} = \nu \frac{\partial^2 \Omega}{\partial \bar{\psi}^2}. \quad (2.25)$$

As variations of  $m$  across the boundary layer may be neglected,  $m$  may be taken to be the function of  $\bar{\phi}$  alone with which it coincides on the bubble surface  $\bar{\psi} = 0$ . Equation (2.25) then reduces to

$$\partial \Omega / \partial X = \nu \partial^2 \Omega / \partial \bar{\psi}^2, \quad (2.26)$$

if  $X = [\bar{\phi}]^2 d\bar{\phi}$ . To a boundary layer approximation the perturbation tangential velocity  $u'_\alpha = u'_\theta$  is given by

$$u'_\alpha(X, \bar{\psi}) = -\frac{1}{\bar{v}} \int_{\bar{\psi}}^{\infty} \Omega(X, \bar{\psi}) d\bar{\psi}, \quad (2.27)$$

because  $u'_\alpha$  and  $\Omega$  both tend to zero at the outer limit of the boundary layer, to a first approximation in which we neglect the secondary flow due to displacement thickness (Lighthill, 1958). Hence  $\bar{v}u'_\alpha$  also obeys the same one-dimensional diffusion equation (2.26) as  $\Omega$ . Note that if  $\bar{\phi}$  on the bubble surface is proportional to distance  $s$  measured parallel to the axis of symmetry (and it is for spheres and spheroids), then  $X$  is proportional to the volume of the bubble upstream from a plane of constant  $s$ .

The subsequent working is simplified if we choose dimensionless variables  $x \propto X$ ,  $z \propto \bar{\psi}$ , and  $f(x, z) \propto \bar{v}u'_\alpha$  such that  $0 \leq x \leq 1$  on the surface of the bubble,  $f(x, z)$  is of order unity in the boundary layer, and Eq. (2.26) becomes

$$4 \partial f / \partial x = \partial^2 f / \partial z^2. \quad (2.28)$$

These requirements are met for a spherical bubble by putting

$$x = \frac{1}{4}(2 - 3\mu + \mu^3) = \frac{1}{4}(1 - \mu)^2(2 + \mu), \quad (2.29)$$

where  $\mu = \cos \theta$  as before,

$$\begin{aligned} z &= 3R^{1/2}(r - a)\sin^2 \theta / 8a \\ &= \bar{\psi} R^{1/2} / 4Ua^2, \end{aligned} \quad (2.30)$$

and

$$f(x, z) = R^{1/2} u'_\alpha \sin \theta / U. \quad (2.31)$$

The boundary conditions on  $f$  are, firstly, the initial condition that the fluid entering the boundary layer near the front stagnation point has no velocity perturbations, i.e.

$$f(0, z) = 0 \quad \text{for } z > 0, \quad (2.32)$$

and secondly, the surface shear stress condition which reduces to

$$\frac{\partial f}{\partial z}(x, 0) = 8 \quad \text{for } 0 < x < 1. \quad (2.33)$$

The solution of Eq. (2.28) with these conditions is immediately found to be  $\partial f / \partial z = 8 \operatorname{erfc}(z/x^{1/2})$ , or, on integrating,

$$f(x, z) = -8x^{1/2} \operatorname{ierfc}(z/x^{1/2}) = -8x^{1/2} \int_{z/x^{1/2}}^{\infty} \operatorname{erfc}(t) dt. \quad (2.34)$$

This result was first found correctly by Moore (1963) in a different notation from that used here; Levich (1962) and Chao (1962) used erroneous forms of the continuity and stress equations, respectively.

The perturbation pressure is extraordinarily difficult to find. Chao took the difference between the actual pressure in the fluid and the pressure in the irrotational flow to be  $o(\rho U^2 R^{-1})$ ; Moore (1963) showed that it was  $O(\rho U^2 R^{-1})$ , but he has since pointed out (personal communication) that he neglected the secondary flow due to displacement thickness, which contributes additional terms to his paper's Eqs. (2.22), (2.36), and (2.37) of the same order as the ones which he did take into account. Moore's drag calculation does not depend on those equations and is correct to the order given by him, but Chao's is vitiated by his error in determining the pressure. Before describing Moore's method for the drag, we must look into the behavior of  $u_\theta' \doteq u_\theta'$  near the rear stagnation point, as it has been widely misunderstood. It is clear from our Eq. (2.34) that on the surface  $z = 0$ , near the rear stagnation point  $x = 1$ ,  $f(x, z) \doteq -8\pi^{-1/2}$ , or  $u_\theta' \doteq -8UR^{-1/2} \pi^{1/2} \operatorname{cosec} \theta$ , and  $\bar{u}_\theta = (3/2)U \sin \theta$ . It would therefore seem that the resultant  $\theta$ -velocity  $u_\theta = \bar{u}_\theta + u_\theta'$  must reverse and the boundary layer must separate, where  $\sin^2 \theta = 16/(3\pi^{1/2} R^{1/2})$ , i.e.  $\pi - \theta = O(R^{1/4})$ . But Moore (1963) showed that if  $\pi - \theta = O(R^{-1/6})$  the above theory giving  $u_\theta'$  is not valid and must be replaced by a different one, which predicts  $u_\theta' \ll \bar{u}_\theta$  and hence no boundary layer separation.

Moore's theory for the rear stagnation region proceeds as follows. One writes down the full equations of motion, and evaluates the order of magnitude of each term with the aid of the boundary layer solution (2.34). The result is that if  $\varphi = \pi - \theta$  is in the range  $R^{-1/6} \ll \varphi \ll 1$  then the terms retained in the approximation (2.28) do dominate those neglected, making the approximation still consistent, and the inertial terms also dominate the

viscous ones. (Some of the retained terms are therefore negligible, but that is merely harmless additional complication in the theory: for consistency one requires only that all neglected terms be negligible.) In other words, if  $R^{-1/6} \ll \varphi \ll 1$  the assumption of a thin boundary layer still holds and the perturbation velocity is still much smaller than the irrotational velocity at each point, but viscous diffusion of circulation density may be ignored, as if the fluid were inviscid. The physical explanation for this inviscid behavior is simply that streamlines must be further apart near stagnation points than in the flow generally, and so space derivatives of circulation density are reduced, which impedes its diffusion and leaves what is already there to be carried along the streamlines.

This reason for the flow to be effectively inviscid where  $R^{-1/6} \ll \varphi \ll 1$  still holds where  $\varphi = O(R^{-1/6})$  and the fluid which was formerly in the boundary layer around the surface turns the corner and passes down the wake. Streamlines whose distances from most of the bubble surface are of order  $aR^{-1/2}$  pass the stagnation points at distances of order  $aR^{-1/6}$  and lie at distances of order  $aR^{-1/4} \gg aR^{-1/2}$  from the center-line of the wake, and so diffusion of circulation density across them is a much slower process in the rear stagnation region and wake than in the viscous part of the boundary layer around the surface. This argument could fail if the "inviscid" flow did not obey the viscous boundary condition of zero shear stress on the surface, but (unusually for an inviscid flow) that condition turns out to be satisfied near the rear stagnation point, to leading order. It is not satisfied near the front stagnation point, which explains why the viscous layer begins there, rather than at some small distance downstream.

Because the "inviscid" region has  $\varphi \ll 1$ , we may use cylindrical polar coordinates  $(m, s)$  to describe it, where  $m$  is the perpendicular distance from the axis of symmetry,  $s$  is the distance downstream from the rear stagnation point measured parallel to the axis, and the bubble surface approximates to the plane  $s = 0$  if  $\varphi$  is small. Then, if  $\bar{\psi}$  and  $\psi'$  are the stream functions of the irrotational flow and the perturbation to it, the circulation density  $\Omega = \omega/m$  obeys

$$\Omega = \frac{1}{m^2} \left( \frac{\partial^2 \bar{\psi}}{\partial m^2} - \frac{1}{m} \frac{\partial \bar{\psi}}{\partial m} + \frac{\partial^2 \psi'}{\partial s^2} \right) = B(\bar{\psi} + \psi'), \quad (2.35)$$

in the inviscid region, where  $B$  is a function to be determined from the requirement of matching to the upstream flow at  $a \gg m \gg aR^{-1/6}$ . There,  $\bar{\psi} \gg \psi'$  and

$$\Omega \doteq \frac{1}{a \sin \theta} \frac{\partial u_\theta'}{\partial r} \doteq \frac{3U}{a} \operatorname{erfc} z, \quad (2.36)$$



and hence, in the stagnation region,

$$B(\bar{\psi}) \doteq \frac{3U}{a^2} \operatorname{erfc} \left( \frac{\bar{\psi} R^{1/2}}{4\bar{U}a^2} \right) \doteq \frac{3U}{a^2} \operatorname{erfc} \left( \frac{3R^{1/2}m^2s}{8a^3} \right) = b(m^2s), \quad (2.37)$$

say. One can now find a self-consistent approximation to the solution of (2.35) and (2.37). Let us define dimensionless stagnation region variables  $m_1, s_1$ , to be  $mR^{1/6}/a, sR^{1/6}/a$ , respectively, and assume that  $\psi' \ll \bar{\psi}$  in the region where  $m_1$  and  $s_1$  are of finite order. Then

$$\frac{\partial^2 \psi'}{\partial m_1^2} - \frac{1}{m_1} \frac{\partial \psi'}{\partial m_1} + \frac{\partial^2 \psi'}{\partial s_1^2} = 3Ua^2 R^{-2/3} \operatorname{erfc}(\frac{3}{2}m_1 s_1), \quad (2.38)$$

and  $\psi' = 0$  on  $s_1 = 0, m_1 = 0$ . The chief quantity of interest is  $u'_0 = -u_m' = (1/m)(\partial \psi'/\partial s)$  evaluated on the bubble surface  $s = 0$ . From (2.38) that is given in terms of  $m_1$  by

$$u'_0 = -3UR^{-1/3} \int_0^\infty \int_0^\infty s^2 k e^{-ks} J_1(ks) J_1(km_1) \operatorname{erfc}(\frac{3}{2}s^2 z) \, dz \, ds \, dh. \quad (2.39)$$

In the limit  $R \rightarrow \infty$  this equation holds for all  $m_1$ . For large  $m_1$ ,  $u'_0$  can be shown (Harper and Moore, 1968) to be

$$u'_0 \sim -\frac{1}{m_1} \int_0^\infty b(t) \, dt \sim -\frac{8UR^{-1/3}}{\pi^{1/2}m_1} \sim -\frac{8UR^{-1/2}}{\pi^{1/2}\varphi}, \quad (2.40)$$

where  $b(t)$  is the function defined in (2.37). This form agrees with the boundary layer solution for small  $\varphi$ , so that the present theory, derived for finite  $m_1 = \varphi R^{1/6}$ , is also valid in the region of overlap with the boundary layer,  $R^{-1/6} \ll \varphi \ll 1$  or  $R^{1/24} \ll m_1 \ll R^{1/6}$ . However,  $|u'_0|$  does not go on increasing at the rate indicated by (2.40) as  $m_1$  decreases to order unity, but remains  $O(UR^{-1/3})$  in the stagnation region where  $u_0 = O(UR^{-1/6})$ . Near the rear stagnation point where  $m_1$  is small,  $J_1(km_1) \sim \frac{1}{2}km_1$  in (2.39), and so

$$u'_0 \sim -0.5749m \int_0^\infty b(t^3) \, dt \sim -1.83UR^{-1/3}m_1 \sim -1.83UR^{-1/6}\varphi \sim -1.22R^{-1/6}\bar{u}_0, \quad (2.41)$$

from Harper and Moore's (1968) equations (7.4), (7.9) with the sign error corrected, and (7.10).

We now see that  $u'_0 \ll \bar{u}_0$  everywhere around the bubble if the Reynolds number is high. The ratio  $|u'_0/\bar{u}_0|$  is of order  $R^{-1/2}$  over most of the surface ( $\varphi > O(1)$ ), of order  $R^{-1/2}/\varphi^2$  if  $\varphi \gg R^{-1/6}$ , and of order  $R^{-1/6}$  if  $\varphi = O(R^{-1/6})$ . Therefore the boundary layer does not separate,  $\bar{\psi} \gg \psi'$  even

in the stagnation region, and so our approximations are consistent. The point has been made here at some length, because several authors (Lewich, 1962; Chao, 1962; Winnikow and Chao, 1966; Taunton and Lightfoot, 1969) have used the simple viscous boundary layer analysis well beyond its domain of validity and deduced incorrect results about separation.

None of this theory says, of course, that separation and the associated back-eddies in the wake do not occur in contaminated fluids or at Reynolds numbers of order 10: we have given only an asymptotic analysis for spherical bubbles in pure fluids at high Reynolds numbers. The theory predicts, for example, that there is a neighborhood of the rear stagnation point where  $|u'_0| > \bar{u}_0$  if  $R < 3.3$  and one where  $|u'_0| > \frac{1}{2}\bar{u}_0$  if  $R < 210$ . Even  $\frac{1}{2}u'_0$  is not a very small perturbation, but the region in which the perturbations are this large is of limited size; this presumably explains the good agreement sometimes obtained between theoretical and experimental values of  $C_D$  (see below).

Having determined the nature of the velocity perturbations, we can now evaluate the viscous drag on the bubble. One makes most efficient use of the available information by choosing a method which gives the drag correctly to first order without any knowledge of the details of the boundary layers. It is then possible to find a second approximation to the drag from the first-order perturbations to the irrotational flow. We therefore reject the obvious methods of integrating the momentum deficit in the wake [but see Moore's (1963) proof that it gives the first-order drag correctly], or the normal stress on the surface, in favor of an energy argument. In steady flow, the rate of working of gravity on the bubble, which is the drag force times the velocity  $U$ , is equal to the rate of working against the surface stress plus the rate of viscous dissipation of energy throughout the fluid. Moore's (1963) final result from this method is

$$C_D = \frac{48}{R} \left[ 1 - \frac{2.211}{R^{1/2}} + O(R^{-5/6}) \right], \quad (2.42)$$

where the leading term represents the irrotational dissipation, the next is due to the boundary layer and wake, and the error term comes principally from neglecting viscous dissipation and surface stress in the rear stagnation region. It is of interest to observe that a necessary condition for the analysis to hold is therefore  $R^{-5/6} \ll R^{-1/2}$ , or  $R^{-1/3} \ll 1$ , but the best sufficient condition we have is  $R^{-1/6} \ll 1$ .

Equation (2.42) is plotted in Fig. 1 as curve D. It gives a good description of the experimental facts for bubbles which satisfy its conditions of validity, i.e. high  $R$  (over 50 appears to suffice), low enough  $M$  for the bubble to be almost spherical for some range of  $R$  over 50 ( $M < 10^{-8}$  will do), and fluids pure enough for  $\sigma$  to be effectively constant. But Fig. 1 also

shows that  $C_D$  does not continue to decrease in the way indicated by (2.42) for any fluid, but begins after a certain value of  $R$  to rise steeply, especially if  $M$  is very small. We now turn to the theory of that effect.

#### D. SPHEROIDAL BUBBLES AT HIGH REYNOLDS NUMBERS

So far, the theory for high Reynolds numbers has described only spherical bubbles, but in practice the bubbles are frequently of very different shapes. It is not hard to see why: let the equation of the surface be, as in Section II, C, 1,

$$r = a[1 + \xi(\mu)] = a[1 + \xi(\cos \theta)], \quad (2.14)$$

and suppose that  $\max |\xi| \ll 1$ , so that

$$\int_{-1}^1 \xi(\mu) d\mu = \int_{-1}^1 \mu \xi(\mu) d\mu = 0. \quad (2.15)$$

Suppose also that the flow has the general nature of an irrotational motion slightly perturbed by boundary layers, as above, and then the pressure is nearly (minus) the normal stress component at the surface. The error is of order  $\rho U^2/R$  (Moore, 1959), and so the surface condition is

$$p_1 = p_0 + \sigma(\kappa_1 + \kappa_2) + O(\rho U^2/R), \quad (2.43)$$

where  $p_1$ ,  $p_0$  are the pressures just inside and outside the surface and  $\kappa_1$ ,  $\kappa_2$  are its principal curvatures. Bernoulli's theorem and elementary differential geometry then give

$$\begin{aligned} -a(\kappa_1 + \kappa_2) &= -2 + (1 - \mu^2)\xi'' - 2\mu\xi' + 2\xi + O(\xi^2) \\ &= -\frac{1}{r_0^3}W + O(\xi^2) + O(WC_D) + O(W/R) + \text{constant}, \end{aligned} \quad (2.44)$$

where  $W$  is the Weber number  $2\rho U^2 a/\sigma$ , the term in  $WC_D$  comes from hydrostatic pressure differences around the bubble, and the constant term appears because the pressure  $p_1$  inside the bubble is, so far, unspecified. The solution to (2.44) with the conditions (2.15) is

$$\begin{aligned} \xi &= -\frac{3}{8}W^2 P_2(\mu) + O(W^2) + O(WC_D) + O(W/R) \\ &= -\frac{1}{64}W(3\mu^2 - 1) + O(W^2) + O(WC_D) + O(W/R), \end{aligned} \quad (2.45)$$

which is a useful approximation if  $W \ll 1$ ,  $R \gg 1$  and  $C_D \ll 1$ . It gives an axis ratio  $\chi$  of the bubble equal to  $1 + 9W/64$ , to leading order. The bubble's distortion is initially to the same oblate spheroidal shape at high or low Reynolds numbers, and the coefficients of  $W$  differ only by 10%,  $\chi$  being  $1 + 5W/32$  for  $R \ll 1$ .

In spite of the limitations imposed in the above theory, oblate spheroids are found to be fair approximations to the true shapes of bubbles for quite large values of  $W$ . Accordingly Moore (1965) developed the theory for spheroids analogous to his previous one (Moore, 1963) for spheres. As in Section II.3 above, one calculates the viscous boundary-layer corrections to the irrotational axially symmetric flow, and obtains the first two terms for the drag as

$$C_D = \frac{48}{R} G(\chi) \left( 1 + \frac{H(\chi)}{R^{1/2}} \right) \quad (2.46)$$

where  $G(\chi)$  and  $H(\chi)$  are functions given in Table 1.  $G(\chi)$  represents the

TABLE 1  
MOORE'S FUNCTIONS FOR DISTORTED BUBBLES\*

$\chi$	$W(\chi)$	$G(\chi)$	$H(\chi)$	$\chi$	$W(\chi)$	$G(\chi)$	$H(\chi)$
1.0	0.000	1.000	-2.211	2.6	3.278	4.278	+1.499
1.1	0.624	1.137	-2.129	2.7	3.325	4.565	1.884
1.2	1.168	1.283	-2.025	2.8	3.368	4.862	2.286
1.3	1.492	1.437	-1.899	2.9	3.406	5.169	2.684
1.4	1.802	1.600	-1.751	3.0	3.441	5.487	3.112
1.5	2.056	1.772	-1.583	3.1	3.473	5.816	3.555
1.6	2.268	1.952	-1.394	3.2	3.501	6.155	4.013
1.7	2.446	2.142	-1.186	3.3	3.527	6.505	4.484
1.8	2.597	2.341	-0.959	3.4	3.550	6.866	4.971
1.9	2.727	2.549	-0.714	3.5	3.572	7.237	5.472
2.0	2.839	2.767	-0.450	3.6	3.591	7.620	5.987
2.1	2.937	2.994	-0.168	3.7	3.608	8.013	6.517
2.2	3.022	3.231	+0.131	3.8	3.624	8.418	7.061
2.3	3.098	3.478	+0.448	3.9	3.639	8.834	7.618
2.4	3.165	3.735	+0.781	4.0	3.652	9.261	+8.189
2.5	3.224	4.001	+1.131				

\* The values of  $W(\chi)$  and  $G(\chi)$  have been calculated from Moore's (1965) formulas; the values of  $H(\chi)$  have been copied from his paper, by permission of the Cambridge University Press.

irrotational dissipation rate  $E$ , which can for a general three-dimensional body (Harper, 1970, 1971) be put in either of the forms

$$E = -\eta \iint_S \frac{\partial v^2}{\partial n} dS = 2\eta \iint_S \left( u_\theta^2 h_\theta \frac{\partial h_\theta}{\partial n} + u_\gamma^2 h_\gamma \frac{\partial h_\gamma}{\partial n} \right) dB dy. \quad (2.47)$$

Here  $(\alpha, \beta, \gamma)$  are orthogonal curvilinear coordinates in which the bubble  $S$  has the equation  $\alpha = \text{constant}$ ,  $\partial/\partial n = (1/h_\alpha)(\partial/\partial \alpha)$  denotes differentiation in the direction normal to  $S$  and into the fluid, the element of length  $ds$  is given by  $(dh_\alpha)^2 = h_\alpha^2(d\alpha)^2 + h_\beta^2(d\beta)^2 + h_\gamma^2(d\gamma)^2$ ,  $v$  is the speed of the fluid, and  $u_\alpha, u_\beta, u_\gamma$  the components of velocity in the  $\beta$  and  $\gamma$  directions. The first form for  $E$  in (2.47) is classical (see Lamb, 1932) but has the drawback of requiring velocity gradients. The second requires gradients of metric components instead, which are usually easier to find.

A spheroid will not satisfy the pressure condition (2.43) everywhere around the surface, and so some approximation has to be made. Two methods spring to mind: either equating as many terms as possible of a series expansion near the front stagnation point (R. M. Davies and Taylor, 1950; Saffman, 1956), or satisfying the condition only at the equator and poles (Hartunian and Sears, 1957; Moore, 1959, 1965). The latter method gives results which agree better with experiments, and the values of  $W(\chi)$  predicted by it are shown in Table 1. The data in that table, together with the identity

$$C_D = \frac{4}{3}MR^4W^{-3}, \quad (2.48)$$

allow one to calculate  $C_D(R, M)$ . Curves for  $M = 10^{-6}, 10^{-8}, 10^{-10}$ , and  $10^{-12}$  will be found in Fig. 1. Each curve extends from  $\chi = 0$  to  $\chi = 4.0$ , where  $C_D$  is close to the value for spherical bubbles (Moore, 1963), to  $\chi = 4.0$ , where  $W$  has become nearly constant, making  $C_D \propto R^4$  approximately. The limiting value of  $W$  from Moore's theory is 3.745. Although the theory is then beyond its range of validity (see the next paragraph), experiments indicate that  $W$  is not far from that value when it becomes a slowly varying function of  $\chi$ . The shape of the bubble is then very sensitive to small changes in  $W$ , which might be caused by small currents in the surrounding fluid. It is therefore not surprising that bubbles in pure low- $M$  liquids become unstable for values of  $W$  greater than about 3.

The type of motion which appears when a steady rise of bubbles in a straight line becomes unstable is either steady motion relative to the bubble up a helix with a vertical axis, or else zigzagging in a vertical plane on either side of a vertical line. In spite of many careful experiments, reviewed by Saffman (1956) and Hartunian and Sears (1957), who also performed their own, there is no agreement as to the conditions which decide between the two modes of instability. The above-named authors also gave approximate theories to account for the motion. Saffman used a series expansion of the irrotational-flow pressure condition near the top stagnation point, and showed that steady motion became unstable to zigzags for axis ratios  $\chi > 1.2$ , and that spiraling was possible for  $1.2 < \chi < 2.2$ , although it would only occur for motions suitably started. Experimentally, these

values of  $\chi$  are too low. Hartunian and Sears obtained a more realistic result for the onset of zigzagging by satisfying the pressure condition at the poles and equator, namely  $\chi > 2.2$ , but they did not find any criterion for spiraling. Both methods gave exponentially increasing sideways displacements instead of the oscillatory behavior actually seen in zigzagging bubbles. Saffman suggested that the oscillations might be akin to those seen in the wakes of solid bodies at Reynolds numbers of a few hundred.

A glance at Fig. 1 will show that the rising theoretical curves for  $C_D(R, M)$  are fairly close to the experimental ones provided that  $C_D < 1$ . This limitation shows the importance of the hydrostatic error term in Eq. (2.45), but it is less clear why Moore's (1965) theory works as well as it does for distorted bubbles. The predicted perturbations are not small. To see this, let us assume that the bubble is a very flattened spheroid and keep only the leading terms for large  $\chi$  in Moore's analysis. His equation analogous to (2.32) can be written

$$u_\theta' = \frac{-2\sqrt{2}U(1 + \chi^2 \cos^2 \theta)^{1/2}}{\sqrt{3\pi\chi^{1/6}R^{1/2}} \sin \theta} \int_0^\chi \frac{S(\tau)}{(X - \tau)^{1/2}} \exp\left\{-\frac{Y^2}{4(X - \tau)}\right\} d\tau, \quad (2.49)$$

where  $\theta$  is the eccentric angle of a meridian section of the spheroid,  $\theta = 0$  at the top stagnation point,  $u_\theta'$  is the tangential component of perturbation velocity,

$$X = \frac{8}{3}(2 - 3 \cos \theta + \cos^3 \theta),$$

$$Y = (\frac{8}{3}\pi)^{1/2}(\bar{\psi}/Ua^2)\chi^{1/2}R^{1/2},$$

and

$$S(X) = 3\chi^2/(1 + \chi^2 \cos^2 \theta)^2.$$

The irrotational tangential velocity is  $\bar{u}_\theta = 2U\chi \sin \theta/[\pi(1 + \chi^2 \cos^2 \theta)^{1/2}]$ . If  $\chi$  is large,  $S(X)$  can be approximated by a delta function in the form  $\pi\chi\delta(X - \frac{8}{3})$ , because  $S(X)$  is of order  $\chi^2$  if  $|\cos \theta| = O(1/\chi)$ , a small region near  $\theta = \frac{1}{2}\pi$  or  $X = \frac{8}{3}$ , and  $S(X)$  is of order  $1/\chi^2 \ll \chi^2$  if  $|\cos \theta|$  is of order unity. Physically, this amounts to saying that the surface shear stress in the irrotational flow is concentrated at the equator, where  $\bar{u}_\theta$  and its gradient are highest. It is a good approximation for positions downstream from there where  $-\cos \theta \gg 1/\chi$ . The rear stagnation vorticity is calculated as before, the equation analogous to (2.37) being

$$B(\psi) = b(m^2s)$$

$$= (3\sqrt{6}R^{1/2}U/4\pi\chi^{1/2}a^3)m^2s \exp(-3Rm^4s^2/8\pi\chi^3a^6). \quad (2.50)$$

We therefore find the ratio of perturbation to irrotational velocity at the surface as

$$\frac{u'_0}{\bar{u}_0} \doteq - \frac{\pi \chi^{11/6} \cos^2 \theta}{R^{1/2} \sin^2 \theta (-\cos \theta + \frac{1}{3} \cos^3 \theta)^{1/2}}, \quad (2.51)$$

in the main part of the boundary layer on the rear half of the bubble, where  $\pi - \theta \gg R^{-1/6} \chi^{-1/12}$ , and

$$u'_0/\bar{u}_0 \doteq -1.48 \chi^{35/12} / R^{1/6}, \quad (2.52)$$

in the immediate neighborhood of the rear stagnation point where  $\pi - \theta \ll R^{-1/6} \chi^{-1/12}$ . Equation (2.52) gives  $|u'_0/\bar{u}_0| > 1$  for all values of  $R$  likely to occur in practice even at quite modest values of  $\chi$ . With  $\chi = 3$ ,  $R = 600$ , for example, we obtain  $u'_0/\bar{u}_0 = -4.3$  at the rear stagnation point, and  $u'_0 < -\bar{u}_0$  whenever  $\theta > 131^\circ$ , where  $\sin \theta = 0.76$ . To put it another way, the perturbations are small only if

$$R \gg 10 \chi^{35/12} > 10 \chi^{11}. \quad (2.53)$$

It is tempting to identify the prediction of reversed flow at the rear of the bubble with separation of the boundary layer. But the numerical estimates above suffer from three important errors: we neglected higher terms in  $\chi$ , higher boundary layer approximations, and deviations from spheroidal shape, and so the results can at best indicate general trends. Even if an exact theory predicted a region of reversed flow ( $u_0 < 0$ ) on the surface, that alone would not show whether the back-eddy remained within the boundary layer or grew to a size comparable with the bubble. To answer that question would probably be as difficult and subtle as for flow past a rigid body, and no one has attempted it theoretically.

The question remains of why Moore's values of  $C_D(R, M)$  are so insensitive to the breakdown in his model of the flow for large  $\chi$ . If separation does not occur, but only a back-eddy inside a thin boundary layer, then his leading term (see Eq. 2.46) is unaffected although his second term involving  $H(\chi)$  is wrong, and so one would not expect serious errors in  $C_D$ . If, on the other hand, separation does take place, then the back-eddy will contain slowly circulating fluid. In the irrotational flow for large  $\chi$  the region behind the bubble where the back-eddy is situated would have contained small velocity gradients in any case; most of the viscous dissipation occurs near the equator where velocity gradients take their maximum values. In this case the error affects Moore's leading term, but not very much.

Recently, El Sawi (1970) has developed a new method of finding the function  $W(\chi)$ . He integrated the first moment of the inviscid equation of motion for a spheroid throughout the space occupied by fluid and showed

that it yielded the required function. His maximum value of  $W$  was 3.271 instead of Moore's 3.745. El Sawi also considered bubble shapes slightly perturbed from either his or Moore's spheroids, and found the perturbed shapes closer to each other than the unperturbed, as one would hope. His best final result was that  $W$  tends to a limit near 3.2 as  $\chi \rightarrow \infty$ , instead of having a finite maximum at a finite  $\chi$  as in the theories for spheroids. But an inviscid theory carried to this degree of precision is likely to be unrealistic in practice when viscous effects must be considered too.

#### E. SPHERICAL-CAP BUBBLES AT HIGH REYNOLDS NUMBERS

We have seen in the preceding section that two complications arise for large bubbles. Their boundary layers may separate and the hydrostatic term must be taken into account when evaluating the pressure in the fluid. As a result, a theoretical understanding of the motion is less complete than in the preceding cases. The first real advance was due to R. M. Davies and Taylor (1950), who related the speed of rise  $U$  to the radius of curvature  $r_0$  at the top stagnation point by the simple formula

$$U^2 = \frac{4}{3} g r_0. \quad (2.54)$$

This equation is semiempirical, being based on some experimental results which were not themselves explained theoretically. They are that the upper surface of the bubble is very nearly a cap of a sphere, and the pressure over that surface is very nearly the pressure calculated from Bernoulli's theorem for flow of an ideal fluid past the completed sphere of radius  $r_0$ , even though the wakes might be quite different. Then constancy of pressure inside the bubble requires constancy of

$$-\frac{1}{2} \rho \left( \frac{2}{3} U \sin \theta \right)^2 - \rho g r_0 \cos \theta + (2\sigma/r_0) \quad (2.55)$$

around its surface, where  $\theta$  is the polar angle measured from the top stagnation point around the completed sphere. Equation (2.54) follows on expanding the expression (2.55) in powers of  $\theta$  and equating the first non-trivial coefficient, of  $\theta^2$ , to zero.

This simple theory agrees well with experiments, but it is not self-consistent (higher terms in  $\theta$  do not vanish) and it does not predict other properties of the bubble and its wake. It is, nevertheless, better than the theory for large bubbles given by Levich (1962, Section 84). He ignored the hydrostatic pressure and made approximations which yielded a velocity independent of bubble size. That result occurs in practice only for bubbles in narrow tubes (Haberman and Morton, 1953, 1956; Peebles and Garber, 1953) but even then hydrostatic pressure determines the flow (R. M. Davies and Taylor, 1950).

1. *Theory for Low M*

Moore (1959) ignored surface tension for bubbles with large Reynolds and Weber numbers, and suggested a model for the flow analogous to Helmholtz's well-known free-streamline flow past a flat plate set across a stream (see Lamb, 1932). In Fig. 3, ABC is a cross section of the bubble,

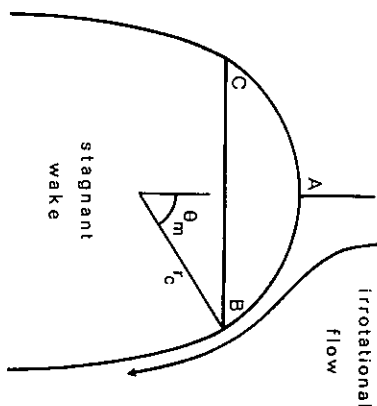


FIG. 3. The inviscid free-streamline model for spherical cap bubbles.

below which a wake containing fluid at rest extends to infinity. Outside the bubble and wake the flow is irrotational, with velocity  $U$  downwards at infinity. By Bernoulli's theorem,  $U$  is also the speed of the fluid at  $B$  and all points on the dividing streamline below  $B$ . Moore took the upper surface to be a spherical cap extending to  $\theta = \theta_m$ , and with Davies and Taylor's results (2.54) obtained the condition for equality of pressure at  $A$  and  $B$  in the form

$$gr_0(1 - \cos \theta_m) = \frac{1}{2}U^2 = \frac{2}{3}gr_0. \quad (2.56)$$

Hence  $\cos \theta_m = 7/9$ , or  $\theta_m \doteq 39^\circ$ . The condition of R. M. Davies and Taylor (1950) that the flow be like that over the complete sphere then gives the velocity at  $B$  as  $\frac{2}{3}U \sin \theta_m = 0.943U$ , not the  $U$  required for consistency. This error of some 6% is a measure of the roughness of Moore's approximation to the shape and the flow field. If one proceeds with it, one finds the volume  $V$  to be

$$V = \frac{1}{3}\pi r_0^3(1 - \cos \theta_m)^2(2 + \cos \theta_m) = \frac{1}{3}\pi \bar{d}^3, \quad (2.57)$$

and so the drag coefficient  $C_D = 8gd/(3U^2) \doteq 1.95$ .

Of course, a spherical cap is not the exact solution to the inviscid problem. We need instead that surface the irrotational flow past which satisfies  $v^2 = 2gy$  on  $AB$  and has  $v = U$  on the dividing streamline below  $B$ , where

$v$  is the speed of the fluid and  $y$  the vertical distance below  $A$ . Rippin and Davidson (1967) calculated it numerically. They found that the shape is indeed close to a spherical cap, with  $\theta_m = 50^\circ$ , that  $C_D = 1.83$ , and  $U^2 = 0.62gr_0$ . Moore's simple theory is thus a fair guide to the general form of Rippin and Davidson's more precise solution.

Unfortunately they both misrepresent the wake. Davies and Taylor's experiments were performed in nitrobenzene, which has an optical anisotropy allowing one to see where the fluid is strongly sheared. They found a turbulent region under the bubble, filling the remainder of the sphere defined by its upper surface. Maxworthy (1967) used more direct flow-visualization techniques and showed that there is also a turbulent wake, of the same order of width as the bubble, extending a considerable distance below it. The turbulence is not surprising: steady flow past bubbles of the size used by Davies and Taylor or by Maxworthy would have been highly unstable.

Before Maxworthy had shown that the wake was not closed if turbulent, Collins (1966) had tried a model for the flow in which the bubble and its recirculating wake formed a closed surface whose spherical polar equation was assumed to be  $r = a_0(1 - \epsilon \sin^4 \theta)$ . He obtained  $\epsilon = 0.0785$  by requiring the flow past the surface to be irrotational and making it satisfy the pressure condition near  $\theta = 0$  to order  $\theta^4$  instead of Davies and Taylor's  $\theta^2$  only. The upper part ( $\theta < 36^\circ$ ) of Collins's assumed surface closely resembles a spherical cap with radius  $\bar{a} = 0.953a$ . Collins's result is  $U^2 = 0.425g\bar{a}$  instead of Davies and Taylor's  $0.444g\bar{a}$ , and it fits the experiments somewhat better. It is interesting to test the way in which the results depend on the function of  $\theta$  assumed for  $r$ . If one repeats Collins's calculation with the well-known irrotational flow past a spheroid (see Lamb, 1932), one finds that the spheroid must be oblate, with eccentricity  $\frac{1}{2}$ , so that the ratio of equatorial to polar diameter is  $2/\sqrt{3} = 1.155$  (cf. Collins's 0.9215), and  $U^2 = 0.414g\bar{a}$  (which fits the experiments about as well as Collins's 0.425).

One can therefore obtain fairly good estimates of  $U^2/g\bar{a}$  from theories of this sort, but they do not readily yield information about the true shape of the wake, not even whether it is elongated or flattened from a sphere. In addition, closed-wake models which ignore viscosity and surface tension cannot possibly give the size of the bubble correctly. Figure 4 shows why. If ABCD represents a cross section of the bubble and BCDE its wake, the inviscid flow must be more or less as shown.  $A$ ,  $C$ , and  $E$  are all stagnation points and so Bernoulli's theorem gives the pressure difference  $p(C) - p(A)$  as  $\rho g \times CA$ . But if surface tension and the density of the gas can be neglected,  $p(C) = p(A)$  and so the bubble must have zero height.

This objection does not apply to Moore's model as improved by Rippin



Wakes in high- $M$  liquids are quite unlike the turbulent chaotic eddies seen by Maxworthy (1967). Slaughter and Wraith (1968) gave a good photograph of a spherical-cap bubble rising in a glycerol solution with  $M$  probably between  $10^{-2}$  and  $10^{-3}$  (not stated by the authors). The wake was a toroidal vortex resembling Hill's (1894) spherical vortex, but somewhat elongated in the direction of flow, and followed by a wake of the usual type in laminar flow far behind an axially symmetric body (Rosenhead, 1963) in which the velocity perturbation gradually decays to zero but the momentum defect remains finite. The only theory so far available for such flows is due to Parlange (1969), who exploited the analogy between the circulating wake and the circulating interior of a drop of one fluid moving in another (see Section III). He assumed that the bubble has little effect on the dynamics of the flow in the wake (except causing it to exist!), so that the vortex was near enough to a sphere for Harper and Moore's (1968) drag theory to apply. If so,

$$\frac{4}{3}\pi\rho a^3g = 30\pi\eta U\tau[1 - (6.6 - 0.14 \ln R/R^{1/2})], \quad (2.58)$$

where  $a$  is the equivalent spherical radius as before,  $\tau$  the radius of the wake sphere, and  $R' = 2U\tau/\nu$ . Parlange also assumed R. M. Davies and Taylor's (1950) relation,  $U^2 = \frac{8}{3}gr$  (see Eq. 2.54). From these equations and the definition of  $C_D$  (Eq. 2.3) one deduces that

$$R = \frac{1}{6}R'C_D, \quad (2.59)$$

and

$$C_D = 6 \left[ \frac{20}{R'} \left( 1 - \frac{6.6 - 0.14 \ln R'}{R'^{1/2}} \right) \right]^{1/3}, \quad (2.60)$$

and finds  $C_D$  and  $R$  in terms of  $R'$ . The resulting graph of  $C_D(R)$  is shown in Fig. 1 as curve 1, down to  $R' = 100$ , below which value Harper and Moore's theory must be seriously in error. It is evidently in the right part of the  $(R, C_D)$  plane at this point ( $R = 44.6$ ,  $C_D = 2.56$ ), and the trend for  $C_D$  to decrease slowly as  $R$  increases is experimentally plausible. No experimental test of the asymptotic form for large  $R$  has yet been published; the prediction is that  $C_D \sim 26.8R^{-1/2}$  as  $R \rightarrow \infty$ . Angelino's (1966) results do not inspire much confidence in it, but they cease at  $R = 300$ .

Parlange's theory is at best a first approximation for high  $R$ , when the bubble occupies a very small fraction of the wake sphere. It is debatable whether the logarithmic term is worth including in Eqs. (2.58) and (2.60), because Harper and Moore's arguments for including it in the theory of drops (see Section III, B, 2) do not apply when a bubble occupies the top stagnation region.

Parlange's assumption that the closed-wake region should be nearly spherical seems easier to justify; Hill's spherical vortex is the only known simply connected shape for which the irrotational flow outside and the flow with constant circulation density  $\Omega$  inside can have the same surface speeds.  $\Omega$  must be constant inside the "wake sphere," by the Prandtl-Batchelor circulation theorem (Prandtl, 1905; Batchelor, 1956). It seems reasonable to suppose that in Parlange's case, where the bubble occupies only a small part of the "wake sphere," the shape of the latter would be slightly perturbed from Hill's vortex. To find these perturbations will not be easy. The shape will depend on the differences between internal and external velocities which give rise to dynamic pressure differences of order  $\rho U^2 R^{-1/2}$  (Harper and Moore, 1968). In many experiments these are of the same order as surface-tension pressures,  $\sigma/r$ , and neither may be neglected. Furthermore, much of the bubble lies within the stagnation regions, whose theory we have already seen to be very complicated in Section II, C.

### 3. Skirts

In some liquids with very high values of  $M$  (0.2 or more), spherical-cap bubbles develop thin "skirts" trailing downwards (Jones, 1965; Davenport *et al.*, 1967b; Guthrie and Bradshaw, 1969), as shown schematically in Fig. 5. The thickness of the skirt was calculated by Guthrie and Bradshaw (1969) by equating the pressure rises down the skirt in the gas inside it

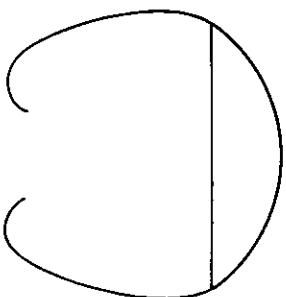


FIG. 5. Cross section of a spherical cap bubble with trailing skirt, after Guthrie and Bradshaw (1969).

and the liquid outside. The gas was treated as a two-dimensional Poiseuille flow and the hydrostatic pressure was assumed to dominate in the liquid. Guthrie and Bradshaw's experimental bubbles of volume  $53 \text{ cm}^3$  had skirts  $41 \text{ }\mu\text{m}$  thick. Their theory gave thicknesses of  $54 \text{ }\mu\text{m}$  for stagnant liquid inside the skirt or  $76 \text{ }\mu\text{m}$  for the same liquid velocity inside and out.

It is not clear what determines whether a skirt is present. Davenport *et al.* (1967b) found them on sufficiently large bubbles in polyvinyl alcohol solutions with  $M = 0.185$ , but Jones (1965), who observed them in glycerol with  $M = 6720$  did not observe them in mineral oil with  $M = 318$ . Nor are the lengths of the skirts well understood. Davenport *et al.* observed a steady length and shape resembling Fig. 5, Jones found them to be shorter and variable, and Astarita (1970) has had them extend right down the path of the bubble.

#### F. THE WAVE ANALOGY

Mendelson (1967), Cole (1967), and Malenkov (1968) have recently tried to draw an analogy between spherical-cap bubbles rising in low- $M$  liquids and waves traveling along a plane free surface. The motion of both waves and bubbles depends mainly on  $g$ ,  $\rho$ , and  $\sigma$ , viscosity being unimportant to first order (but, see, Walbridge and Woodward, 1970), and in both cases the problem is to predict a velocity as a function of a length scale (bubble size in one case, wavelength in the other). But the theory of surface waves is very much easier.

If one identifies the speed of rise of the bubble with the phase velocity of the wave given by Kelvin (see Lamb, 1932) as

$$U^2 = \frac{g\lambda}{2\pi} + \frac{2\pi\sigma}{\lambda\rho}, \quad (2.61)$$

where  $\lambda$  is the wavelength, it remains to ascertain which parameter of the bubble is best to call  $\lambda$ . R. M. Davies and Taylor (1950) give  $U^2 = \frac{1}{2}gd$  as a good approximation for large bubbles, and so Mendelson (1967) suggested that  $\lambda$  should be put equal to the equatorial circumference of the equivalent sphere,  $\pi d$ . This substitution yields graphs of  $U$  against  $d$  which agree reasonably well with the rather scattered data, but it does not give a smooth transition between the limit of large spheroidal bubbles ( $M$  constant near 3) and spherical caps ( $C_D$  constant near 8/3). This is because Eq. (2.61) with Mendelson's substitution  $\lambda = \pi d$  gives

$$C_D = \frac{8}{3} \left( 1 - \frac{1}{2W} \right), \quad (2.62)$$

after a little algebra using Eqs. (2.3) and (2.6). Clearly (2.62) is inconsistent with  $C_D$  varying while  $W$  has any constant value. The wave theory therefore does not offer a short cut to the very difficult theory of the spheroid-spherical cap transition.

### III. A Drop with Constant Surface Tension Moving Under Gravity

#### A. INTRODUCTION

The theory of moving liquid drops is in most respects very like that of gas bubbles, but more complicated. That is why bubbles were described separately in Section II. Instead of one ( $M$ ), there are now three independent dimensionless parameters which characterize the liquids, inside and outside the drop. These are  $\rho_0/\rho_1$ ,  $\eta_0/\eta_1$ , and

$$M_0 = g\eta_0^4 | \rho_0 - \rho_1 | / \rho_0^2 \sigma, \quad (3.1)$$

the reciprocal of Hu and Kintner's (1955) parameter  $P$ . Here  $\sigma$  is the interfacial tension and  $g$  the acceleration due to gravity as before, and  $\rho_1$  and  $\eta_1$  are the density and viscosity, for  $i = 0$  outside the drop (the continuous phase) and for  $i = 1$  inside it (the dispersed phase). Guided by Section II, A we define the Reynolds number  $R_0$ , drag coefficient  $C_{D0}$ , and Weber number  $W_0$  by the equations

$$R_0 = U d / \nu_0 = U d \rho_0 / \eta_0, \quad (3.2)$$

$$C_{D0} = \text{force on drop} / \frac{1}{2} \rho_0 U^2 \pi a^2 = 4gd | \rho_0 - \rho_1 | / 3 \rho_0 U^2, \quad (3.3)$$

$$W_0 = \rho_0 U^2 d / \sigma = (4M_0 R_0^4 / 3 C_{D0})^{1/2}. \quad (3.4)$$

As before,  $d = 2a$  is the diameter of the sphere with the same volume as the drop (the equivalent sphere). The modulus of  $\rho_0 - \rho_1$  appears in the formulas because it is convenient to have positive drag coefficients whether the drop moves up or down. One can define  $M_1$ ,  $R_1$ ,  $C_{D1}$  and  $W_1$  by interchanging subscripts 0 and 1 in Eqs. (3.1)–(3.4), but the parameters  $M_0$ ,  $R_0$ ,  $C_{D0}$ , and  $W_0$  are more often useful.

Figure 1 illustrates the behavior of bubbles, but would serve also for drops with very large values of both  $\rho_0/\rho_1$  and  $\eta_0/\eta_1$ . We shall not attempt to draw the corresponding graphs for general values of  $\rho_0/\rho_1$  and  $\eta_0/\eta_1$ , but instead indicate how the theories of bubble motion must be modified for drops. As we shall see, information is even less complete than for bubbles.

#### B. THEORY FOR A SPHERICAL DROP

##### 1. Low Reynolds Number

The analysis of Section II, C, 1 for bubbles follows the original work first of Hadamard (1911) and Rybczynski (1911) and then of Taylor and Acrivos (1964). It presents the special case  $\eta_1 = \rho_1 = 0$  of the same



authors' theories of drops, which use the same methods. The boundary conditions at the surface are now continuity of tangential velocity and shear stress, and zero values of normal velocity both inside and out. Uniqueness of the solution for sufficiently small  $R_0$  is ensured by the additional conditions that the velocity be a finite continuous function of position at the center  $r=0$ , and that it tend to a constant vertical vector of magnitude  $U$  as  $r \rightarrow \infty$ , downwards if  $\rho_1 < \rho_0$ , upwards if  $\rho_1 > \rho_0$ .

Equations (2.7)-(2.9) still describe the flow both inside and out, in the limits  $R_1 \rightarrow 0$ ,  $rR_0 \rightarrow 0$ , and Eq. (2.10) is still the general solution outside the drop. Inside it, the stream function  $\psi$  is given by

$$\frac{\psi}{Ua^2} = \sum_{n=2}^{\infty} \left( \gamma_n \frac{r^{n+2}}{a^{n+2}} - \delta_n \frac{r^n}{a^n} \right) \mathcal{J}_n(\mu), \quad (3.5)$$

if it is (without loss of generality) required to vanish at the origin. As before,  $\mathcal{J}_n(\mu)$  is the integrated Legendre polynomial of Eq. (2.11). The coefficients  $\gamma_n$ ,  $\delta_n$  must be evaluated from the boundary conditions. For a spherical bubble  $\gamma_n = \delta_n$  for all  $n$ , and continuity of tangential velocity and shear stress at  $r=a$  gives, on substitution from (2.10) and (3.5),

$$\begin{aligned} \frac{u_\theta \sin \theta}{U} &= \frac{1}{Ua} \frac{\partial \psi}{\partial r} \\ &= (3 - 2\alpha_2) \mathcal{J}_2(\mu) - \sum_{n=3}^{\infty} 2\alpha_n \mathcal{J}_n(\mu) \\ &= 2 \sum_{n=2}^{\infty} \gamma_n \mathcal{J}_n(\mu), \end{aligned} \quad (3.6)$$

$$\begin{aligned} \frac{p_0 a \sin \theta}{U} &= \frac{\eta_1}{U} \frac{\partial}{\partial r} \left( \frac{1}{r^2} \frac{\partial \psi}{\partial r} \right) \\ &= \eta_0 \{ 6(\alpha_2 - 1) \mathcal{J}_2(\mu) + \sum_{n=3}^{\infty} (4n - 2) \alpha_n \mathcal{J}_n(\mu) \} \\ &= \eta_1 \sum_{n=2}^{\infty} (4n - 2) \gamma_n \mathcal{J}_n(\mu), \end{aligned} \quad (3.7)$$

for all  $\mu = \cos \theta$  in  $-1 \leq \mu \leq 1$ . We may now equate coefficients of  $\mathcal{J}_n(\mu)$ , and find  $\alpha_n = \gamma_n = 0$  for  $n \geq 3$  as before, while  $\alpha_2 = (2\eta_0 + 3\eta_1)/(2\eta_0 + 2\eta_1)$ ,  $\gamma_2 = \eta_0/(2\eta_0 + 2\eta_1)$ . Hence

$$C_{D0} = 8(2\eta_0 + 3\eta_1)/R_0(\eta_0 + \eta_1), \quad (3.8)$$

and

$$u_\theta = U\eta_0 \sin \theta / (2\eta_0 + \eta_1) = v_0 \sin \theta, \quad (3.9)$$

on  $r=a$ . As  $\eta_0/\eta_1 \rightarrow \infty$  we recover the previous results for bubbles:  $C_{D0} \rightarrow 16/R_0$  and  $v_0 \rightarrow \frac{1}{2}U$ . As  $\eta_0/\eta_1 \rightarrow 0$  we recover Stokes's results for rigid spheres:  $C_{D0} \rightarrow 24/R_0$  and  $v_0 \rightarrow 0$ . For intermediate values of  $\eta_0/\eta_1$ ,  $C_{D0}$  and  $v_0$  take intermediate values.

Inside the drop the stream function and hence the velocity components are simple fixed functions of position, multiplied by  $v_0$ . One streamline pattern will therefore serve for any value of  $v_0$ , and it is shown in Fig. 6. It is given by

$$\psi = \frac{1}{2}v_0[(r^4/a^2) - r^2]\sin^2 \theta \leq 0 \quad (3.10)$$

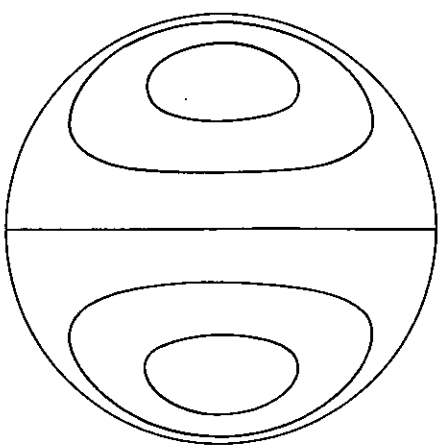


FIG. 6. Streamline pattern inside Hill's spherical vortex.

inside the drop. The flow goes round the surface and back up the middle. The maximum speed is  $v_0$  at the equator and the center, and there is a stagnation ring at  $r = a/\sqrt{2}$ ,  $\theta = \frac{1}{2}\pi$ . This flow pattern was discovered by Hill (1894) as a solution of the equations of inviscid motion; it satisfies the Navier-Stokes equations exactly for any value of the Reynolds number if the boundary conditions are suitable. So does Hill's (1894) spheroidal vortex whose stream function is

$$\psi = Ar^2 \sin^2 \theta (Br^2 \cos^2 \theta + Cr^2 \sin^2 \theta - 1),$$

where  $A$ ,  $B$ ,  $C$  are constants. Both vortices appear below in the theory for high Reynolds numbers. The internal motion has been elegantly observed by Tyrolier *et al.* (1971) and its general features confirmed, although their Reynolds numbers were not small enough to make the theory strictly applicable.

The theory above holds only in the Stokes flow limit  $R_0 \rightarrow 0$ . Higher

terms in the expansion for small  $R_0$  were given by Taylor and Acrivos (1964). We quote here their result for  $R_0 C_{D0}$ , but only to order  $R_0$ :

$$R_0 C_{D0} = \frac{8(2\eta_0 + 3\eta_1)}{\eta_0 + \eta_1} \left( 1 + \frac{R_0(2\eta_0 + 3\eta_1)}{16(\eta_0 + \eta_1)} + O(R_0^2 \ln R_0) + O(W_0) \right). \quad (3.11)$$

Taylor and Acrivos also gave the coefficients of  $R_0^2 \ln R_0$  and  $W_0$ , but not that of  $R_0^2$  which often contributes to  $R_0 C_{D0}$  to the same order. The practical value of these higher terms is in any case disputable for solid spheres (see Chester and Breach, 1969; Pruppacher *et al.*, 1970) and we have no reason to believe the situation is better for fluid spheres. To take many terms of a divergent asymptotic series only gives a close approximation to its sum very near the point where a small number of terms would be adequate.

The shape of the drop was also investigated by Taylor and Acrivos. To leading order, the axis ratio  $\chi$  is given by

$$\begin{aligned} \chi - 1 = & \frac{3W_0}{16(\kappa + 1)^3} \left[ \left( \frac{81}{80} \kappa^3 + \frac{57}{20} \kappa^2 + \frac{103}{40} \kappa + \frac{3}{4} \right) - \frac{\rho_1 - \rho_0}{12\rho_0} (\kappa + 1) \right] \\ & + O(W_0 R_0) + O(W_0^2 R_0^{-1}), \end{aligned} \quad (3.12)$$

where  $\kappa = \eta_1/\eta_0$ . The drop is, to first order, a spheroid, but it may be either prolate or oblate, unlike a bubble. Prolate (elongated) shapes require the inner fluid to be the denser, and either less viscous than the outer fluid, or else very little more. Liquid drops in gases, for example, are normally oblate, as are mercury drops in water. In the limit  $\kappa \rightarrow \infty$  (drop behaving like a solid sphere),  $R_0 C_{D0} \rightarrow 24(1 + \frac{3}{8}R_0)$  and  $\chi - 1 \rightarrow (243/1280)W_0 \doteq 0.190W_0$ . As  $\chi - 1 \doteq 0.156W_0$  for a gas bubble, the shape is not very sensitive to the interior viscosity if the drop rises and so  $\rho_1 < \rho_0$ .

## 2. High Reynolds Number

If the Reynolds number is large, the analogy between drop and bubble motion is less close than for small  $R_0$ . Internal circulation cannot be neglected for drops, and it brings fluid particles repeatedly around closed loops in steady motion. We must therefore impose the condition that the circulation density  $\Omega$  of each fluid particle returns to its original value on completing the path. Inside the drop and away from the thin boundary layers, that requires  $\Omega$  to be constant if  $R_0$  is large, by Prandtl's (1905) and Batchelor's (1956) theorem.

But if  $\Omega$  is constant inside a sphere the flow must be Hill's spherical vortex (Eq. 3.10), with surface velocity,  $v_1 \sin \theta = (2\Omega a^2 \sin \theta)/5$ . We

therefore envisage the motion of the drop as follows, as it starts from rest. Initially there is no motion inside the drop ( $\psi = \Omega = 0$ ), and irrotational flow with surface velocity  $v_0 \sin \theta = \frac{2}{5}U \sin \theta$  outside. A boundary layer must develop around the surface because of this velocity discontinuity, and the circulation density  $\Omega$  within it will be carried along with the fluid and diffused across streamlines. The beginning of this process is described by Sumner and Moore (1969), who gave the first two terms of an expansion in powers of the time. But the boundary layer cannot remain a transition region between irrotational flow and none. The circulation density in the layer must be of order  $U/(\delta a)$  initially both inside and outside the surface if  $\eta_0$  and  $\eta_1$  are of the same order and the surface tension is constant, and  $\delta$  is the boundary layer thickness.  $\Omega$  will then diffuse both inwards and outwards until in a steady state reached after a time  $O(a^2/\nu)$  it has the same order of magnitude throughout the interior, the boundary layer, and the wake. In the interior it is then of order  $v_1/a^2$  and in the boundary layer  $(v_0 - v_1)/(\delta a)$ , and so

$$v_0 - v_1 = O(v_0 \delta a/a^2) = O(v_1 \delta/a) \ll v_1, \quad (3.13)$$

if the Reynolds number is high.

To a first, inviscid approximation we may take  $v_0 = v_1$  if  $R_0$  is high, the flow steady, the drop spherical, the surface tension constant, and the interior viscosity of the same order as the exterior. Sumner and Moore (1969) argue against this conclusion, but prove only that denying any of the assumptions invalidates it. A separate question is whether the assumptions can all be true for real drops in real fluids. We investigate this more fully below; the answer is that they can, to a good approximation, but only for a restricted class of drops.

The importance of spherical shape to the argument is interesting. It enables the tangential velocity to be continuous across the surface (as Hill realized in 1894), unlike any other known simply-connected closed surface. No proof has ever been given that other such surfaces do not exist, however. Recently Fraenkel (1970) suggested that doubly-connected ones do. He found a one-parameter family of toroidal vortices with  $\Omega$  constant inside, irrotational flow outside, and velocity continuous everywhere.

Having arrived at a velocity distribution which is continuous across the surface of the drop for the limiting case  $\sigma \rightarrow \infty$ ,  $R_0 \rightarrow \infty$  (in that order), we can now use the methods described for spherical bubbles in Section II, C, 2 to analyze the boundary layers. As in the case of bubbles, these layers must exist because the inviscid velocity field does not satisfy the tangential stress condition, and the velocity perturbation is of order  $\delta/a = O(R^{-1/2})$  of the inviscid velocity. But there is a major complication. The boundary layers merge into the rear stagnation regions inside and outside the drop, and the

fluid in them turns through  $90^\circ$  to travel up and down the vertical axis of symmetry. Outside the drop, this fluid forms the upstream end of the wake, but inside it, it travels with very little diffusion of circulation density (see Harper and Moore, 1968) until it rejoins the boundary layer at the front stagnation point (see Fig. 7). The distribution of  $\Omega$  therefore cannot

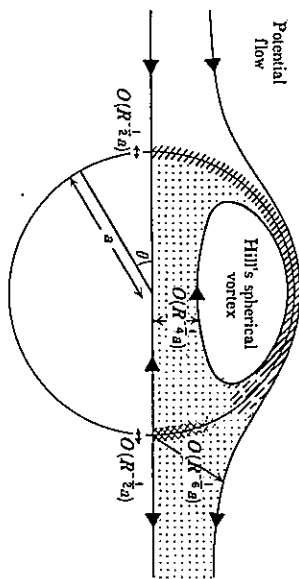


FIG. 7. The form of the boundary layers and wakes of a spherical drop at high Reynolds numbers. Diagonally shaded: the stress-induced viscous boundary layer. Dotted: the essentially inviscid stagnation regions and wakes. Cross-hatched: the inner viscous boundary layer near the rear stagnation point. [From Harper and Moore (1968), by permission of the Cambridge University Press.]

be specified at the front stagnation point without solving the problem of its diffusion in the boundary layer. One has to let  $\Omega$  be some arbitrary function of  $\psi$  inside the drop at the front stagnation point, follow its variation around the surface and back up the middle, and use the condition that the starting and finishing values be the same.

Similar considerations apply (Brignell, 1970) to convective diffusion of a solute. Boundary layer analyses which ignore the coupling between rear and front stagnation regions of a drop must be in error, whether they purport to describe the distribution of circulation density or of solute, unless the effects of internal diffusion are negligible or the motion has been going for such a short time that fluid from the rear stagnation region has not yet reached the front. This fact was realized, though not corrected for in the theory, by Ruckenstein (1967) and Taunton and Lightfoot (1969). It was unfortunately ignored by Winnikow and Chao (1966).

The closed-loop condition on  $\Omega$  was studied by Harper and Moore (1968). It can be written as an integral equation to be solved for a function  $g(z)$  in  $0 \leq z < \infty$ , namely

$$\pi^{-1/2} \int_0^\infty g(z') \{ \exp[-(z-z')^2] + \lambda_a \exp[-(z+z')^2] \} dz' = g(z) + h(z), \quad (3.14)$$

where  $\lambda_a$  is a parameter between  $-1$  and  $1$ , and  $h(z)$  is a known function. Special cases of this equation, which also appears in magnetohydrodynamics and the theory of evolution of comet orbits, have been studied by Hammersley (1961), Kendall (1961), and Stewartson (1968) for  $\lambda_a = 0$ , and by Kochina (1969) for  $\lambda_a = -1$ .

In Harper and Moore's paper,  $z$  is defined to be  $3R_1^{1/2}(a-r)\sin^2\theta/8a$ . This differs from Eq. (2.31) above by the substitution of  $R_1$  for  $R_0$  and by its sign. Both changes make it more convenient for use inside the drop. The values of  $\lambda_a$ ,  $g(z)$ , and  $h(z)$  are

$$\lambda_a = (1 - V')/(1 + V'), \quad (3.15)$$

$$g(z) = \frac{4\sqrt{2}a^2}{3U} \int_z^\infty \Omega'(z') dz', \quad (3.16)$$

$$h(z) = \frac{2\sqrt{2}(2V' + 3)}{V' + 1} \lambda_b \operatorname{ierfc}(z) + \frac{3V' \mu C_1}{V' + 1} \int_{-1}^1 \mu \operatorname{erfc}\left(\frac{2z}{(1+\mu)(2-\mu)^{1/2}}\right) d\mu + \lambda_b g_b(z, \lambda_a) + C g_c(z, \lambda_a), \quad (3.17)$$

say, where  $\Omega'(z)$  is the perturbation circulation density in a stagnation region,  $V' = \eta_0/\eta_1$ ,  $V' = (\eta_0 \rho_0/\eta_1 \rho_1)^{1/2}$ , and  $\lambda_b = (2V' + 3)/(2V' + 3)$ . The expression for  $g_c(z, \lambda_a)$  is simpler than that of Harper and Moore but is equivalent to it.  $C$  in Eq. (3.17) is related to the strength of the Hill's vortex, which is  $1 + (2/R_1)^{1/2}$  times its unperturbed value. One finds  $C$  from the condition that the tangential velocity perturbation in a boundary layer must tend to zero as the layer merges into effectively inviscid flow at its outer limit, i.e.  $g(z) \rightarrow 0$  as  $z \rightarrow \infty$ . Only one value of  $C$  will give that result in Eqs. (3.14) and (3.17), and it is negative. This corresponds to the internal vortex being slowed down by viscosity, which seems reasonable. The values of  $C/\lambda_b$  are within 2% of  $-2.5(2 + V')/V'\sqrt{2}$ . With that approximation the internal circulation is less than that of Hill's classical vortex by a factor of

$$1 + \frac{C\sqrt{2}}{R_1^{1/2}} = 1 - \frac{2.5(2V' + 3)(V' + 2)}{R_0^{1/2}V'(2V' + 3)} \quad (3.18)$$

More precise values of  $C/\lambda_b$  will be found in Table 3, with data on the drag.

With that major complication of allowing for recirculation out of the way, there is now a minor one to be considered. The theory of the stagnation regions predicts velocity discontinuities of order  $UR_1^{-1/3}$  developing at

distances of order  $aR_0^{-1/6}$  from the stagnation points. Such discontinuities in an inviscid model imply viscous boundary layers in the real flow. Near the rear stagnation point this layer develops after the main viscous layer has died out, but it turns out to be of little dynamical significance. Near the

TABLE 3  
DRAG FUNCTIONS FOR SPHERICAL BUBBLES<sup>a</sup>

$V'$	0.2	0.5	1.0	2.0	5.0	$\infty$
$3\lambda_a$	2	1	0	-1	-2	-3
$c_1$	0.0275	0.0935	0.177	0.262	0.335	0.390
$c_2$	8.89	7.56	6.15	5.15	4.22	3.56
$c_3$	-9.72	-9.00	-8.22	-7.41	-6.59	-5.77
$C/\lambda_b$	-19.86	-8.900	-5.282	-3.500	-2.452	-1.772

<sup>a</sup> The second-order terms  $c_1, c_2, c_3$  in Eq. (3.18) for the drag coefficient, and the internal flow perturbation parameter  $C/\lambda_b$ , as functions of  $\lambda_a$  or of  $V'$ , copied from Harper and Moore (1968) by permission of the Cambridge University Press.

front it merges into the main layer. It does not appreciably affect Eq. (3.14) but it does contain viscous dissipation of energy at a rate sufficient to add a term  $O(R_0^{-3/2} \ln R_0)$  to the drag coefficient. The other terms in the drag are calculated from the viscous dissipation in the irrotational flow, the internal vortex, the boundary layers, and the wake as for bubbles, and the final result is

$$C_{D0} = \frac{48}{R_0} \left\{ 1 + \frac{3}{2V} + \frac{\lambda_b(V' + 1)}{R_0^{1/2}V} \left[ \frac{\lambda_b c_1(\lambda_a) \ln R_0}{V} + \frac{\lambda_b(1 + V') c_2(\lambda_a)}{V} + \left( 1 + \frac{3}{2V'} \right) c_3(\lambda_a) \right] \right\}, \quad (3.19)$$

where  $c_1, c_2$ , and  $c_3$  are functions of  $\lambda_a$  given in Table 3. The approximations made near stagnation points have the effect on  $C_{D0}$  of producing errors of the same order as the logarithmic term (which is, fortunately, small). It is therefore worthwhile when comparing the theory with experiments, or predicting drop velocities, to do the calculation both with and without that term.

Such an elaborate theory would not be worth using if it did not agree better with experiments than the available alternatives. It does in carefully

purified liquids, provided that  $M_0$  is low enough for drops to remain nearly spherical up to Reynolds numbers of several hundred and provided that the calculated perturbations are reasonably small. The values of  $C_{D0}$  then come within 20% of the experimental data, whereas  $C_{D0}$  for a rigid sphere is a factor of 2 too high and Winnikow and Chao's (1966) oversimple theory is a factor of 2 or 3 too low. The experiments in question were done by Licht and Narasimhamurti (1955), Elzinga and Banchero (1961), Winnikow and Chao (1966), and Thorsen *et al.* (1968). Graphs of  $C_{D0}$  against  $R$  plotted logarithmically on both axes are presented in Fig. 8. The curves are generally similar to those for bubbles in low- $M_0$  liquids, except for two liquids in which there was a sharp break in the curves at about  $R_0 = 400$ , due probably to surface contamination.

Agreement between experiment and theory is worse than for bubbles in general, although it is better than for bubbles in water. All the drop experiments had water as continuous phase, except one which had it as dispersed phase. Perturbations predicted in the theory are often larger fractions of the first-order terms than for bubbles, especially if the dispersed phase is the more viscous; if  $\eta_1 > 2\eta_0$  the theory is unlikely to be applicable. But Sumner and Moore (1969) exaggerate when they suggest that it is useless whenever  $\eta_1$  is of the same order as  $\eta_0$ .

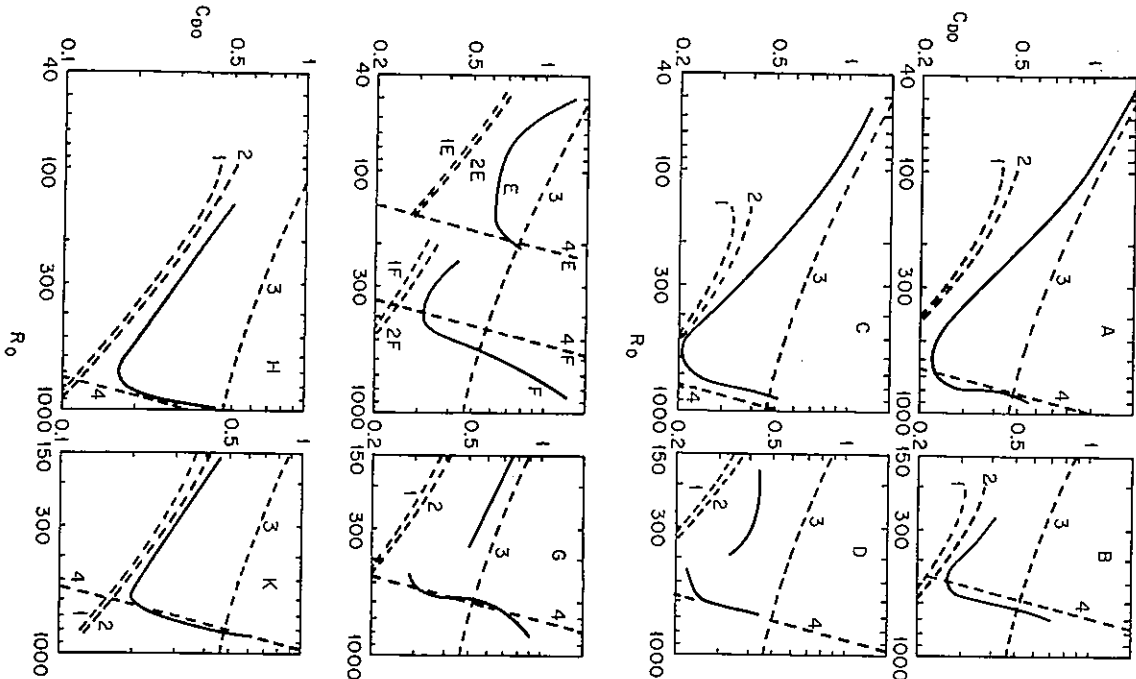
The theory is also inapplicable if the first-order drag coefficient  $48(1 + 3/2V)/R_0$  is larger than that of a rigid sphere at the same  $R_0$ , or if the predicted internal circulation is less than about half of its value in the inviscid theory (see Eq. 3.18). One then gets a better result by assuming the drop to behave as if rigid.

### C. DISTORTIONS FROM SPHERICITY

If  $R_0$  is high enough, drops, like bubbles, will not be spherical. Experimentally, the effects on drops and bubbles are rather similar; see Winnikow and Chao (1966) and Thorsen *et al.* (1968). As  $R_0$  increases  $C_{D0}$  passes a minimum value and then increases; at slightly higher  $R_0$  the drops begin to oscillate (either sideways like bubbles or oblate-to-prolate while rising vertically). Then, if it was initially well below the solid sphere value,  $C_{D0}$  becomes proportional to  $R_0^4$ , as  $W_0$  is constant at about 4 (making  $C_{D0} \approx M_0 R_0^{4/48}$ ) until about  $C_{D0} = 1$ . Beyond that value  $C_{D0}$  rises rather less steeply, but the curves do not level off to a constant value as they do for bubbles. Oscillating falling drops emitted from nozzles are so much less stable than rising bubbles released from dumping cups that they break up when  $W_0$  is of order 10 (see Lane and Green, 1956). It is a pity that no data seem to be available for rising drops in low- $M_0$  fluids at high Weber

numbers nor for drops released from dumping cups. (Bubbles from nozzles may also break up.)

One might hope that a theory like that of Moore (1965) could account for the deformations of drops as successfully as it has for bubbles. Unfortunately, the flow past a spheroid can never be slightly perturbed from a condition of irrotational outside and constant  $\Omega$  inside unless the shape is



very close to a sphere. The reason, given by Hill (1894), is that the tangential velocity has a discontinuity across the surface which increases with the distortion. For very flattened spheroids the form of the discontinuities is sketched in Fig. 9. Outside the surface the irrotational velocity is greatest at the equator, but inside it the greatest velocities in Hill's (1894) spheroidal vortex occur at a finite fraction of the radius. In the cylindrical polar coordinates ( $m, s$ ) shown in Fig. 9, the velocity just inside the very flattened spheroid is approximately  $\omega s = \Omega m s \propto m s$ , where  $\omega$  is the vorticity, and  $m s$  is a maximum where the eccentric angle is  $\frac{1}{2}\pi$ , i.e. at  $1/\sqrt{2}$  of the distance from the axis to the equator. Consequently, the boundary layer around the surface contains velocity variations of the same order as the velocity itself, and its theory would be as complicated as that of the boundary layer on a solid body. It does not seem to have been developed, and so the shapes of drops can be accounted for only qualitatively.

Falling drops tend to be of the shape shown in Fig. 10, with the leading surface flatter than the trailing (Lane and Green, 1956; Winnikow and

FIG. 8. Drag coefficients plotted against Reynolds numbers for liquid drops. Experimental curves are drawn solid, theoretical curves dotted. Curves 1 and 2: Harper and Moore's theory (1968) without and with the logarithmic term. Curve 3: rigid spheres. Curve 4: Weber number  $We = 4$ .

System	$M_0$	Dispersed phase	Continuous phase	Reference
A	$5.1 \times 10^{-11}$	Carbon tetrachloride	Water	Thorsen <i>et al.</i> (1968)
B	$2.2 \times 10^{-10}$	Ethylene bromide	Water	Thorsen <i>et al.</i> (1968)
C	$3.1 \times 10^{-11}$	<i>o</i> -dichlorobenzene	Water	Thorsen <i>et al.</i> (1968)
D	$9.1 \times 10^{-11}$	Ethyl bromide	Water	Thorsen <i>et al.</i> (1968)
E	$2.55 \times 10^{-6}$	Water	Finol	Elzinga and Bancho (1968)
F	$7.1 \times 10^{-10}$	Ethyl chloroacetate	Water	Licht and Narasimhamurthy (1961)
G	$1.9 \times 10^{-10}$	Methylene bromide	Water	Thorsen <i>et al.</i> (1968)
H	$1.7 \times 10^{-11}$	Chlorobenzene	Water	Winnikow and Chao (1966)
K	$5.8 \times 10^{-11}$	Bromobenzene	Water	Winnikow and Chao (1966)

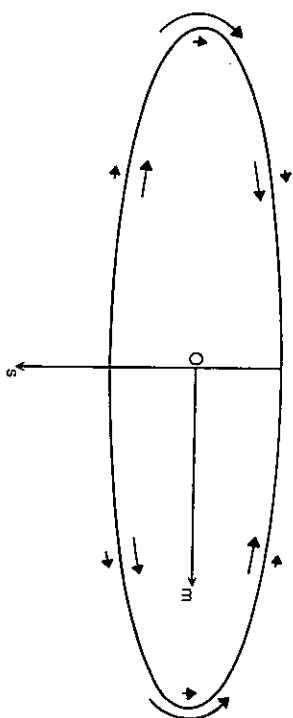


FIG. 9. Schematic indication of velocity variations around the surface of a falling spheroidal drop when very oblate. (Potential flow outside, Hill's spheroidal vortex inside.)

Chao, 1966). This is the opposite way round to bubbles. It seems that the high dynamic pressure near the front stagnation point A pushes it inwards, and surface tension is less impeded than it is for bubbles in its tendency to make the rear surface spherical because the density difference between inner and outer fluids is smaller in the experiments which have been reported,

Shoemaker and Marc de Chazal (1969) studied drops rising in high- $M_0$  fluids at high Weber numbers. They found skirts like those behind some bubbles (Section II, E, 3), and also reentrant "dimples" in the rear stagnation regions. So did Thomson and Newall (1885), for falling drops.

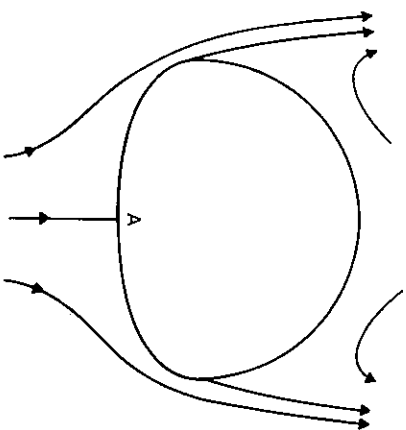


FIG. 10. A typical shape for a distorted falling drop, after Lane and Green (1956), with flow pattern sketched.

## IV. Surface Activity

### A. INTRODUCTION

It will be obvious to anyone familiar with the literature that the experimental data cited above as agreeing with theory are a very small fraction of those which have been published. Experimental liquids (especially water) are very easily contaminated with substances which lower the surface tension by an amount depending on the concentration. Fluid motions at the surface are then retarded, by the following mechanism. If the motion expands an element of area at the surface, a given amount of surfactant will have more surface to occupy (until diffusion restores equilibrium), the surface concentration will fall, and the surface tension will rise. This causes a tangential stress tending to drag fluid in along the surface towards the element of area, which opposes the original motion. Similarly contractions of elements of surface are also opposed.

### B. SURFACE CONCENTRATIONS

Although there are several different ways to define surface concentrations (see Defay *et al.*, 1966; Adam, 1968), most authors do not take the trouble to show that the same definition is being used in their equations for surface tension changes and conservation of mass of surfactant. This can be done by using Guggenheim's (1949) surface model and Landau and Lifshitz's (1959) theory of convective diffusion. The differences between the definitions are important for weakly surface-active solutes, such as ethyl alcohol in water.

We shall use the "continuum approximation," assuming quantities to vary continuously with position and ignoring molecular fluctuations, and we also assume that the relations between thermodynamical variables which hold at equilibrium remain good approximations for individual "infinitesimal" fluid elements, even when the system as a whole is in motion and its state varies from place to place. In this context, "infinitesimal" means "much smaller than macroscopic length-scales of variation, such as boundary-layer thicknesses, but much larger than the distances between molecules or their mean free paths." For a fuller discussion of this approximation, see Lighthill's Chapter I in Rosenhead (1963).

We follow Guggenheim (1949) in ignoring effects of curvature of the interface. These can be allowed for (see Defay *et al.*, 1966; Melrose, 1968), but they do not significantly modify the argument given below except for really minute bubbles or drops. The corrections become important at radii

of curvature of about  $1\ \mu\text{m}$  (apart from the Young-Laplace pressure difference across the surface which may matter mechanically whenever the radius is less than  $1\ \text{cm}$  or thereabouts, but which has little effect on the surface thermodynamics at such large radii).

The Gibbs-Duhem equation connecting changes in surfactant concentration and surface tension may be derived as follows. Let us indicate the bulk phases as before by subscripts 0 and 1, and let phase  $i$  be a solution of surfactant (chemical component number 2) in a solvent (component number  $i$ ). Let the mole fraction of surfactant be  $x_i$ , i.e. in a volume of phase  $i$  which contains  $k_i$  moles altogether, there are  $k_i x_i$  moles of component 2 and  $k_i(1 - x_i)$  moles of component  $i$ . Throughout this section,  $i = 0$  or  $1$ . To simplify the algebra we suppose that there are only these three components in the system, that none of them associates, dissociates, or reacts chemically with another, and that components 0 and 1 are mutually insoluble. (Otherwise there would be at least three different components in one or both phases.)

On each side of the interface and parallel to it, imagine planes drawn in the bulk phases, a distance  $l$  apart (Fig. 11). Suppose that  $l$  is large enough for conditions in each phase at its dividing plane to be uniform and unaffected by the presence of the other phase. Except in dilute ionic solutions  $l$  need only be a few molecular lengths; but  $l$  in an ionic solution must be several times the mean thickness of the double layer, which is  $0.3c^{-1/2}\text{nm}$  if  $c$  is the concentration of a dilute uni-univalent solute in  $\text{mol dm}^{-3}$  (see Parsons, 1954; J. T. Davies and Rideal, 1963). Ionic solutions, of course, require at least three chemical components to be considered in the same phase: positive and negative ions and bulk solvent. Their general theory is beyond the scope of this article.

The material between the two dividing planes (see Fig. 11) forms the

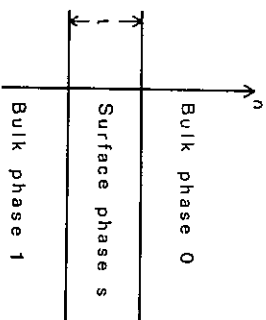


Fig. 11. Diagram of a fluid interface, showing the conventions for numbering phases and the direction of the normal. Bulk phase 0: component 2 dissolved in component 0. Surface "phase"  $s$ : all three components. Bulk phase 1: component 2 dissolved in component 1.

"surface phase" which we indicate by a subscript  $s$ . Unlike the bulk phases it is not even approximately homogeneous, and many of its properties depend on the value of  $l$  and the exact position within it of the true phase boundary. We shall be concerned in our final equations only with quantities independent of these geometrical parameters.

If the number of moles of component  $i$  ( $i = 0, 1$ , or  $2$ ) and the total entropy in area  $A$  of the surface phase are respectively  $n_{si}$  and  $S_s$ , let us define the surface concentration  $\Gamma_i$  and entropy per unit area  $s_s$  by

$$\Gamma_i = n_{si}/A, \quad (4.1)$$

$$s_s = S_s/A. \quad (4.2)$$

Guggenheim (1949) obtains the Gibbs-Duhem equation relating infinitesimal changes in intensive variables in the surface phase as

$$s_s dT - l dP + d\sigma + \sum_{i=0}^2 \Gamma_i d\mu_i = 0, \quad (4.3)$$

in our notation, where  $T$ ,  $P$ ,  $\sigma$ ,  $\mu_i$  are the temperature, pressure, surface tension, and the chemical potential of component  $i$ , and where we imagine infinitesimal changes in these quantities to occur with the dividing planes fixed. The corresponding equations for the two bulk phases are (Guggenheim, 1949)

$$x_0 d\mu_2 + (1 - x_0) d\mu_0 = 0, \quad (4.4)$$

$$x_1 d\mu_2 + (1 - x_1) d\mu_1 = 0, \quad (4.5)$$

if temperature changes are negligible. If  $l$  is so small that  $l dP \ll d\sigma$ , and if temperature changes are negligible, two terms in (4.3) disappear and the remaining ones give

$$-\left(\frac{\partial\sigma}{\partial\mu_2}\right)_T = \Gamma_2 - \Gamma_0 \frac{x_0}{1 - x_0} - \Gamma_1 \frac{x_1}{1 - x_1} = \Gamma, \quad (4.6)$$

say, when we substitute for  $d\mu_1$  and  $d\mu_0$  from (4.4) and (4.5), and use the fact that chemical potentials are uniform throughout the system. In a real system which may have large changes of  $\mu_i$  over large distances, we must choose  $l$  so small that the  $\mu_i$  are sensibly constant across the surface phase, having the same values at each dividing plane. Unless  $\mu_i$  can have discontinuities, this requires only that  $l$  be much smaller than the diffusion boundary layer thickness. The question of possible discontinuities in  $\mu_i$  is important and is taken up in Section IV, I below. For the moment we assume that they do not appear.

The quantity  $\Gamma$  defined by Eq. (4.6) is the "surface excess" of component 2, and is unaffected by movement of the imaginary dividing planes,

unlike the three  $\Gamma_i$ . This can be seen either from the definitions of the  $\Gamma_i$  and of mole fractions, or from the invariance of the left-hand side of (4.6) under changes of position of the dividing planes. Physically,  $\Gamma_i$  is the amount of surfactant between the dividing planes, less the amount which would have been there if each bulk phase had contained unaltered right up to the plane of separation.

Further progress depends on knowledge of  $\mu_i$  as a function of  $\Gamma$  or  $x_i$ . Let us suppose that the surfactant is dilute enough for it to be an ideal solution with  $x_i \ll 1$  in each bulk phase and a "gaseous film" (see Adam, 1968) at the interface, i.e.

$$\begin{aligned}\mu_2 &= \bar{\mu}_{20} + R_g T \ln x_0 \\ &= \bar{\mu}_{21} + R_g T \ln x_1 \\ &= R_g T \ln(\Gamma/\bar{\Gamma}),\end{aligned}\quad (4.7)$$

where  $\bar{\mu}_{20}$ ,  $\bar{\mu}_{21}$ , and  $\bar{\Gamma}$  depend only on  $T$ ,  $p$ , and the chemical natures of the three components, and  $R_g$  is the gas constant. Then  $x_0 \propto x_1 \propto \Gamma$ , and Eq. (4.6) gives

$$\Pi = c_p - \sigma = R_g T \Gamma, \quad (4.8)$$

where  $c_p$  is the interfacial tension between pure components 0 and 1,  $\sigma$  the tension when surface excess of component 2 is adsorbed on the interface, and  $\Pi$  is the "surface pressure."

### C. DIFFUSION BOUNDARY CONDITIONS

Mole fractions are convenient units for chemistry, but if one has to deal also with dynamics and diffusion it is helpful to use mass fractions  $w_0$ ,  $w_1$  in the two phases. These are analogous to the mole fractions  $x_0$ ,  $x_1$ , being the ratio of the mass of component 2 to the total mass of fluid in a given volume element. Landau and Lifshitz (1959) refer to a mass fraction as a concentration,  $c$ , but we follow the physical chemists' convention (McGlashan, 1968) of using this name and the symbol  $c_i$  for the amount of component 2 measured in moles per unit volume of phase  $i$ . If the molar masses of the three components are  $m_0$ ,  $m_1$ , and  $m_2$ , and the total density of phase  $i$  is  $\rho_i$ , we have

$$\frac{m_2 c_i}{\rho_i} = w_i = \frac{m_2 x_i}{m_i(1 - x_i) + m_2 x_i} \doteq \frac{m_2 x_i}{m_i}, \quad (4.9)$$

where the last form on the right-hand side is an approximation for dilute solutions. In the bulk phase  $i$ , the mass flux of component 2 is  $\rho_i w_i \mathbf{u}_i$  by

convection with the fluid and, to a dilute solution approximation (Landau and Lifshitz, 1959),

$$\mathbf{j}_i = -\rho_i D_i \nabla w_i \doteq -m_2 D_i \nabla c_i \quad (4.10)$$

by diffusion, where  $\mathbf{u}_i$  is the velocity vector (= momentum of unit mass),  $\mathbf{j}_i$  the diffusion flux, and  $D_i$  the diffusivity. With these definitions of density and velocity, the usual equation of continuity and the Navier-Stokes equation hold in the bulk phase. Equation (4.10) for the diffusion flux holds, as Landau and Lifshitz explain, in the absence of thermal diffusion and barodiffusion, and then conservation of mass of solute gives

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{j}_i + D_i \nabla c_i) = D_i \nabla^2 c_i, \quad (4.11)$$

if we can ignore the variations of  $\rho_i$  and  $D_i$  with concentration. Whether variations of  $\rho_i$  are important or not depends on the type of fluid motion under discussion. They usually do not matter for bubbles and drops, where they are much smaller than the density difference between the two bulk phases. They can, of course, be the cause of fluid motion in a system which would otherwise be in mechanical equilibrium, and then they must be taken into account.

We have not yet used the condition that mass of each chemical component must be conserved. Let the two dividing surfaces of Fig. 11 be fixed relative to the interface, so close to it that the tangential velocity  $\mathbf{u}_s$  is effectively the same at all points between them. (This condition is usually less restrictive than the one that the chemical potentials be effectively uniform across the "surface phase.") Let the normal velocity components in the two phases at the dividing surfaces be  $u_{n0}$ ,  $u_{n1}$ , both measured positively if in the direction of the vector from phase 1 to phase 0 in Fig. 11. As Levich (1962) pointed out, one cannot assume that the tangential mass flux  $\mathbf{j}_{si}$  of component  $i$  is the same as its convective part  $\Gamma_i m_i \mathbf{u}_s$ , and we shall follow his course of taking the next simplest assumption. This is to suppose that  $\mathbf{j}_{si} - \Gamma_i m_i \mathbf{u}_s$  is linearly dependent on the surface concentration gradients. Because any one of the  $\Gamma_i$  determines the other two if the temperature, pressure, and dividing surfaces are fixed, by the phase rule, we may use the surface gradient (Weatherburn, 1927; Scriven, 1960) of surface excess,  $\nabla_s \Gamma$ , to specify the surface concentration gradients. Then

$$\mathbf{j}_{si} = m_i(\Gamma_i \mathbf{u}_s - D_{si} \nabla_s \Gamma), \quad (4.12)$$

where the  $D_{si}$  are three constants of proportionality with the dimensions ( $L^2 T^{-1}$ ) of diffusivity. At most two of them can be independent, for

$$\sum_{i=0}^2 \mathbf{j}_{si} = \left( \sum_{i=0}^2 m_i \Gamma_i \right) \mathbf{u}_s = \left( \sum_{i=0}^2 m_i \Gamma_i \right) \mathbf{u}_s - \left( \sum_{i=0}^2 m_i D_{si} \right) \nabla_s \Gamma, \quad (4.13)$$



where the first part of (4.13) comes from the definition of total mass flux and the second from (4.12). Hence

$$\sum_{i=0}^2 m_i D_{si} = 0. \quad (4.14)$$

By considering the total mass flux of the three components into an element of surface phase, we may now obtain

$$\frac{\partial \Gamma_0}{\partial t} + \text{div}_s \mathbf{j}_{s0} = \frac{1}{m_0} \left( -\rho_0 (1 - w_0) u_{n0} - \rho_0 D_0 \frac{\partial w_0}{\partial n} \right), \quad (4.15)$$

$$\frac{\partial \Gamma_1}{\partial t} + \text{div}_s \mathbf{j}_{s1} = \frac{1}{m_1} \left( \rho_1 (1 - w_1) u_{n1} + \rho_1 D_1 \frac{\partial w_1}{\partial n} \right), \quad (4.16)$$

$$\frac{\partial \Gamma_2}{\partial t} + \text{div}_s \mathbf{j}_{s2} = \frac{1}{m_2} \left( -\rho_0 w_0 u_{n0} + \rho_1 w_1 u_{n1} + \rho_0 D_0 \frac{\partial w_0}{\partial n} - \rho_1 D_1 \frac{\partial w_1}{\partial n} \right), \quad (4.17)$$

where  $\text{div}_s \mathbf{j}_{si}$  denotes the surface divergence of the vector  $\mathbf{j}_{si}$  (Weatherburn, 1927); i.e. Scriven's (1960)  $\nabla_s \cdot \mathbf{j}_{si}$ . Because the surface tension depends on  $\Gamma$ , we must take a linear combination of the above equations of the form

$$(4.17) - \frac{x_0}{1 - x_0} (4.15) - \frac{x_1}{1 - x_1} (4.16),$$

and we obtain

$$\begin{aligned} \frac{\partial \Gamma}{\partial t} + \text{div}_s (\Gamma \mathbf{u}_s) + \sum_{i=0}^1 \frac{\Gamma_i m_i}{m_2} \left( \frac{\partial}{\partial t} + \mathbf{u}_s \cdot \nabla \right) \left( \frac{w_i}{1 - w_i} \right) \\ = - \sum_{i=0}^1 \left( \frac{1}{m_2 (1 - x_i)} \text{div}_s (D_{si} m_i \nabla_s \Gamma) + \frac{(-1)^i \rho_i D_i}{m_2 (1 - w_i)} \frac{\partial w_i}{\partial n} \right). \end{aligned} \quad (4.18)$$

This equation simplifies, if we use the bulk diffusion equation (4.13), the dilute-solution approximations  $w_i \ll 1$ ,  $x_i \ll 1$ ,  $D_i$  constant, and  $D_{si}$  constant, and the definition  $c_i = w_i \rho_i / m_2$ , to

$$\begin{aligned} \frac{\partial \Gamma}{\partial t} + \text{div}_s (\Gamma \mathbf{u}_s) + \sum_{i=0}^1 \frac{\Gamma_i m_i}{m_2} \left( D_i \nabla^2 w_i - u_{ni} \frac{\partial w_i}{\partial n} \right) \\ = D_{s2} \nabla_s^2 \Gamma + \sum_{i=0}^1 (-1)^i D_i \frac{\partial c_i}{\partial n}. \end{aligned} \quad (4.19)$$

If we assume that  $l$ , the thickness of the interfacial region, is much smaller than the diffusion boundary layer thickness, then the terms in  $\Gamma$ , in (4.19) are negligible. Here the boundary layer thickness is best thought of as the

shorter of the distances in the  $n$  direction over which  $\partial w_0 / \partial n$  and  $\partial w_1 / \partial n$  change by significant fractions of themselves. If  $l$  is not this small, then using it as a thickness of a surface phase is unhelpful. We shall therefore neglect those terms in  $\Gamma$ , and recover Levich's (1962) surface condition

$$\frac{\partial \Gamma}{\partial t} + \text{div}_s (\Gamma \mathbf{u}_s) = D_s \nabla_s^2 \Gamma + D_0 \frac{\partial c_0}{\partial n} - D_1 \frac{\partial c_1}{\partial n} \quad (4.20)$$

on writing  $D_{s2} = D_s$ , but we have used a definition of  $\Gamma$  and hence of  $D_s$  more explicit than his.

Equation (4.20) now appears as one of the two boundary conditions interconnecting the concentration and velocity fields at an interface between surfactant solutions. The other condition derives from the fact that for small  $l$  there is so little mass in the surface phase that the forces on it can be taken to be in equilibrium. The normal component gives the Young-Laplace relation between normal stresses, surface tension, and curvature (see Section II, C, 1 and Eq. 2.44), and the tangential component gives the condition we seek, in the form (Scriven, 1960)

$$\nabla_s \sigma = -\nabla_s \Pi = p_{ns1} - p_{ns0} \quad (4.21)$$

where  $p_{nsi}$  is the shear stress at the surface in phase  $i$ . The relation between (4.21) and concentrations is clear from Eqs. (4.7)-(4.9), which we may use to write

$$\nabla_s \sigma = -(R_g T \Gamma / c_i) \nabla_s c_i = -R_g T \nabla_s \Gamma, \quad \text{for } i = 0, 1, \quad (4.22)$$

for ideal dilute solutions.

The thermodynamics of ideal solutions gives no information about the distribution coefficients  $c_0/c_1$  and  $\Gamma/c_i$  except that they are constants relating the concentrations of the solute in the two bulk phases and the surface. Their values are determined by the chemical natures of the three components. We define "adsorption depths"  $h_0$ ,  $h_1$  by

$$h_i = \Gamma / c_i, \quad \text{for } i = 0, 1; \quad (4.23)$$

they have the dimensions of length because  $\Gamma$  is an amount of substance per unit area and  $c_i$  an amount per unit volume. The depth  $h_i$  of phase  $i$  obviously contains the same amount of dissolved solute (component 2) as is adsorbed on its surface. Numerical values of  $h_i$  cover a very wide range. In water, at an air-water interface,  $h_i$  is of the order of a molecular length for a weakly adsorbed solute like ethyl alcohol  $\text{C}_2\text{H}_5\text{OH}$  [4 nm according to Adam (1968), 7 nm according to Bakker *et al.* (1966)], but for strongly adsorbed substances it is much higher, especially if they are sparingly soluble. [1  $\mu\text{m}$  for sodium dodecyl sulphate,  $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$  (Durham, 1961; Rubin and Jorrie, 1969), 0.3 mm for dodecanol,  $\text{C}_{12}\text{H}_{25}\text{OH}$  (Shinoda

and Nakanishi, 1963).] By Traube's rule (see Adam, 1968),  $h_i$  increases by a factor of about 3 for each additional  $\text{CH}_2$  group in a homologous series of long chain organic compounds. But the values are difficult to determine; discrepancies by nearly a factor of 2 occur for the same substance, as in the two values given above for ethyl alcohol, and the "Traube factor" is sometimes nearer 4 than 3, as in Fig. 7.1 of Defay *et al.* (1966), reporting work of Hommelen on the  $n$ -aliphatic alcohols  $\text{C}_m\text{H}_{2m+1}\text{OH}$  for  $m = 6, 7, 8, 9$ , and 10. Hommelen's solutions, however, were too concentrated to behave as if ideal.

If more than one surfactant is present, but all of them are very dilute, Eq. (4.20) still holds for each unless the rate of chemical change of one into another is comparable with the rate of transfer along or into the surface. Equation (4.22) becomes

$$\begin{aligned} \nabla_s \sigma &= -R_g T \sum_{j=2}^n \frac{\Gamma_j'}{\nabla_s c_{ij}} \\ &= -R_g T \sum_{j=2}^n \nabla_s \Gamma_j', \quad \text{for } i = 0, 1, \end{aligned} \quad (4.24)$$

where  $c_{ij}$  is the concentration of component  $j$  in bulk phase  $i$ , the bulk solutes in phases 0, 1 are components 0, 1 as before, and the surface-active solutes are components 2, 3, ...,  $n$ .  $\Gamma_j'$  is the generalization of  $\Gamma_j$  obtained in the following way. Let  $x_{ij}$  be the mole fraction of component  $j$  in phase  $i$ , so that

$$\sum_{j=0}^n x_{ij} = 0 \quad \text{for } i = 0, 1, \quad (4.25)$$

and in dilute solutions  $x_{00} \doteq 1$ , and  $x_{11} \doteq 1$ . The Gibbs-Duhem equations for the surface and the bulk phases are, at constant temperature and pressure,

$$-d\sigma = \sum_{j=0}^n \Gamma_j d\mu_j, \quad (4.26)$$

$$0 = \sum_{j=0}^n x_{ij} d\mu_j, \quad \text{for } i = 0, 1, \quad (4.27)$$

where  $\mu_j$  is the chemical potential of component  $j$ . On eliminating  $d\mu_0$  and  $d\mu_1$  from Eqs. (4.26) and (4.27) we obtain an equation giving  $-d\sigma$  in terms of  $d\mu_2, d\mu_3, \dots, d\mu_n$ , and define  $\Gamma_j'$  to be the coefficient of  $d\mu_j$  in it. In very dilute solutions

$$\begin{aligned} \Gamma_j' &= -\partial\sigma/\partial\mu_j \\ &\doteq \Gamma_j - x_{0j}\Gamma_0 - x_{1j}\Gamma_1, \quad \text{for } j, k = 2, 3, \dots, n, j \neq k. \end{aligned} \quad (4.28)$$

In an ionic solution this type of analysis is necessary because there must be at least the two oppositely charged ions present together with the solute. Then one has also to use the condition of electrical neutrality in the bulk phases to show that the effective diffusivity  $D_0$  is

$$D_0 = \frac{D^+ D^- (z^+ + z^-)}{z^+ D^+ + z^- D^-}, \quad (4.29)$$

when there are two types of ion with electrovalencies  $z^+$ ,  $z^-$  and diffusivities  $D^+$ ,  $D^-$  (see Deryagin *et al.*, 1959; Levich, 1962). In addition the surface layer as a whole must be electrically neutral although the actual surface is usually charged, so that the immediately subjacent fluid has an excess of ions of the opposite charge. We shall not discuss these "double layers" here (see J. T. Davies and Rideal, 1963; Parsons, 1954), nor the sort of complication which arises with acetic acid at the benzene-water interface, when  $(\text{CH}_3\text{COOH})_2$  and  $\text{CH}_3\text{COOH}$  molecules occur in the benzene, and  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  as well in the water, and reversible reactions occur between the various species. Such behavior is common among organic acids, at air-water or benzene-water interfaces (Glasstone, 1953).

Heat can also be considered as a surfactant, because changes in temperature, like changes in chemical potential, affect the surface tension and give rise to diffusion. One can draw up a list of quantities analogous to one another in the theory (see Harper *et al.*, 1967):  $D_i$  to the heat diffusivity  $K_i = K/\rho_i c_{pi}$ , where  $K_i$  is the heat conductivity and  $c_{pi}$  the specific heat at constant pressure of phase  $i$ ,  $\mu_j$  to  $R_g T$ ,  $\Gamma$  to  $-(1/R_g)(\partial\sigma/\partial T)_{\mu_j}$ ,  $h_i$  to  $-(1/\rho_i c_{pi})(\partial\sigma/\partial T)_{\mu_j}$ , where  $\mu_j$  is the chemical potential. Because its " $h_i$ " is very small (0.037 nm for water at room temperature) the surface effects of heat can usually be ignored in practice unless, of course, they cause the motion, as in some Bénard cells (Pearson, 1958; Scriven and Sternling, 1960, 1964), or are artificially increased as in the work of Young *et al.* (1959) on bubbles held fixed against gravity in a vertical temperature gradient.

Dimensional analysis takes a form in this subject which may be a little unfamiliar. Besides the usual mass  $M$ , length  $L$ , and time  $T$  of mechanics as dimensionally independent variables, we have temperature  $\theta$  and amount of substance  $\tilde{Q}$  (McGlashan, 1968). The unit for  $\tilde{Q}$  in the metric system is the mole. The analogies in the previous paragraph have been altered slightly from those of Harper *et al.* (1967) to make analogous quantities have the same dimensions. We collect the quantities used in this chapter with their dimensions, in Table 4.

TABLE 4

DIMENSIONS OF PHYSICO-CHEMICAL QUANTITIES

$c_i, c_y$	concentration	$QL^{-3}$
$\epsilon_p$	specific heat	$L^2T^{-2}\theta^{-1}$
$D_0, D_a, D_i$	diffusivity	$L^2T^{-1}$
$h_i$	adsorption depth	$L$
$j_i$	volume mass flux	$ML^{-2}T^{-1}$
$j_{si}$	surface mass flux	$ML^{-1}T^{-1}$
$K_i$	heat conductivity	$MLT^{-3}\theta^{-1}$
$m_i$	molar mass	$MO^{-1}$
$n_{si}$	amount of $i$ in surface phase	$Q$
$R_g$	gas constant	$ML^2T^{-2}Q^{-1}\theta^{-1}$
$S_g$	entropy	$ML^2T^{-2}\theta^{-1}$
$s_p$	entropy per unit area	$ML^2T^{-2}\theta^{-1}$
$T$	temperature	$MT^{-2}\theta^{-1}$
$\omega_i$	mass fraction	$\theta$
$x_i$	mole fraction	1
$\Gamma_i, \Gamma_i'$	surface excess	1
$\Gamma_i$	surface phase concentration	$QL^{-2}$
$k_i$	heat diffusivity	$QL^{-2}$
$\mu_i$	chemical potential	$L^2T^{-1}$
$\sigma$	surface tension	$ML^2T^{-2}Q^{-1}$
$\Pi$	surface pressure	$MT^{-2}$

## D. A DROP OR BUBBLE MOVING AT LOW PÉCLET NUMBER

To illustrate the interaction of fluid motion and solute diffusion, let us consider the case of a steadily moving drop which is small enough to be considered spherical and whose Péclet numbers  $Ud/D_i$ ,  $Ud/D_s$  are much smaller than one. Because  $D_i$  is usually much less than  $\nu_i$ , the Reynolds numbers will be small too. Bubbles obey the same theory if  $\eta_i$  is neglected (see Levich, 1962; Harper *et al.* (1967); and Kenning (1969).

The equation of motion is  $D^4\psi = 0$  in each phase (Sections II, C, 1 and III, B, 1), and that of diffusion is  $\nabla^2 c_i = 0$  for  $i = 0, 1$ , if the Péclet numbers are small. The boundary conditions are Eqs. (4.20) to (4.23), together with continuity of velocity at the interface, finiteness of velocity and  $c_i$  at the origin, and uniform limiting values  $U$  and  $c_\infty$  for velocity and  $c_i$  at the infinity. It is convenient to define a fictitious "surface pressure" throughout the space as

$$\Pi = R_g T h_i c_i, \quad (4.30)$$

where  $h_i$  takes its interfacial value everywhere in phase  $i$ . This definition makes  $\Pi$  a harmonic function in each phase and continuous across the

interface  $r = a$ . At the interface it keeps its previous value and meaning, defined in (4.8). The value of  $\Pi$  at infinity,  $\Pi_\infty$ , is a convenient measure of the strength of the solution, being given by

$$\Pi_\infty = R_g T h_0 c_\infty, \quad (4.31)$$

the amount by which the equilibrium interfacial tension between phases 0 and 1 is lowered by the presence of the surfactant. Then

$$\Pi = \Pi_\infty + \sum_{n=0}^{\infty} \epsilon_n \frac{r^n}{a^n} P_n(\mu) \quad (4.32)$$

inside the drop and

$$\Pi = \Pi_\infty + \sum_{n=0}^{\infty} \epsilon_n \frac{a^{n+1}}{r^{n+1}} P_n(\mu) \quad (4.33)$$

outside it, for some set of constants  $\epsilon_n$ , where  $\mu = \cos \theta$ . The surface stress condition (4.21) can be written

$$\epsilon_1 = \frac{3}{2} U [(3 - 2\alpha_2)\eta_1 - 2(\alpha_2 - 1)\eta_0], \quad (4.34)$$

$$\epsilon_n = -(4n + 2)U\alpha_{n+1}(\eta_0 + \eta_1)/n(n + 1) \quad \text{for } n \geq 2, \quad (4.35)$$

if we use Eqs. (3.6) and (3.7), and equate coefficients of  $\mathcal{P}_n(\mu)$ . No information comes from this source about  $\epsilon_0$ , the difference between the surface mean value of  $\Pi$  and  $\Pi_\infty$ . The surface mass balance equation (4.20) becomes

$$U \frac{d}{d\mu} \left\{ \left[ \Pi_\infty + \sum_{n=0}^{\infty} \epsilon_n P_n(\mu) \right] \left[ (3 - 2\alpha_2) \mathcal{P}_2(\mu) - 2 \sum_{n=2}^{\infty} \alpha_n \mathcal{P}_n(\mu) \right] \right\} \\ = \sum_{n=0}^{\infty} \epsilon_n P_n(\mu) \left\{ n(n + 1) \frac{D_s}{a} + (n + 1) \frac{D_0}{h_0} + n \frac{D_1}{h_1} \right\}. \quad (4.36)$$

By integrating this equation from  $\mu = -1$  to  $\mu = 1$  and using the definition of  $\mathcal{P}_n(\mu)$  (Eq. 2.11), it can be shown that  $\epsilon_0 = 0$ . We do not attempt to equate any other coefficients of  $P_n(\mu)$  in the general case. It would require the expansion of  $P_n(\mu) \mathcal{P}_n(\mu)$  in Legendre polynomials, lead to an infinite set of nonlinear equations to solve for the  $\alpha_i$ , and be of spurious physical generality anyway, as we shall see in the discussion following Eq. (4.40). It will appear that in cases likely to arise in real fluids the surface pressure  $\Pi$  is only slightly perturbed from its mean value  $\Pi_\infty$ . With that assumption, to be checked later, we may ignore the term  $\sum_{n=2}^{\infty} \epsilon_n P_n(\mu)$  on the left-hand side of Eq. (4.36) and obtain  $\alpha_{n+1} = \epsilon_n = 0$  for  $n \geq 2$ , while

$$\alpha_2 = R_0 C_{b0}/16 \\ = (2\eta_0 + 3\eta_1 + \Pi_\infty/\nu_D)/(2\eta_0 + 2\eta_1 + 2\Pi_\infty/3\nu_D), \quad (4.37)$$

where the "diffusion velocity"  $v_D$  is defined by

$$v_D = \frac{D_s}{a} + \frac{D_o}{h_o} + \frac{D_1}{2h_1}. \quad (4.38)$$

It is additive over the three routes for diffusion—phase 0, phase 1, and surface—because a given inequality of surface concentration is "smoothed out" by the three "diffusion currents" in parallel. The surface velocity is  $v_o \sin \theta$ , where

$$\begin{aligned} v_o &= U(\frac{3}{2} - \alpha_2) \\ &= U\eta_o/(2\eta_o + 2\eta_1 + 2\Pi_\infty/3v_D), \end{aligned} \quad (4.39)$$

and the surface pressure is  $\Pi_\infty + \epsilon_1 \cos \theta$ , where

$$\begin{aligned} \epsilon_1/\Pi_\infty &= -v_o/v_D \\ &= -U\eta_o/v_D(2\eta_o + 2\eta_1 + 2\Pi_\infty/3v_D). \end{aligned} \quad (4.40)$$

Equation (4.40) shows that for the theory to be valid it is sufficient to require that the two Reynolds and three Péclet numbers,  $Ud/\nu$ ,  $Ud/D_s$ , and  $Ud/D_o$ , be all much less than one, for  $2v_o < U$  and  $v_D > 2D_s/d$ , and so  $|\epsilon_1/\Pi_\infty| < Ud/4D_s \ll 1$ , by hypothesis. Wasserman and Slattery (1969) present a theory in which  $\epsilon_1/\Pi_\infty$  is not small but the Reynolds numbers and two of the Péclet numbers ( $Ud/D_s$ ) are, and they ignore surface diffusion. That part of their work seems unlikely to be a useful generalization unless  $D_s \ll D_o$ , a supposition for which there is no evidence yet.

The dynamical effect of the surfactant on the drag and the surface velocity is effectively to increase the viscosity inside the drop from  $\eta_1$  to  $\eta_1 + \Pi_\infty/3v_D$  and hence bring the motion nearer to that of a solid sphere. Clearly the influence is greater in more concentrated solutions (higher  $\Pi_\infty$ ), but the theory becomes invalid if the concentration is too high. The surface pressure varies from a minimum of  $\Pi_\infty + \epsilon_1$  at the front stagnation point to a maximum of  $\Pi_\infty - \epsilon_1$  at the rear, at least if  $\Pi_\infty > 0$  and the surfactant is positively adsorbed. Some solutes raise the surface tension instead of lowering it, in which case  $\Pi_\infty$ ,  $\Gamma$ ,  $h_1$ , and  $v_D$  are all negative. If so, the solute is never strongly surface-active (see Adam, 1968, Section III.7), and then  $|h_1| \ll a$  for all practical sizes of drops, and surface diffusion can be neglected.

The implications of the theory are easiest to understand for bubbles, where  $\eta_1 \ll \eta_o$  and  $D_1/h_1 \ll D_o/h_o$  (unless the surfactant is volatile). Then  $\Pi_\infty/\eta_o v_D$  reduces for strong surfactants or small bubbles ( $h_o \gg a$ ) to  $\Pi_\infty a/\eta_o D_s$ , and for weak surfactants or large bubbles ( $h_o \ll a$ ) to  $\Pi_\infty h_o/\eta_o D_o$ . For a moderately surface-active substance in water, with  $h_o \doteq 1 \mu\text{m}$  (for example, the dodecyl sulphate ion, or hexanol),

$D_o \doteq 5 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1} = 5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ , and so  $\Pi_\infty h_o/\eta_o D_o = 1$  if  $\Pi_\infty = 0.5 \mu\text{N m}^{-1} = 5 \times 10^{-4} \text{ dyn cm}^{-1}$ . The surface concentration is then  $2 \times 10^{-10} \text{ mol m}^{-2}$  ( $8 \times 10^4$  square Ångström units per molecule) and the bulk concentration  $2 \times 10^{-4} \text{ mol m}^{-3}$ .

Bubble behavior might seem from these figures to provide a good means of experimental research into surface properties of solutions too dilute to measure by other methods, but there is a difficulty. We have assumed the Péclet number to be small. The velocity  $U$  is at least its Stokes law value  $2ga^2/9\nu$ , and so  $Ud/D_o < 1$  only if  $d < 10 \mu\text{m}$ , for the example above. We can therefore apply the present theory in water only for very small bubbles:  $10 \mu\text{m} = 0.01 \text{ mm}$ . The situation is not much better in most other liquids, for  $Ud/D_o \geq ga^2/18D_o\nu_o$ , and the Stokes-Einstein theory of diffusion (see Bird *et al.*, 1960) gives

$$D_o \nu_o = kT/6\pi\rho_o a_m, \quad (4.41)$$

where  $k$  is Boltzmann's constant and  $a_m$  is the radius of a surfactant molecule if it is spherical, or a distance of the order of the molecule's size if not. For a given surfactant, then,  $Ud/D_o \propto d^3\rho_o/T$  if the bubble size and the solute are varied. Larger bubbles can therefore satisfy the conditions of the theory for small Péclet numbers only if the temperature is high, the density low, or the Stokes-Einstein law is not obeyed. There are viscous liquids with that last property, such as Redfield and Houghton's (1965) dextrose solutions in which the diffusivity of carbon dioxide was anomalously high, but carbon dioxide, of course, is not very surface-active.

For drops the conditions are slightly less restrictive, because  $Ud/D_o < |\rho_o - \rho_1|ga^2/12D_o\nu_o\rho$  if we use the fact that

$$U < |\rho_o - \rho_1|ga^2/3\nu_o\rho_o,$$

which is the Rybczynski-Hadamard result for  $\eta_1 = 0$ . The gain is, however, not great. To multiply the permissible value of  $d$  by 10,  $|\rho_o - \rho_1| < 10^{-3}\rho_o$ ; experiments with such small density differences would need elaborate precautions against convection currents.

#### E. A BUBBLE AT LOW REYNOLDS AND HIGH PÉCLET NUMBER

We have seen that bubbles visible to the naked eye are unlikely to obey the requirement of Section IV, D that the Péclet number be small, and so the next simplest case, of low Reynolds and high Péclet numbers, has received a good deal of attention (Deryagin *et al.*, 1959, 1960; Deriaguin and Dukhin, 1961; Dukhin and Deryagin, 1961; Levich, 1962; Griffith, 1962; Dukhin and Buřkov, 1965; Loehiel, 1965; Davis and Acrivos, 1966;

Newman, 1967; Wasserman and Slattery, 1969). Unfortunately some of this work uses unjustified assumptions, and some authors neglect singularities which predict infinite surface excesses at rear stagnation points. Very little has been done for Péclet numbers of order unity except by Wasserman and Slattery (1969), whose numerical method becomes untrustworthy at high Péclet numbers because of those same singularities. All this work ignores transport of surfactant through the interior. To allow for it would involve the difficulties, caused by recirculation of fluid inside the bubble, that we encountered for high Reynolds numbers in Section III,C,2.

For a spherical bubble in steady flow the surface condition (4.20) becomes

$$\frac{\partial}{\partial \theta} (\Pi u_\theta \sin \theta) = D_s \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Pi}{\partial \theta} \right) + \frac{a^2 D_0 \sin \theta}{h_0} \frac{\partial \Pi}{\partial r}, \quad (4.42)$$

in terms of the surface pressure  $\Pi$ , defined on the surface by (4.8) and elsewhere by (4.30).

### 1. *Slightly Contaminated Surface, Weak Surfactant*

Equation (4.42) involves  $\Pi$  and  $u_\theta$ , both of which are unknown in general. This makes the general theory very difficult, and so it is worthwhile to seek special cases of physical interest which are simpler. The first is that in which  $u_\theta$  is very near the value  $v_0 \sin \theta$  given by the Rybczynski-Hadamard theory for a free surface, i.e. the surfactant has had only a slight effect on the motion of the bubble. Equation (4.42) is then linear in its remaining unknown variable  $\Pi$ , but is still complicated. Suppose that the surface diffusion term in (4.42) can be neglected, and that  $\Pi \rightarrow \Pi_\infty$  at a large distance from the bubble. Then, as the Péclet number is high, analysis like that of Section II,C,2 gives

$$4 \frac{\partial \Pi}{\partial x} = \partial^2 \Pi / \partial y^2, \quad (4.43)$$

where  $x = \frac{1}{2}(1 - \cos \theta)^2(2 + \cos \theta)$  as before, and

$$y = \frac{(r-a) \sin^2 \theta}{d} \left( \frac{3v_0 d}{8D_0} \right)^{1/2}. \quad (4.44)$$

In  $(x, y)$  coordinates the boundary condition (4.42) becomes

$$\frac{\partial}{\partial x} (\Pi \sin^2 \theta) = \frac{3}{2P_{vs}} \frac{\partial}{\partial x} \left( \sin^4 \theta \frac{\partial \Pi}{\partial x} \right) + \frac{\delta_0}{h_0} \frac{\partial \Pi}{\partial y}, \quad (4.45)$$

where  $P_{vs} = v_0 d / D_s$  is the Péclet number based on surface velocity and

surface diffusivity, and  $\delta_0$ , a convenient measure of the diffusion boundary layer thickness, is defined by

$$\delta_0^2 = D_0 d / 6v_0 = d^2 / 6P_{vs}, \quad (4.46)$$

where  $P_{vs} = v_0 d / D_0$ .

Equation (4.45), with the conditions  $\Pi \rightarrow \Pi_\infty$  as  $y \rightarrow \infty$ ,  $\Pi = \Pi_\infty$  at  $x=0$ ,  $y>0$ ,  $\Pi$  finite at  $x=y=0$ , uniquely specifies the solution of (4.43). If  $x$  is small,  $\sin^2 \theta \approx 4(\frac{1}{2}x)^{1/2}$ , and on making that approximation we find that

$$\Pi \approx \Pi_\infty - (\Pi_\infty - \Pi_0) \operatorname{erfc}(y/x^{1/2}), \quad (4.47)$$

where the surface pressure  $\Pi_0$  at the front stagnation point obeys

$$\Pi_0 = \Pi_\infty \delta_0 / [\delta_0 + h_0(\pi/3)^{1/2}]. \quad (4.48)$$

This simple calculation shows that  $\Pi_0/\Pi_\infty$  is nearly zero if  $\delta_0 \ll h_0$ , and is nearly one if  $\delta_0 \gg h_0$ . These two cases correspond respectively to there being much less and much more surfactant dissolved in the boundary layer than adsorbed at the surface. For brevity we shall refer to the surfactant in these two cases as being strong and weak respectively.

The first of the two cases to be described in detail was that of a weak surfactant, by Frumkin and Levich in 1949 (see Levich, 1962). They made a rather crude approximation to  $\partial \Pi / \partial y$ , and Derjaguin and Dukhin (1961) improved it. But even they do not deal adequately with the singularities which appear at the rear stagnation point.

For a weak surfactant ( $\delta_0 \gg h_0$ ) in very dilute solution, we may take  $\Pi$  everywhere around the bubble to be close to  $\Pi_\infty$ . The neglect of surface diffusion in (4.45) is easily justified, and the equation reduces to

$$\frac{\partial \Pi}{\partial y} = \frac{h_0 \Pi_\infty}{\delta_0} \frac{\partial}{\partial x} (\sin^2 \theta) = \frac{h_0 \Pi_\infty}{4\delta_0} \frac{\partial^2 N(x, 0)}{\partial y^2}, \quad (4.49)$$

approximately, and the solution to

$$\Pi = \Pi_\infty \left( 1 + \frac{h_0}{4\delta_0} \frac{\partial N(x, y)}{\partial y} \right). \quad (4.50)$$

In these equations  $N(x, y)$  is the solution of the diffusion equation (4.43) with initial condition  $N(0, y) = 0$  and boundary condition  $N(x, 0) = \sin^2 \theta(x) = f(x)$ , say, on  $y=0$ , where  $\theta(x)$  is the inverse function to  $x(\theta)$ . That is (Dukhin, 1966),

$$N(x, y) = \int_0^x \frac{df(t)}{dt} \operatorname{erfc} \frac{y}{(x-t)^{1/2}} dt. \quad (4.51)$$

From Eq. (4.51) we find (see Harper, 1972) that as  $\mu = \cos \theta \rightarrow -1$ ,  $\partial N/\partial y \rightarrow \infty$  on the surface  $y = 0$ , and that  $\partial N/\partial y$  is asymptotic to an exact solution of the full diffusion equation near the rear stagnation point but it does not satisfy all the boundary conditions there. The form of the singularity is that of a line sink, with  $\partial \Pi/\partial m \rightarrow \text{constant}/m$  as distance  $m$  from the axis of symmetry tends to zero. One must therefore add to the expression for  $\Pi$  a line-source solution of the full diffusion equation, of the correct strength to cancel that singularity. The correction is significant only in a small neighborhood  $\pi - \theta = O(P_{\infty}^{2/3})$  of the stagnation point, in which  $\Pi - \Pi_{\infty}$  is of order  $\Pi_{\infty} h_0 \ln P_{\infty} \delta_0$  instead of  $\Pi_{\infty} h_0 \delta_0$ , its order of magnitude at the front stagnation point and in most of the boundary layer.

The drag coefficient is hardly affected by the correction, because the integral from which it is calculated converges even for the singular expression (4.50). To calculate the drag, the most convenient method is to use Eqs. (2.12), (2.13), and (4.21) to prove that

$$C_{D0} = \frac{16}{R_0} \left( 1 + \frac{1}{2U\eta_0} \int_{-1}^1 \mu \sigma(\mu) d\mu \right) = \frac{16}{R_0} \left( 1 - \frac{1}{2U\eta_0} \int_{-1}^1 \mu \Pi(\mu) d\mu \right); \quad (4.52)$$

in this equation  $\sigma(\mu)$ ,  $\Pi(\mu)$  are the values of the surface tension and surface pressure where  $\cos \theta = \mu$ . Hence

$$C_{D0} = \frac{16}{R_0} \left( 1 + 0.608 \frac{h_0 \Pi_{\infty}}{\eta_0 D_0 P_{\infty}^{1/2}} \right), \quad (4.53)$$

where  $P_0 = Ua/D_0 = 2P_{\infty}$ .

## 2. Slightly Contaminated Surface, Strong Surfactant

The quantitative theory for a strong surfactant ( $h_0 \gg \delta_0$ ) was first given by Deryagin *et al.* (1960), but their treatment of the singularity at the rear stagnation point is inadequate. The error is worse than in the previous case. We have already seen in Eq. (4.48) that the surface pressure  $\Pi_0$  at the front stagnation point is very much smaller than  $\Pi_{\infty}$  if surface diffusion is neglected, being  $O(\Pi_{\infty} \delta_0/h_0)$ .

If we assume that  $\Pi_0 \ll \Pi_{\infty}$  even when surface diffusion is allowed for, there will be some part of the bubble's surface over which  $\Pi \ll \Pi_{\infty}$ , and then the normal diffusive flux to the surface will be approximately the same as if  $\Pi$  were put equal to zero. That is,

$$\frac{\partial \Pi}{\partial y} \doteq \frac{2\Pi_{\infty}}{(\pi x)^{1/2}} \exp\left(-\frac{y^2}{x}\right) = \frac{2\Pi_{\infty}}{(\pi x)^{1/2}} \quad \text{at } y = 0, \quad (4.54)$$

from Eq. (4.43). Equation (4.54) can be rewritten in terms of  $\partial \Pi/\partial r$ , and the result substituted into (4.42) and integrated, to obtain the following differential equation for  $\Pi$  on the bubble surface:

$$\Pi + \frac{D_s}{av_0} \frac{\partial \Pi}{\partial \mu} = \frac{2\Pi_{\infty} \delta_0 (2 + \mu)^{1/2}}{\pi^{1/2} h_0 (1 + \mu)}. \quad (4.55)$$

From this equation it appears that  $\Pi$  is of order  $\Pi_{\infty} \delta_0/h_0$  not only at the front stagnation point but over most of the bubble surface, and that surface diffusion may be neglected over most of the surface, because  $D_s/av_0$  is a small parameter. Near the rear stagnation point, however, these estimates fail, because  $\varepsilon = 1 + \mu \sim \frac{1}{2}\varphi^2 \rightarrow 0$ , where  $\varphi = \pi - \theta$ . Hence  $\Pi/\Pi_{\infty}$  does not remain small all the way round the bubble.

Harper (1972) has described how to resolve the singularity, but the complicated details will not be given here. He finds a first approximation to  $C_{D0}$  in the form of

$$C_{D0} = \frac{16}{R_0} \left( 1 + \frac{\Pi_{\infty}}{\sqrt{3}U\eta_0} \right), \quad (4.56)$$

which is independent of  $D_s$ , although the distribution of surfactant at distances of order  $aP_{\infty}^{-1/2}$  from the rear stagnation point is not. At that point

$$\Pi = \Pi_{\infty} P_{\infty}^{1/3} / \sqrt{3}. \quad (4.57)$$

For comparisons with experiments, it is easier to give  $C_{D0}$  for a given liquid and surfactant concentration in the form

$$C_{D0} = (16/R_0)(1 + Ad^n), \quad (4.58)$$

where the correction term  $Ad^n$  is assumed much smaller than unity,  $A$  is a constant,  $n = -\frac{2}{3}$  for a weak surfactant, from (4.53), and  $n = -2$  for a strong one, from (4.56).

## F. DROPS AND HIGH REYNOLDS NUMBERS

If the surfactant is soluble only in the continuous phase, all the theory in Section IV,E is applicable to drops, except that  $v_0$  is now slightly perturbed from  $\frac{1}{2}U\eta_0/(\eta_0 + \eta_1)$  instead of  $\frac{1}{2}U$  (Eq. 3.9), and  $C_{D0}$  is given by a formula more elaborate than (4.52), because Eqs. (3.6) and (3.7) for the internal velocity and shear stress must be taken into account. The result is

$$C_{D0} = \frac{8}{R_0(\eta_0 + \eta_1)} \left( 2\eta_0 + 3\eta_1 - \frac{1}{U} \int_{-1}^1 \mu \Pi(\mu) d\mu \right), \quad (4.59)$$

which generalizes Eq. (4.52), and for a weak surfactant

$$C_{D0} = \frac{8}{R_0(\eta_0 + \eta_1)} \left[ 2\eta_0 + 3\eta_1 + 0.608 \frac{h_0 \Pi_\infty}{D_0 P_0^{1/2}} \left( \frac{\eta_0}{\eta_0 + \eta_1} \right)^{1/2} \right], \quad (4.60)$$

to the first order.

If the Reynolds number  $R_0$  of a bubble is much larger than one, but not large enough for the bubble to be significantly distorted, it can be shown (Harper, 1972) that the analysis is again affected only in the value of  $v_0$  and the final calculation of  $C_{D0}$ , which is now

$$C_{D0} = \frac{48}{R_0} \left( 1 - \frac{1}{2U\eta_0} \int_{-1}^1 \mu \Pi(\mu) d\mu \right) = \frac{48}{R_0} \left( 1 + \frac{1.053h_0 \Pi_\infty}{\eta_0 D_0 P_0^{1/2}} \right) \quad (4.61)$$

for a weak surfactant. In this case the perturbations reach larger fractions of the basic flow than for small  $R_0$ , and there is not much difference in aqueous solutions between the values of  $\Pi_\infty$  which are too small for  $C_{D0}$  to be noticeably affected and too large for the small perturbation theory to be applicable. The situation is worse for a strong surfactant, and the value of  $C_{D0}$  does not seem worth giving.

Unfortunately no theory seems to be available for finite perturbations at high Reynolds numbers. Proportional increases in drag coefficient can occur which are greater than at low Reynolds numbers, because the ratio of  $C_{D0}$  values for spheres with rigid and free surfaces increases with  $R_0$  (see Fig. 1). For distorted bubbles the effect of surfactants diminishes, until it can be neglected for spherical caps, whose shape and drag can be explained fairly well without considering surface tension at all (see Section II,E).

To date, all the theory described in this chapter has been confirmed only qualitatively and semiquantitatively by experiments (Levich, 1962). Surfactant solutions with accurately known concentrations are difficult to prepare, and even more difficult to keep in a known chemical state while bubbles are passed through them. In addition, the main physical parameters,  $h$ ,  $D_s$ , and  $D_g$ , are difficult to measure. Determinations of  $h$ , and  $D_s$ , commonly disagree with one another by factors of 2, and only two measurements of  $D_s$  seem to have been made. That of Sakata and Berg (1969) is probably in error because of their assumptions that bulk diffusion is always much faster than desorption and readsorption, even when times of several hours are in question, and that evaporation of their myristic acid could be neglected. We are left with Imahori's (1952) work, in which  $D_s$  for an adsorbed protein of relative molecular mass 70400 was found to be  $1.1 \times 10^{-10} \text{ m}^2 \text{ sec}^{-1}$ , or about twice its bulk diffusivity.

### G. STAGNANT SURFACES

In many practical applications, enough surfactant is present for rising bubbles and drops to have their surface motion almost completely stopped. Much of the experimental work gives nearly rigid-sphere values of drag coefficients for undistorted bubbles (Haberman and Morton, 1953, 1956; Peebles and Garber, 1953) and drops (Hu and Kintner, 1955; Licht and Narasimhamurti, 1955; Keith and Hixson, 1955; Klee and Treybal, 1956; Elzinga and Bancho, 1961). Because the transfer of heat and mass to bubbles and drops obeys different laws for free and rigid surfaces (Levich, 1962) it is important to know how small the velocity at the surface should be for the rigid-surface theory to apply.

At low Péclet numbers (much less than one) there is no problem: the diffusion equation is  $\partial c / \partial t = D \nabla^2 c$  in either case, and for steady flow involving surfactants the theory is to be found in Section IV,D. But at high Péclet numbers the diffusion equation is no longer  $4\partial c / \partial x = \partial^2 c / \partial y^2$  (see Eqs. 4.43 and 4.44), but (Levich, 1962)

$$9\partial c / \partial X = (1/Y) \partial^2 c / \partial Y^2, \quad (4.62)$$

for flow past a rigid sphere at low Reynolds numbers, for which

$$P_{r0} = 3U\eta_0 \sin \theta / 2a \quad \text{on the surface,} \quad (4.63)$$

$$\psi \doteq \frac{3}{2} U(r - a)^2 \sin^2 \theta \quad \text{near it,} \quad (4.64)$$

$$X = \theta - \frac{1}{2} \sin 2\theta, \quad \text{making} \quad dX/d\theta = 2 \sin^2 \theta, \quad (4.65)$$

$$Y = 2\mu^{1/2} / (3^{5/6} D_0^{1/3} U^{1/6} a^{2/3}) \\ \doteq (P_0/6)^{1/3} [(r - a) \sin \theta / a], \quad (4.66)$$

where  $P_0 = 2Ua/D_0 \gg 1$  as before. The solutions of Eq. (4.62) will normally vary significantly over ranges of  $Y$  of order unity, and so the boundary layer thickness will be of order  $aP_0^{-1/3} \gg aP_0^{-1/2}$ , the value for free surfaces. In the diffusion boundary layer, the fluid velocity is then  $O(U/P_0^{-1/3})$ .

Like Eq. (4.43), Eq. (4.62) has some simple similarity solutions. We need the one which takes values  $c = 0$  on  $X = 0$  for  $Y > 0$ ,  $c \rightarrow 0$  as  $Y \rightarrow \infty$  for  $X > 0$ , and  $c = 1$  on  $Y = 0$  for  $X > 0$ , namely

$$c = \frac{\int_z^\infty \exp(-t^3) dt}{\int_0^\infty \exp(-t^3) dt}$$

$$= \frac{1}{(\frac{2}{3})!} \int_z^\infty \exp(-t^3) dt = h(z), \quad \text{say,} \quad (4.67)$$

where

$$z = Y/X^{1/3}. \quad (4.68)$$

With  $x, y, z$ , and  $\frac{1}{2}$  replacing  $X, Y, 3, \frac{1}{2}$  throughout we recover the corresponding solution of Eq. (4.43).

Equations equivalent to (4.62)–(4.68) are the basis of Levich's (1962) diffusion theory for rigid spheres, and we must now follow Dukhin and Buikov (1965) by investigating what strength of surfactant solution makes bubbles (or drops) obey them. Equation (4.63) specifies the surface shear stress, and so

$$\begin{aligned}\Pi &= R_g T h_0 c = \Pi_0 + \frac{2}{3} U \eta_0 (1 - \cos \theta) \\ &= \Pi_0 + g(X), \text{ say,}\end{aligned}\quad (4.69)$$

on the surface of the bubble or drop, if  $\Pi_0$  denotes the surface pressure at the front stagnation point. Equation (4.69) is one boundary condition to (4.62) in the region  $0 \leq X \leq \pi$ ,  $0 \leq Y < \infty$ , the other being that  $\Pi \rightarrow \Pi_\infty$ , the fictitious surface pressure at a great distance defined by (4.30), as  $Y \rightarrow \infty$  and as  $X \rightarrow 0$  for  $Y > 0$ . The solution resembles Eq. (4.51), being

$$\Pi = \Pi_\infty + (\Pi_0 - \Pi_\infty) h \left( \frac{Y}{X^{1/3}} \right) + \int_0^X \frac{dg(t)}{dt} h \left( \frac{Y}{(X-t)^{1/3}} \right) dt, \quad (4.70)$$

where the functions  $g$  and  $h$  are defined in Eqs. (4.67) and (4.69). From Eq. (4.70) the value of  $\partial \Pi / \partial r$  at the surface is

$$\begin{aligned}\frac{\partial \Pi}{\partial r} &= \left( \frac{P_0}{6} \right)^{1/3} \frac{\sin \theta}{a} \frac{\partial \Pi}{\partial Y} \\ &= \left( \frac{P_0}{6} \right)^{1/3} \frac{\sin \theta}{(\frac{1}{3})^{1/3} a} \left( \frac{\Pi_\infty - \Pi_0}{X^{1/3}} - \int_0^X \frac{dg(t)}{dt} \frac{dt}{(X-t)^{1/3}} \right).\end{aligned}\quad (4.71)$$

Substitution of  $\Pi$  and  $\partial \Pi / \partial r$  into Eq. (4.42),

$$a \frac{\partial}{\partial \theta} (\Pi u_\theta \sin \theta) = D_s \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Pi}{\partial \theta} \right) + \frac{a^2 D_0 \sin \theta}{h_0} \frac{\partial \Pi}{\partial r},$$

allows us to calculate  $u_\theta$ . For the theory to be consistent,  $u_\theta$  must be much less than  $U P_0^{-1/3}$ , or

$$\Pi_0 \gg \max \left( \frac{D_s \eta_0 P_0^{1/3}}{a}, \frac{D_0 \eta_0 P_0^{2/3}}{h_0} \right). \quad (4.72)$$

To find  $\Pi_0$ , we integrate Eq. (4.42) right along the surface to obtain

$$\int_0^\pi \sin \theta \frac{\partial \Pi}{\partial r} d\theta = 0 = \int_0^\pi \frac{\partial \Pi}{\partial Y} dX, \quad (4.73)$$

and hence from (4.71)

$$\begin{aligned}\Pi_\infty - \Pi_0 &= \frac{2U\eta_0}{\pi^{2/3}} \int_0^\pi \int_0^0 \frac{\sin \theta' \sin^2 \theta d\theta' d\theta}{(\theta - \theta' - \frac{1}{2} \sin 2\theta + \frac{1}{2} \sin 2\theta')^{1/3}}, \\ &\equiv 1.768 U \eta_0,\end{aligned}\quad (4.74)$$

a result equivalent to that of Dukhin and Buikov (1965) to the degree of accuracy they used.

For a bubble or drop to behave like a rigid sphere as far as convective diffusion to its surface through the continuous phase is concerned, we see that  $\Pi_\infty = R_g T h_0 c_\infty$  must be large enough for  $\Pi_0$  given by (4.74) to obey the inequality (4.72). If  $\Pi_\infty$  is not this large, the surface velocity  $u_\theta$  will be great enough to nullify equation (4.62) and make the boundary layer diffusion equation take a form like (2.27), i.e.

$$\partial c / \partial x = D_0 \partial^2 c / \partial \psi^2, \quad (4.75)$$

where  $\psi$  is the stream function and

$$x = \int_0^s \{m(s')\}^{1/2} u_\theta(s') ds', \quad (4.76)$$

where  $s$  measures arc length from the front stagnation point ( $a\theta$  for a sphere) and  $m(s)$  is distance from the axis of symmetry to the bubble surface ( $a \sin \theta$  for a sphere). Of course, this set of equations is difficult to work with if  $u_\theta$  is one of the unknowns, and calculations can be found in the literature only for  $u_\theta = v_0 \sin \theta$  (see Section IV, E), the form it takes for surfactants so dilute that the motion is hardly affected. Authors who assume  $u_\theta = v_0 \sin \theta$  in other circumstances may be overoptimistic.

#### H. INSOLUBLE SURFACTANTS

So far, we have considered bubbles moving through solutions of surface-active material when their interfaces have reached a steady state, in which the total rate of diffusion to the more sparsely covered parts of their surfaces balances the rate of diffusion away from the more heavily covered parts. If the surfactant is very strong (i.e. the adsorption depths  $h_i$  are very large) it may happen that the latter process is very slow. (A characteristic time for it is evidently the smaller value of  $h_i \delta_i / D_i$ .) Then we may consider bubbles to be rising with a constant amount of surfactant adsorbed, and bulk diffusion can be neglected. If so, Eq. (4.42) simplifies to

$$a \Pi u_\theta = D_s \partial \Pi / \partial \theta, \quad (4.77)$$



if the bubble is spherical, and so  $\Pi$  increases by a factor  $e$  while  $\theta$  increases by the amount  $au_0/D_s$ , i.e.

$$\Pi = \Pi_0 \exp \left( \int_0^\theta \frac{au_0(\theta')}{D_s} d\theta' \right). \quad (4.78)$$

The surface shear stress  $p_\theta$  is  $(1/a)(\partial\Pi/\partial\theta) = \Pi u_0/D_s$  if the surface excess is small enough, and  $p_\theta$  never exceeds  $O(U\eta_0/a)$  at low Reynolds numbers. Therefore either  $\Pi$  or  $u_0$  is small at each point around the bubble, and the bubble tends to reach a state in which  $u_0$  is of order  $U$  over a part of the surface where  $\Pi$  is very small and may be neglected, whereas  $u_0 \ll U$  over the remainder. The transition region between the two parts has small angular extent at large Peclet numbers, but its details have not been elucidated.

Theories for the motion of such bubbles have been developed by several authors. They all consider the transition between a tangentially stress-free and rigid surface to occur suddenly at an angle  $\theta = \theta^*$ . Savic (1953) began this work both experimentally and theoretically for bubbles. Griffith (1962) reported many observations on drops and suggested an approximate method for adapting Savic's theory to them. The theory for bubbles has since been improved by Davis and Acrivos (1966), who used a series expansion for the shear stress in the range where it was nonzero, and found the coefficients by minimizing the velocity in that range.

Davis and Acrivos found rather sudden transitions from free to rigid behavior of bubbles in a given liquid as their diameter decreased, with  $n = -4$  in the notation of (4.58), whereas Levich's (1962) theory gives a more gradual change with  $n = -\frac{3}{2}$ . Experiments (Bond and Newton, 1928; Griffith, 1962) may give either type, and vary widely among themselves.

### I. SLOW ADSORPTION

Levich (1962) mentions the possibility that the transfer of adsorbed solute from regions of high to low surface excess through the bulk solution might be hindered by slowness of adsorption or desorption, i.e. that there might be an "activation energy" barrier between the dissolved and adsorbed states of a surfactant. His equation (74.18) implies that  $n = -1$  in our Eq. (4.58) for a surfactant whose energy barrier controls its adsorption. In this review such barriers have been ignored. We take the view that no convincing experimental evidence for their existence has yet been put forward, except possibly for systems with several interacting surface-active components.

Many workers who have measured the surface tension of freshly formed liquid surfaces disagree, but Defay and Hommelen (1958a) found no

measurements on surfactant solutions in which proper allowance was made for the effect of the fluid motion on the surfactant distribution. It is, of course, impossible to alter the area of a fluid surface without setting the fluid in motion.

Hansen *et al.* (1958), Defay and Pétrel (1962), and Hansen (1964) have made a start on determining short-term hydrodynamical effects in vibrating-jet measurements of surface tension. It seems that surface ages can be overestimated by a millisecond or so, and surface tensions can be overestimated by a few percent in the first few milliseconds. This casts some doubt on the suggestion of Tsouopoulos *et al.* (1971) that Defay and Hommelen's (1958b) experimental results imply an adsorption barrier for hexanol. For surface ages of several seconds the hydrodynamics may no longer be a problem, but evaporation of the solute may simulate an adsorption barrier with higher alcohols such as decanol (Defay and Hommelen, 1959b).

The above comments apply to systems in which chemical reactions between the components can be ignored. When several reacting surface-active substances are present, it may happen that an element of fluid in the bulk solution contains an equilibrium mixture, but the mixture is no longer in chemical equilibrium if brought to the surface when each component adsorbs according to its own value of  $h = \Gamma/c$ . If so, the approach to surface equilibrium may be delayed by the slowness of the reactions restoring equilibrium among the various chemical components. Hansen and Wallace (1959) found some evidence for this in organic acids, which are known to exist in ionized, unionized, and associated forms. Defay and Hommelen (1959b) found that a slow reaction occurred for the dibasic azelaic acid  $\text{HO}_2\text{C}(\text{CH}_2)_7\text{CO}_2\text{H}$ .

Reaction times of the order of milliseconds are the most important for bubbles, because a bubble small enough to be appreciably affected by surfactants rises through its own diameter in a few milliseconds in water. Unfortunately, there is no very good method of measuring surface tensions which vary as rapidly as this (Defay and Hommelen, 1958a, 1959a; Defay and Pétrel, 1962; Wegener and Parlange, 1964; reviewed by Defay *et al.*, 1966). Another complication is that dissolved ions, especially polyvalent ones, may modify the molecular structure of the water in their neighborhood enough to affect the behavior of bubbles. Ziemiński and Whittemore (1971) discussed their experiments on bubble coalescence from this point of view, but admit that it is controversial.

### ACKNOWLEDGMENTS

This article was written at Imperial College, London, during a period of refresher leave from the Victoria University of Wellington, New Zealand, and I am most grateful to both institutions. I also wish to thank Prof. G. Astarita, Prof. G. K. Batchelor, Dr. T.

Blake, Prof. A. V. Bradshaw, Dr. R. Collins, Dr. A. R. H. Cornish, Dr. G. J. Jameson, Dr. J. A. K. Kitchener, Dr. H. Sawtowski, Prof. L. E. Scriven, and especially Dr. D. W. Moore for discussions, Miss J. Pindelska, Librarian, Mathematics Department, Imperial College, for help in obtaining and copying references, and the Cambridge University Press for permitting Fig. 7, part of Table 1, and Table 3 to be copied from papers in the *Journal of Fluid Mechanics*.

## REFERENCES

- ABRAMOWITZ, M., and STEGUN, I. A. (1965). "Handbook of Mathematical Functions." Dover, New York.
- ACKERT, J. (1952). Über exakte Lösungen der Stokes-Navier-Gleichungen inkompressibler Flüssigkeiten bei veränderten Grenzbedingungen. *Z. Angew. Math. Phys.* 3, 259-271.
- ADAM, N. K. (1968). "The Physics and Chemistry of Surfaces." Dover, New York.
- ANGELINO, H. (1966). Hydrodynamique des grosses bulles dans les liquides visqueux. *Chem. Eng. Sci.* 21, 541-550.
- ASTARITA, G. (1970). Personal communication.
- BAKKER, C. A. P., VAN BUYTENEN, P. M., and BEER, W. J. (1966). Interfacial phenomena and mass transfer. *Chem. Eng. Sci.* 21, 1039-1046.
- BACHELOR, G. K. (1956). On steady laminar flow with closed streamlines at large Reynolds number. *J. Fluid Mech.* 1, 177-190.
- BIRD, W. B., STEWART, W. E., and LIGHTFOOT, E. N. (1960). "Transport Phenomena." Wiley, New York.
- BIRKHOFF, G., and ZARANTONELLO, E. H. (1957). "Jets, Wakes, and Cavities." Academic Press, New York.
- BOND, W. N., and NEWTON, D. A. (1928). Bubbles, drops and Stokes' law. (Paper 2.) *Phil. Mag.* 17 5, 794-800.
- BRIGNEL, A. S. (1970). Ph.D. Thesis, Imperial College, London University.
- BRODKEY, R. S. (1967). "The Phenomena of Fluid Motions." Addison-Wesley, Reading, Massachusetts.
- BRYN, T. (1933). Steiggeschwindigkeit von Luftblasen in Flüssigkeiten. *Forsch. Geb. Ingenieurw.* 4, 27-30.
- CHAN, B. K. C., and PRINCE, R. G. H. (1965). Distillation studies—viscous drag on a gas bubble rising in a liquid. *AIChEJ* 11, 268-273.
- CHAO, B. T. (1962). Motion of spherical gas bubbles in a viscous fluid at large Reynolds numbers. *Phys. Fluids* 5, 69-79.
- CHESTER, W., and BREACH, D. R. (1969). On the flow past a sphere at low Reynolds number. *J. Fluid Mech.* 37, 751-760.
- COLE, R. (1967). Motion of vapor bubbles in saturated liquids. *AIChEJ* 13, 403-404.
- COLLINS, R. (1966). A second approximation for the velocity of a large bubble rising in an infinite liquid. *J. Fluid Mech.* 25, 469-480.
- DAVENPORT, W. G., BRADSHAW, A. V., and RICHARDSON, F. D. (1967a). Behaviour of spherical cap bubbles in liquid metals. *J. Iron Steel Inst., London* 205, 1034-1042.
- DAVENPORT, W. G., RICHARDSON, F. D., and BRADSHAW, A. V. (1967b). Spherical cap bubbles in low density liquids. *Chem. Eng. Sci.* 22, 1221-1235.
- DAVIES, J. T., and RIDDELL, E. K. (1963). "Interfacial Phenomena," 2nd. ed. Academic Press, New York.
- DAVIES, R. M., and TAYLOR, G. I. (1950). The mechanics of large bubbles rising through extended liquids and through liquids in tubes. *Proc. Roy. Soc., Ser. A* 200, 375-390.

- DAVIS, R. E., and ACRIVOS, A. (1966). The influence of surfactants on the creeping motion of small bubbles. *Chem. Eng. Sci.* 21, 681-685.
- DERAY, R., and HOMMELEN, J. (1958a). Bibliographie critique sur les methodes de mesure des tensions superficielles dynamiques. *Ind. Chim. Belge* 23, 597-614.
- DERAY, R., and HOMMELEN, J. (1958b). Measurement of dynamic surface tensions of aqueous solutions by the oscillating jet method. *J. Colloid Sci.* 13, 553-564.
- DERAY, R., and HOMMELEN, J. (1959a). Measurement of dynamic surface tensions of aqueous solutions by the falling meniscus method. *J. Colloid Sci.* 14, 401-410.
- DERAY, R., and HOMMELEN, J. (1959b). The importance of diffusion in the adsorption process of some alcohols and acids in dilute aqueous solutions. *J. Colloid Sci.* 14, 411-418.
- DERAY, R., and PÉRIÉ, G. (1962). Correcting surface tension data obtained by the oscillating jet method. *J. Colloid Sci.* 17, 565-569.
- DERAY, R., PRIGOGINE, I., BELLEMANS, A., and EVERETT, D. H. (1966). "Surface Tension and Adsorption." Longmans, Green, New York.
- DERYAGIN, B. V., and DUKIN, S. S. (1961). Theory of flotation of small and medium-size particles. *Inst. Mining Met., Trans.* 70, 221-246.
- DERYAGIN, B. V. (= DERYAGIN, B. V.), DUKIN, S. S., and LISCHENKO, V. A. (1959). The kinetics of the attachment of mineral particles to bubbles during flotation. I. The electric field of a moving bubble. *Russ. J. Phys. Chem.* 33, 389-393.
- DERYAGIN, B. V., DUKIN, S. S., and LISCHENKO, V. A. (1960). The kinetics of the attachment of mineral particles to bubbles during flotation. II. The electric field of a moving bubble when the surface activity of the ionogenic substance is high. *Russ. J. Phys. Chem.* 34, 248-251.
- DUKIN, S. S. (1966). An electrical diffusion theory of the Dorn effect and a discussion of the possibility of measuring zeta potentials. *Rev. Surface Forces, Proc. Conf.*, 2nd, 1962 Vol. 2, pp. 54-74.
- DUKIN, S. S., and BUKOV, M. V. (1965). Theory of the dynamic adsorption layer of moving spherical particles. II. Theory of the dynamic adsorption layer of a bubble (drop) at a Reynolds number  $Re \ll 1$  in the presence of strong retardation of the surface. *Russ. J. Phys. Chem.* 39, 482-485.
- DUKIN, S. S., and DERYAGIN, B. V. (1961). Kinetics of the attachment of mineral particles to bubbles during flotation. V. Motion of the bubble surface strongly retarded by surface-active substances. Distribution of the surface-active material and electric field of the bubble. *Russ. J. Phys. Chem.* 35, 715-717.
- DURNAM, K., ed. (1961). "Surface Activity and Detergency." Macmillan, New York.
- EL SAWI, M. (1970). Ph.D. Thesis, Imperial College, London University.
- ELZINCA, E. R., and BANCHEK, J. T. (1961). Some observations on the mechanics of drops in liquid-liquid systems. *AIChEJ* 7, 394-399.
- FRANKEL, L. E. (1970). On steady vortex rings of small cross-section in an ideal fluid. *Proc. Roy. Soc., Ser. A* 316, 29-62.
- GAL-OR, B., KLINGING, G. E., and TAVLADIS, L. L. (1969). Bubble and drop phenomena. *Ind. Eng. Chem.* 61, 2, 21-34.
- GARBEDIAN, P. R. (1957). On steady-state bubbles generated by Taylor instability. *Proc. Roy. Soc., Ser. A* 241, 423-431.
- GILL, W. N., COLE, R., ESTRIN, J., and NUNGE, R. J. (1969). Fluid dynamics. *Ind. Eng. Chem.* 61, 1, 41-75.
- GILL, W. N., COLE, R., DAVIS, E. J., ESTRIN, J., NUNGE, R. J., and LUTTMAN, H. (1970). Fluid dynamics. *Ind. Eng. Chem.* 62, 4, 49-79.
- GLASTONE, S. (1953). "The Elements of Physical Chemistry." Macmillan, New York.

- GOLDSTEIN, S., ed. (1938). "Modern Developments in Fluid Dynamics," 2 vols. Cambridge Univ. Press, London and New York.
- GOMEZPATLA, A., and REGAN, T. M. (1968). Mass transfer. *Ind. Eng. Chem.* **60**, 12, 53-62.
- GOUSE, S. W., Jr. (1966). "An Index to the Two-phase Gas-liquid Flow Literature." MIT Press, Cambridge, Massachusetts.
- GURETIN, R. M. (1962). The effect of surfactants on the terminal velocity of drops and bubbles. *Chem. Eng. Sci.* **17**, 1057-1070.
- GUGGENHEIM, E. A. (1949). "Thermodynamics." North-Holland Publ., Amsterdam.
- GUTHRIE, R. I. L., and BRADSHAW, A. V. (1969). The stability of gas envelopes trailed behind large spherical cap bubbles rising through viscous liquids. *Chem. Eng. Sci.* **24**, 913-917.
- HABERMAN, W. L., and MORTON, R. K. (1953). An experimental investigation of the drag and shape of air bubbles rising in various liquids. *David Taylor Model Basin Rep.* No. 802.
- HABERMAN, W. L., and MORTON, R. K. (1956). An experimental study of bubbles moving in liquids. *Trans. Amer. Soc. Civil Eng.* **121**, 227-252.
- HADAMARD, J. (1911). Mouvement permanent lent d'une sphère liquide et visqueuse dans une liquide visqueux. *C. R. Acad. Sci.* **152**, 1735-1738.
- HAMMERSLEY, J. H. (1961). On the statistical loss of long-period comets from the solar system. II. *Proc. Symp. Math. Stat. Probability*, 4th, 1960, Vol. 3, pp. 17-78.
- HANSEN, R. S. (1964). The calculation of surface age in vibrating jet measurements. *J. Phys. Chem.* **68**, 2012-2014.
- HANSEN, R. S., and WALLACE, T. C. (1959). The kinetics of adsorption of organic acids at the water-air interface. *J. Phys. Chem.* **63**, 1085-1091.
- HANSEN, R. S., PUNCHASE, M. E., WALLACE, T. C., and WOODY, R. W. (1958). Extension of the vibrating jet method for surface tension measurement to jets of nonuniform velocity profiles. *J. Phys. Chem.* **62**, 210-214.
- HARPER, J., and BRENNER, H. (1965). "Low Reynolds Number Hydrodynamics." Prentice-Hall, Englewood Cliffs, New Jersey.
- HARPER, J. F. (1970). Viscous drag in steady potential flow past a bubble. *Chem. Eng. Sci.* **25**, 342-343.
- HARPER, J. F. (1971). Errata to "Viscous drag in steady potential flow past a bubble." *Chem. Eng. Sci.* **26**, 501.
- HARPER, J. F. (1972). On spherical bubbles rising steadily in dilute surfactant solutions. (to be published).
- HARPER, J. F., and MOORE, D. W. (1968). The motion of a spherical liquid drop at high Reynolds number. *J. Fluid Mech.* **32**, 367-391.
- HARPER, J. F., MOORE, D. W., and PEARSON, J. R. A. (1967). The effect of the variation of surface tension with temperature on the motion of bubbles and drops. *J. Fluid Mech.* **27**, 361-366.
- HARTUNIAN, R. A., and SEARS, W. R. (1957). On the instability of small gas bubbles moving uniformly in various liquids. *J. Fluid Mech.* **3**, 27-47.
- HILL, M. J. M. (1894). On a spherical vortex. *Phil. Trans. Roy. Soc. London, Ser. A* **185**, 213-245.
- HU, S., and KRITNER, R. C. (1955). The fall of single liquid drops through water. *AIChEJ.* **1**, 42-48.
- IMANORI, K. (1952). The structure of surface-denatured protein. III. Determination of the shape of surface-denatured horse serum albumin. *Bull. Chem. Soc. Jap.* **25**, 13-16.
- JONES, D. R. M. (1965). Ph.D. Thesis, University of Cambridge.

- KERTH, F. W., and HIXSON, A. N. (1955). Liquid-liquid extraction spray columns. *Ind. Eng. Chem.* **47**, 258-267.
- KENDALL, D. G. (1961). Some problems in the theory of comets. II. *Proc. Symp. Math. Stat. Probability*, 4th, 1960 Vol. 3, pp. 121-147.
- KENNEDY, D. B. R. (1969). The effect of surface energy variations on the motion of bubbles and drops. *Chem. Eng. Sci.* **24**, 1385-1386.
- KLEE, A. J., and THERYAL, R. E. (1956). Rate of rise or fall of liquid drops. *AIChEJ.* **2**, 444-447.
- KOSHINA, N. N. (1969). Some solutions of the inhomogeneous heat equation. (In Russian.) *Dokl. Akad. Nauk SSSR* **186**, 54-57; see *Sov. Phys.—Dokl.* **14**, 419-421.
- KOJIMA, E., AKENAGA, T., and SHIRAI, T. (1968). Rising velocity and shape of single air bubbles in highly viscous liquids. *J. Chem. Eng. Jap.* **1**, 45-50.
- LACROIX, P. A., and COLE, J. D. (1955). Examples illustrating expansion procedures for the Navier-Stokes equations. *J. Rat. Mech. Anal.* **4**, 817-882.
- LAMB, H. (1932). "Hydrodynamics," 6th ed. Cambridge Univ. Press, London and New York.
- LANDAU, L. D., and LIFSHITZ, E. M. (1959). "Fluid Mechanics." Pergamon, Oxford.
- LANE, W. R., and GREEN, H. L. (1956). The mechanics of drops and bubbles. In "Surveys in Mechanics" (G. K. Batchelor and R. M. Davies, eds.), pp. 162-215. Cambridge Univ. Press, London and New York.
- LEVICH, V. G. (1949). Motion of gaseous bubbles with high Reynolds numbers. (In Russian.) *Zh. Eksp. Teor. Fiz.* **19**, 18-24.
- LEVICH, V. G. (1962). "Physicochemical Hydrodynamics." Prentice-Hall, Englewood Cliffs, New Jersey.
- LICHT, W., and NARASIMAMURTHY, G. S. R. (1955). Rate of fall of single liquid droplets. *AIChEJ.* **1**, 366-373.
- LIGHTHILL, M. J. (1958). On displacement thickness. *J. Fluid Mech.* **4**, 383-392.
- LOCHIE, A. C. (1965). The influence of surfactants on mass transfer around spheres. *Can. J. Chem. Eng.* **43**, 40-44.
- MCGILVER, M. L. (1968). "Physico-Chemical Quantities and Units." Roy. Inst. Chem., London.
- MALENKOV, E. G. (1968). Motion of large gas bubbles rising into fluids (in Russian). *Zh. Prikl. Mekh. Tekh. Fiz.* **6**, 130-133; to be translated in *J. Appl. Mech. Tech. Phys. (USSR)*.
- MAXWORTHY, T. (1967). A note on the existence of wakes behind large, rising bubbles. *J. Fluid Mech.* **27**, 367-368 and 2 plates.
- MELROSE, J. C. (1968). Thermodynamic aspects of capillarity. *Ind. Eng. Chem.* **60**, 3, 53-70.
- MENDLSON, H. D. (1967). The prediction of bubble terminal velocities from wave theory. *AIChEJ.* **13**, 250-253.
- MOORE, D. W. (1959). The rise of a gas bubble in a viscous liquid. *J. Fluid Mech.* **6**, 113-130.
- MOORE, D. W. (1963). The boundary layer on a spherical gas bubble. *J. Fluid Mech.* **16**, 161-176.
- MOORE, D. W. (1965). The velocity of rise of distorted gas bubbles in a liquid of small viscosity. *J. Fluid Mech.* **23**, 749-766.
- NEWMAN, J. (1967). Retardation of falling drops. *Chem. Eng. Sci.* **22**, 83-85.
- PAN, Y. F., and ACRIVOS, A. (1968). Shape of a drop or bubble at low Reynolds number. *Ind. Eng. Chem., Fundam.* **7**, 227-232.
- PARRANCE, J. Y. (1969). Spherical bubbles with laminar wakes. *J. Fluid Mech.* **37**, 257-263.

- PANSONS, R. (1954). Equilibrium properties of electrified interphases. In "Modern Aspects of Electrochemistry" (J. O'M. Bockris, ed.), Vol. 1, pp. 103-179. Butterworth, London.
- PEARSON, J. R. A. (1958). On convection cells induced by surface tension. *J. Fluid Mech.* 4, 489-500.
- PEREULE, F. N., and GARBER, H. J. (1953). Studies on the motion of gas bubbles in liquids. *Chem. Eng. Progr.* 49, 88-97.
- PERRY, R. H., CHILTON, C. H., and KIRKPATRICK, S. D., eds. (1963). "Chemical Engineers Handbook," 4th ed. McGraw-Hill, New York.
- PLESSER, M. S. (1964). Bubble dynamics. In "Cavitation in Real Liquids" (R. Davies, ed.), pp. 1-18. Elsevier, Amsterdam.
- PRANDTL, L. (1905). Über Flüssigkeitsbewegung bei sehr kleiner Reibung. *Verh. Int. Math.-Kongr.*, 3rd, 1904 pp. 484-491.
- PRANDTL, L., and TETJENS, O. G. (1957). "Applied Hydro- and Aerodynamics." Dover, New York.
- PROUDMAN, I., and PEARSON, J. R. A. (1957). Expansions at small Reynolds numbers for the flow past a sphere and a circular cylinder. *J. Fluid Mech.* 2, 237-262.
- PRUPPACHER, H. R., LE CLAIR, B. P., and HAMMEL, A. E. (1970). Some relations between drag and flow pattern of viscous flow past a sphere and a cylinder at low and intermediate Reynolds numbers. *J. Fluid Mech.* 44, 781-790.
- RADPILL, J. A., and HOUNGTON, G. (1965). Mass transfer and drag coefficients for single bubbles at Reynolds numbers of 0.2-5000. *Chem. Eng. Sci.* 20, 131-139.
- REGAN, T. M., and GONZALEZ, A. (1970). Mass transfer. *Ind. Eng. Chem.* 62, 2, 41-53.
- RIPPIN, D. W. T., and DAVIDSON, J. F. (1967). Free streamline theory for a large gas bubble in a liquid. *Chem. Eng. Sci.* 22, 217-227.
- ROSENHEAD, L., ed. (1963). "Laminar Boundary Layers." Oxford Univ. Press, London and New York.
- RUBIN, E., and JORNE, J. (1969). Foam separation of solutions containing two ionic surface-active agents. *Ind. Eng. Chem., Fundam.* 8, 474-482.
- RUCKENSTEIN, E. (1967). Mass transfer between a single drop and a continuous phase. *Int. J. Heat Mass Transfer* 10, 1785-1792.
- RYNCHYNSKI, W. (1911). On the transitory motion of a fluid sphere in a viscous medium (in German). *Bull. Int. Acad. Pol. Sci. Math. Natur., Ser. A* pp. 40-46.
- SAFFMAN, P. G. (1956). On the rise of small air bubbles in water. *J. Fluid Mech.* 1, 249-275.
- SAKATA, E. K., and BRIG, J. C. (1969). Surface diffusion in monolayers. *Ind. Eng. Chem., Fundam.* 8, 570-575.
- SAVIC, P. (1953). Circulation and distortion of liquid drops falling through a viscous medium. *Nat. Res. Comm. Can., Div. Mech. Eng. Rep.* MT-22.
- SCHMIDT, E. (1933). Über die Bewegung von Flüssigkeits-Gas-Gemischen. *VDI (Ver. Dett. Ing.) Z.* 77, 1159-1160.
- SCRIVEN, L. E. (1960). Dynamics of a fluid interface. *Chem. Eng. Sci.* 12, 98-108.
- SCRIVEN, L. E., and STERNLING, C. V. (1960). The Marangoni effects. *Nature (London)* 187, 186-188.
- SCRIVEN, L. E., and STERNLING, C. V. (1964). On cellular convection driven by surface-tension gradients: Effects of mean surface tension and surface viscosity. *J. Fluid Mech.* 19, 321-340.
- SHEDLOVSKY, L. (1968). Interface properties of detergent films. *Ind. Eng. Chem.* 60, 10, 47-52.
- SHINODA, K., and NAKANISHI, J. (1963). Selective adsorption studies by radio tracer techniques. IV. Selective adsorptivity of alcohol against surface active agent at the air-solution interface. *J. Phys. Chem.* 67, 2547-2549.

- SHODMAKER, P. D., and MARC DE CHAZAL, L. E. (1969). Dimpled and skirted liquid drops moving through viscous liquid media. *Chem. Eng. Sci.* 24, 795-797.
- SLUGHTER, I., and WRAITH, A. E. (1968). The wake of a large gas bubble. *Chem. Eng. Sci.* 23, 932 and plate.
- STANLEY, E. P., and FERRILL, J. K. (1968). Heat transfer. *Ind. Eng. Chem.* 60, 1, 75-83.
- STEWARTSON, K. (1968). On an integral equation. *Mathematika* 15, 22-29.
- SUMNER, B. S., and MOORE, F. K. (1969). Comments on the nature of the outside boundary layer on a liquid sphere in a steady, uniform stream. *NASA Contract. Rep. NASACR-1362.*
- TAUNTON, J. W., and LIGHTFOOT, E. N. (1969). Transient effects in mass transfer to circulating drops. *Int. J. Heat Mass Transfer* 12, 1718-1722.
- TAVLARIDES, L. L., COULIOPOULOS, C. A., ZEITLIN, M. A., KUNZING, G. E., and GAL-OR, B. (1970). Bubble and drop phenomena. *Ind. Eng. Chem.* 62, 11, 6-27.
- TAYLOR, T. D., and ACRIVOS, A. (1964). On the deformation and drag of a falling viscous drop at low Reynolds number. *J. Fluid Mech.* 18, 466-476.
- THOMSON, J. J., and NEWALL, H. F. (1885). On the formation of vortex rings by drops falling into liquids, and some allied phenomena. *Proc. Roy. Soc.* 39, 417-437.
- THOMSEN, G., STORDALEN, R. M., and TEJESSEN, S. G. (1968). On the terminal velocity of circulating and oscillating liquid drops. *Chem. Eng. Sci.* 23, 413-426.
- TSONOPoulos, C., NEWMAN, J., and PRAUSNITZ, J. M. (1971). Rapid aging and dynamic surface tension of dilute aqueous solutions. *Chem. Eng. Sci.* 26, 817-827.
- TYROLER, G., HAMMEL, A. E., JOHNSON, A. I., and LECLAIR, B. P. (1971). Mass transfer with fast chemical reaction in drops. *Can. J. Chem. Eng.* 49, 56-61.
- WALBRIDGE, N. L., and WOODWARD, L. A. (1970). Phase velocity of surface capillary-gravity waves. *Phys. Fluids* 13, 2461-2465.
- WASSERMAN, M. L., and SLATTERY, J. C. (1969). Creeping flow past a fluid globule when a trace of surfactant is present. *AIChEJ.* 15, 533-547.
- WATKINSON, C. E. (1927). "Differential Geometry of Three Dimensions," Vol. I. Cambridge Univ. Press, London and New York.
- WEGENER, P. P., and PARLANGE, J.-Y. (1964). Surface tension of liquids from water-bell experiments. *Z. Phys. Chem. (Frankfurt am Main)* 43, 245-259.
- WINNIKOW, S., and CHAO, B. T. (1966). Droplet motion in purified systems. *Phys. Fluids* 9, 50-61.
- YOUNG, N. O., GOLDSTEIN, J. S., and BLOCK, M. J. (1959). The motion of bubbles in a vertical temperature gradient. *J. Fluid Mech.* 6, 350-356.
- ZIMENSKI, S. A., and WHITTEMORE, R. C. (1971). Behavior of gas bubbles in aqueous electrolyte solutions. *Chem. Eng. Sci.* 26, 509-520.

Wegener Sundell + Farlangessee Album Fluid 1971, 2107

(1972) JFM 53

(1962) JFM 22 47, 435

at (1967) AIC 13 213 3, 330-4

(JFM 55 629 637 + 4 pages)