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# Fluid dynamics of two miscible liquids with diffusion and gradient stresses

D. D. JOSEPH *

ABSTRACT. – The density of incompressible fluids can vary with concentration $\varphi$ and temperature, but not with pressure. The velocity field $\mathbf{u}$ of such incompressible fluids is not in general solenoidal, $\operatorname{div}\mathbf{u}\neq 0$. A conservation form for the left hand side of the diffusion equation which differs from the usual substantial derivative of $\varphi$ by the addition of $\varphi \operatorname{div}\mathbf{u}$, is implied by requiring that the mass per unit total volume of one liquid in a material volume is conserved in the absence of diffusion. The possibility that stresses are induced by gradients of concentration and density in slow diffusion of incompressible miscible liquids, as in the theory of Korteweg [1901] is considered. Such stresses could be important in regions of high gradients giving rise to effects which can mimic surface tension. The small but interesting history of thought about interfacial tension between miscible liquids is collected here. The presence of a sharp interface in the case of slow diffusion in rising bubbles and falling drops has been documented in many experiments and in the experiments reported here. The shape of such interfaces can scarcely be distinguished from the shapes of bubbles and drops of immiscible liquids with surface tension. The usual description of interface problems for miscible liquids with classical interface conditions but with zero interfacial tension misses out on slow diffusion on the one hand and gradient stresses on the other. The usual description of diffusion with $\operatorname{div} \quad =0$ is also inexact, though it is a good approximation in some cases.

## 1. Motivation and problem statement

In Figure 1 we have presented a sequence of photographs documenting the change in the shape of a water bubble ($\rho=1$ gm/cc) as it rises in a container filled with glycerin ($\rho=1.2$ gm/cc). Since water and glycerin are miscible we must admit that our perceptions trick us and that our eyes do not resolve the diffusion layer of aqueous glycerol in which the transition from pure glycerin to pure water must take place. The shape of the water bubble we see, however, is not so different than what we might expect to see in the case of a rising bubble or falling drop of one immiscible liquid in another, provided that the immiscible liquids are otherwise similar, with the same densities and viscosities and a small, but not zero, interfacial tension.

In Figure 2 we show a sequence of photographs of a molasses and water mixture in glycerin. The densities are nearly matched, so that the bubble rises slowly.

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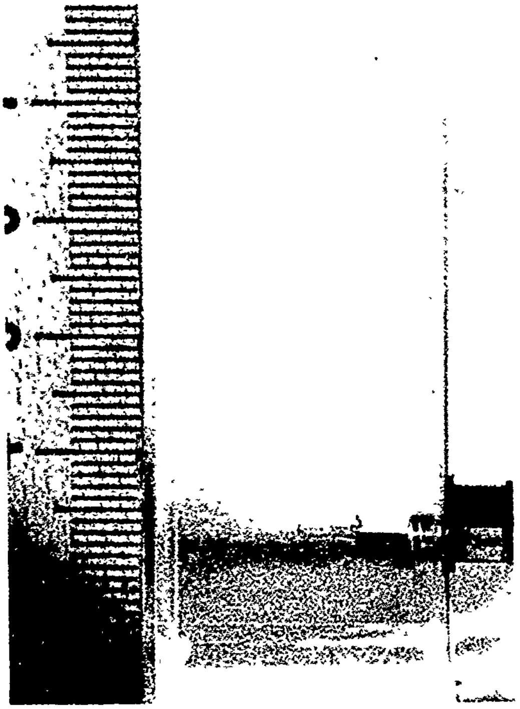


Fig. 1a

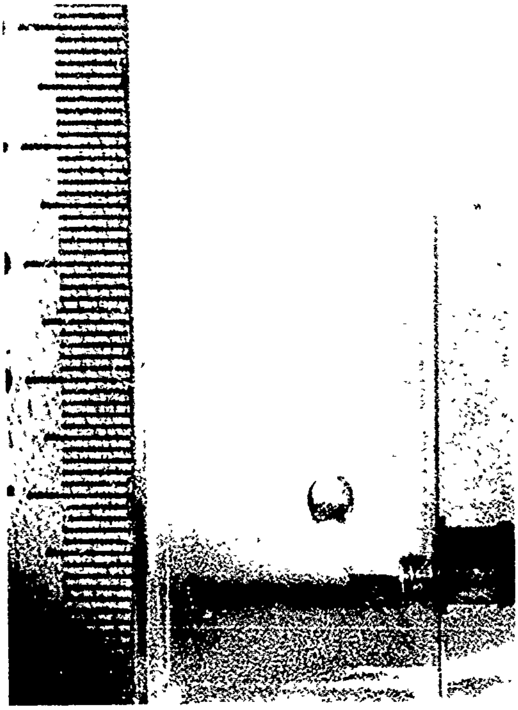


Fig. 1b

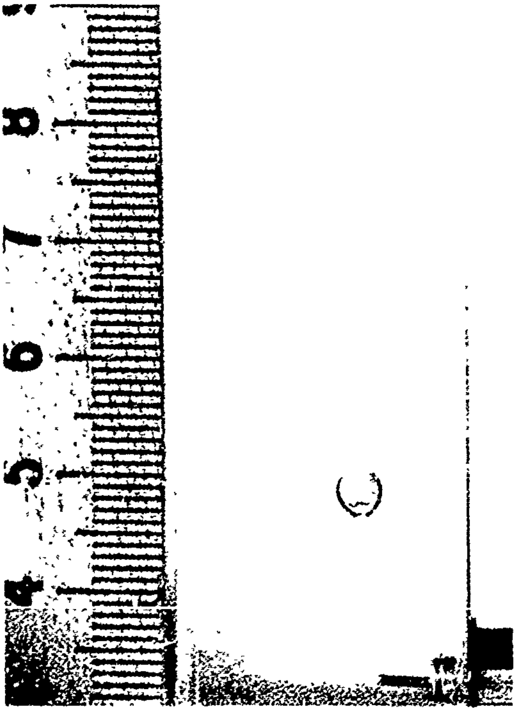


Fig. 1c

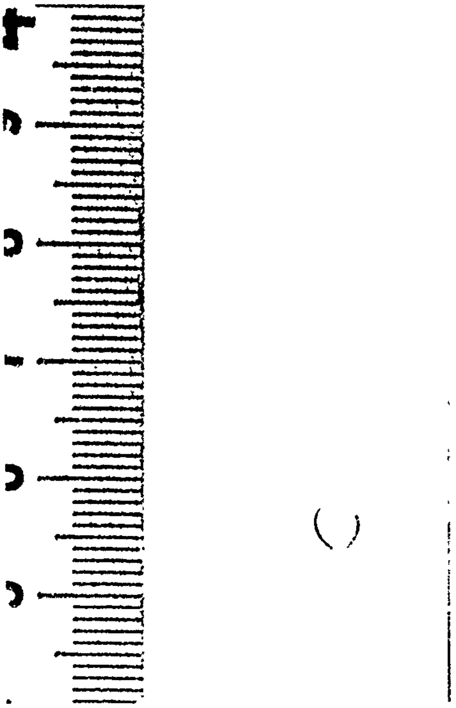


Fig. 1d

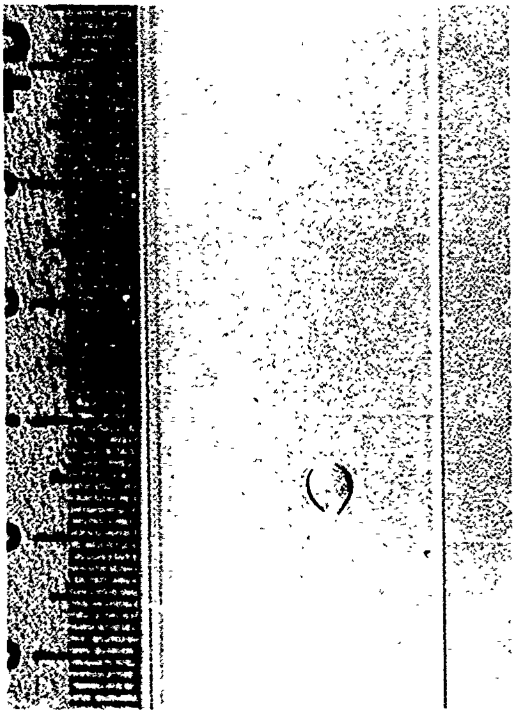


Fig. 1e

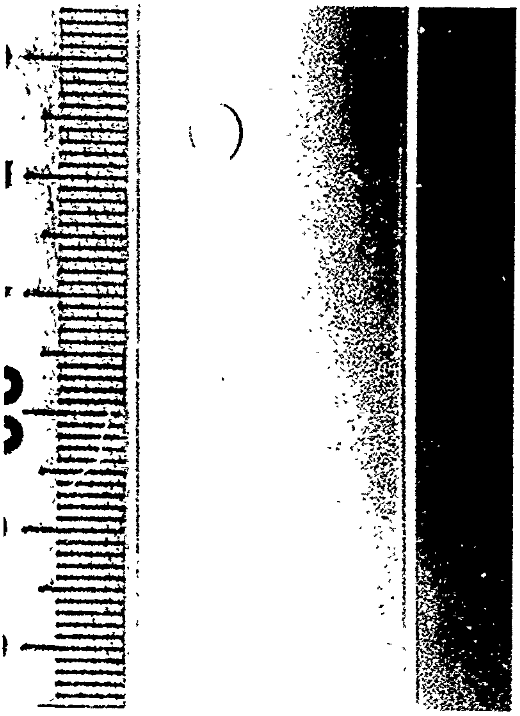


Fig 1f

Fig. 1 — Water bubbles rising in a column of glycerin. The photographs (*a*) through (*e*) were taken at approximately two-second intervals with an interval of 1 to 1-1 2 seconds between (*a*) and (*b*). (*f*) follows (*d*) after 40 sec. The density ratio is 1.21 and the viscosity ratio is 69. The water bubble appears to want to pull into a sphere even and especially at the instant of injection. The spherical shape in (*c*) is nearly perfect. However, there is always a rearward protrusion followed by an extruded thread of water left behind as the bubble rises. A small "capillary bubble" is visible on the water thread in (*c*) and (*d*). The sharp spherical interface at the leading edge and the protruding tail at the trailing edge are persistent. The drop shapes strongly resemble shapes of unstable spherical drops with nonzero interfacial tension which were computed by Koh&Leal [1989] (their Figs 7 and 9), by Pozrikidis [1990] (his Fig 6) and observed by Koh&Leal [1990] (see Fig. 5 in this report). The computed shapes for zero interfacial tension and no diffusion always have intrusions near the trailing edge even when a thread is ejected at the trailing edge. We have the impression that glycerin has been entrained and possibly diffused in the bubble shown in (*e*) and (*f*), as in the thermal drops studied by Griffiths [1986*a*].

In Figure 3 we show a sequence of photographs of a molasses drop falling in glycerin. Diffusion is very slow. Even after vigorous mixing, it takes two days for the small amount of molasses to dissolve completely in the glycerin. Is it possible to find a pair of

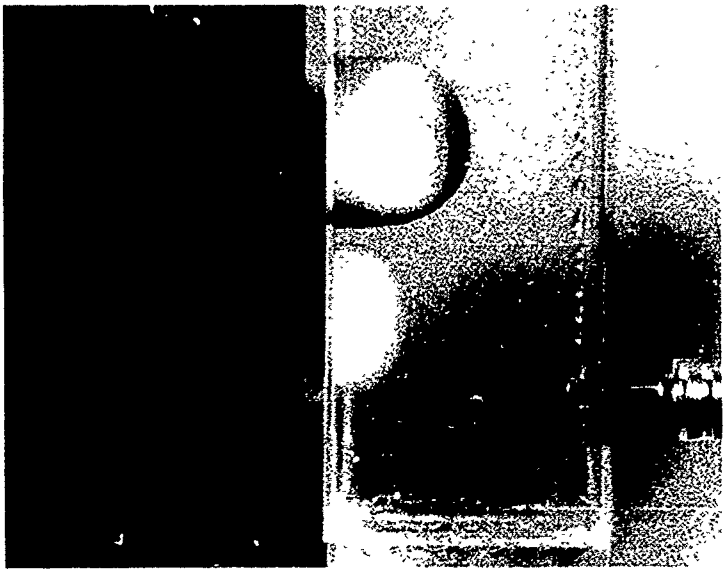


Fig. 2a

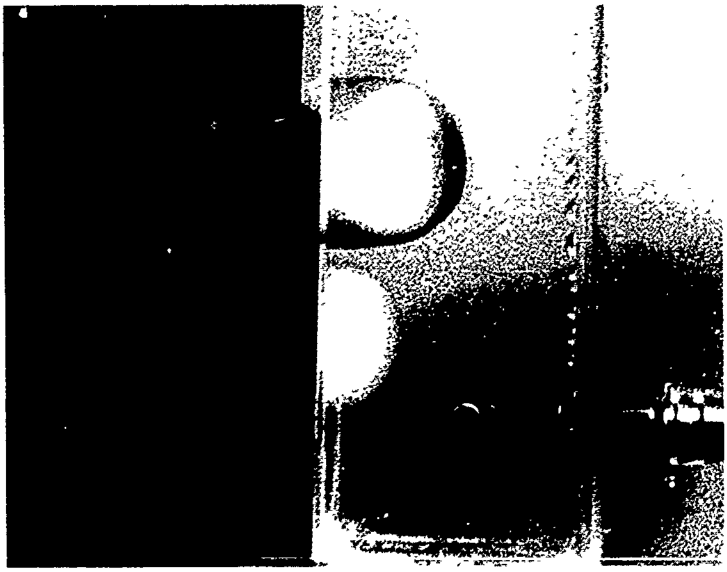
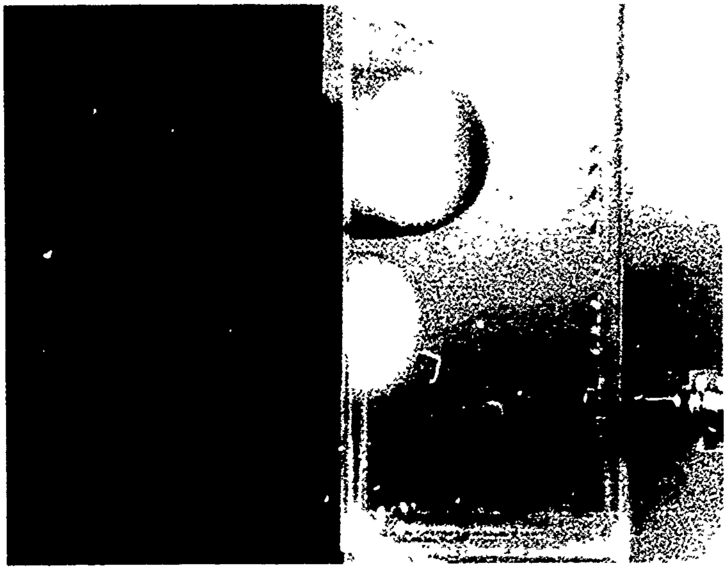


Fig. 2b



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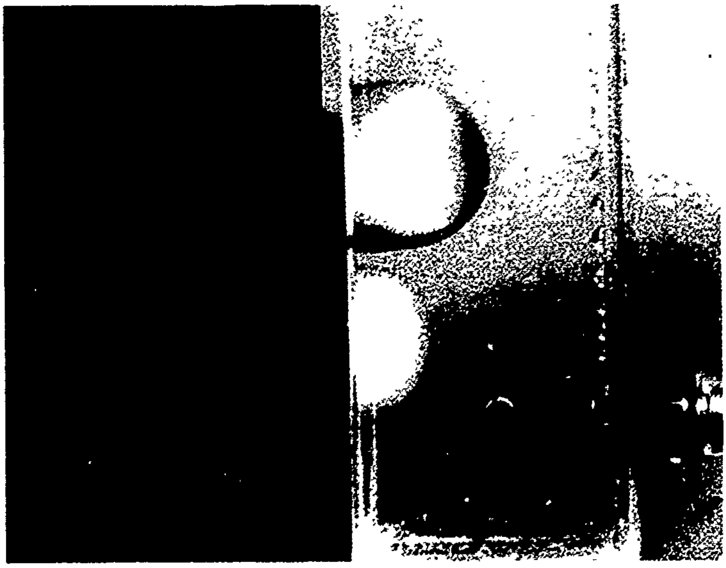


Fig. 2d

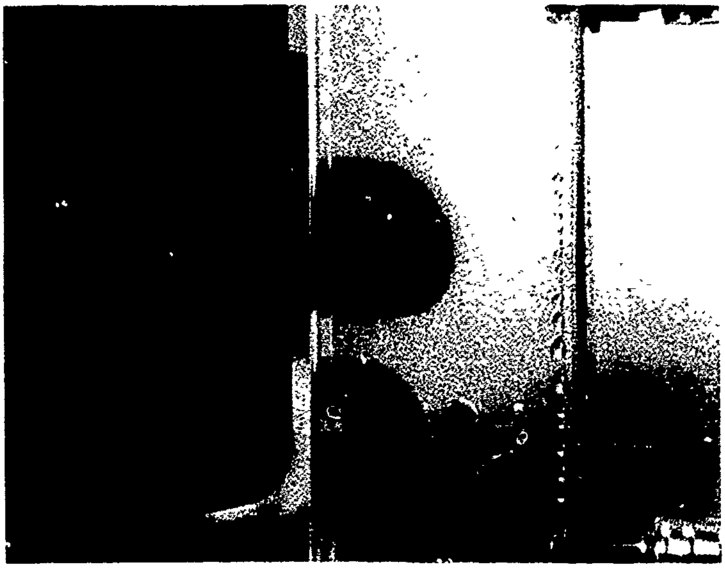


Fig. 2*e*

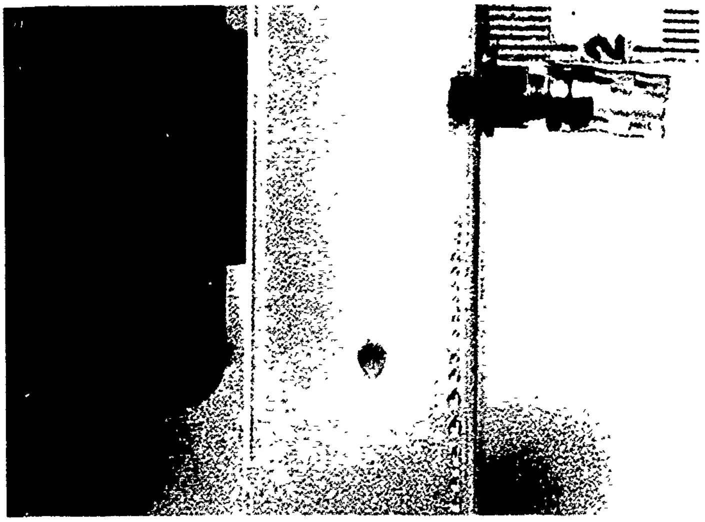


Fig. 2*f*

Fig. 2. – A mixture of molasses and water in glycerin rises slowly The density is nearly matched The essentially "static" configurations in (*a*) through (*c*) possibly suggest action of capillary-like forces. Time on the clock is in seconds: (*a*) 00.98, (*b*) 01.14, (*c*) 01 23, (*d*) 01.99, (*e*) 09.01, (*f*) 15.68.

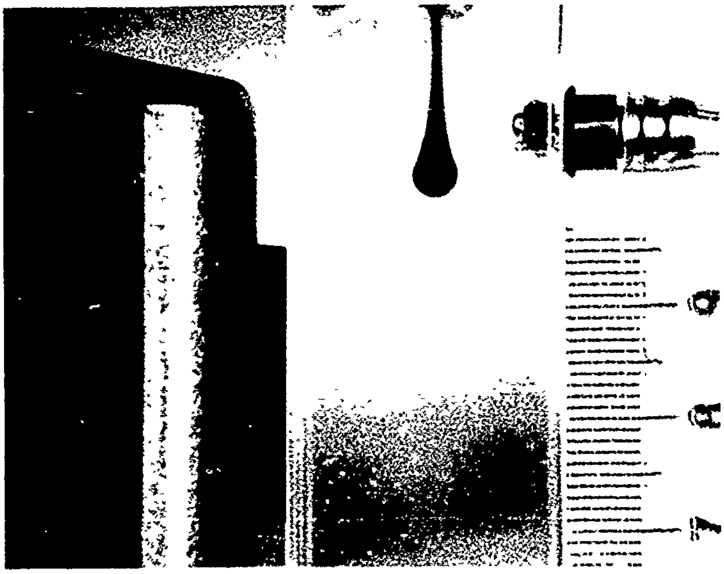


Fig.3 *a*

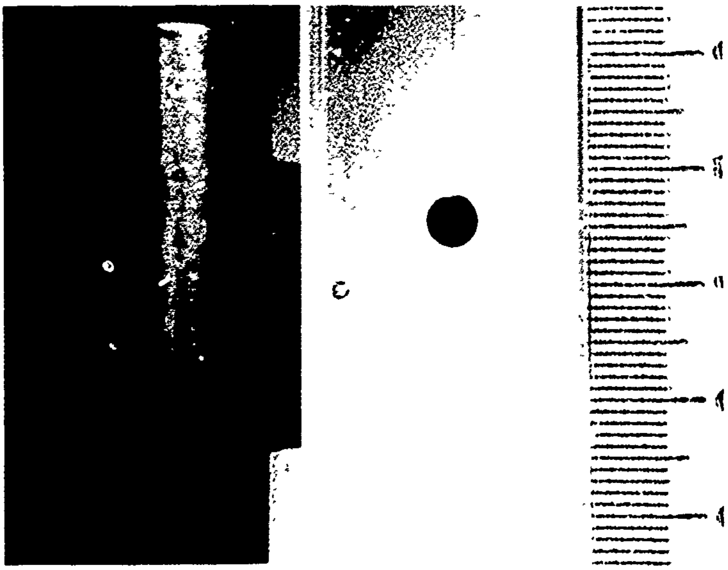


Fig 3 *b*

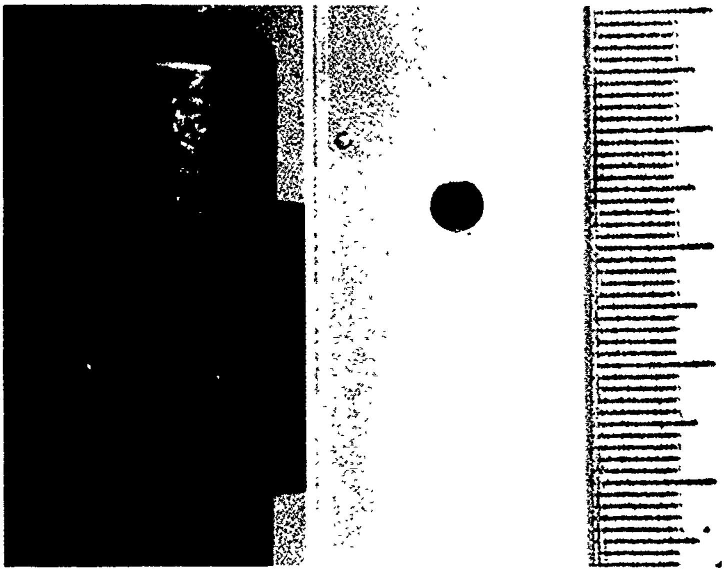


Fig. 3*c*

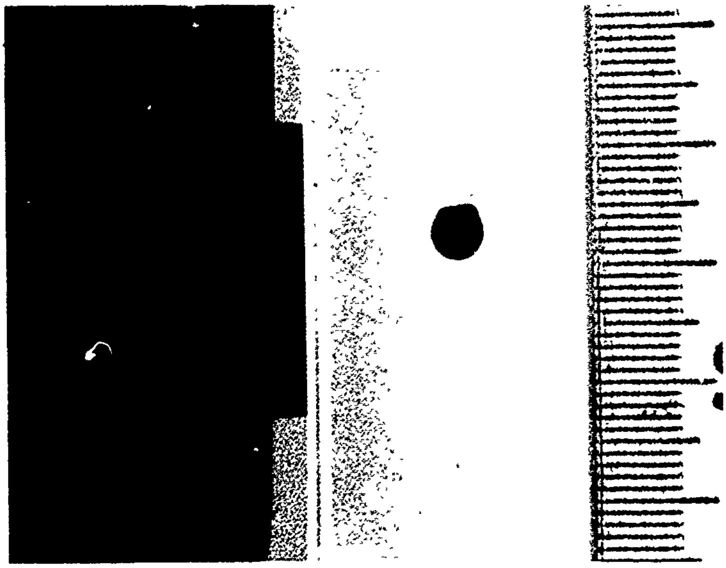


Fig. 3*d*

Fig. 3*e*

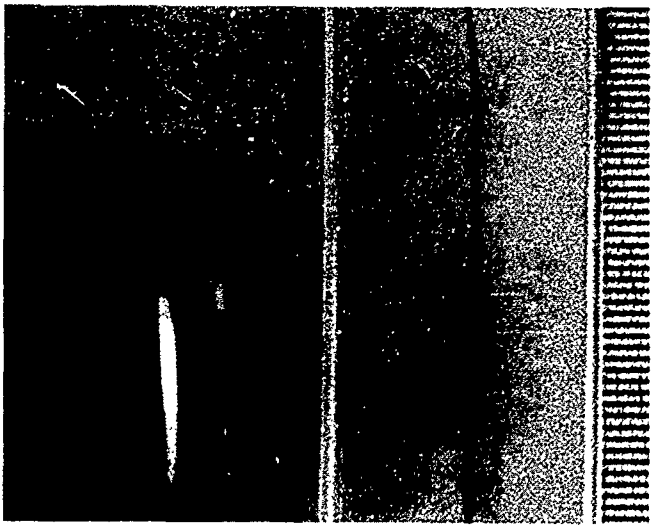


Fig. 3*f*

Fig. 3. — Molasses drops falling in glycerin. The fall is timed in seconds (*a*) 21.61, (*b*) 41.25, (*c*) 45.86, (*d*) 54.34, (*e*) 113.48, (*f*) 203. Frictional drag on the falling drop creates circulation. The drop eats the thread in (*a*), (*b*), (*c*). In (*d*) a kind of spherical cap develops In (*e*) and (*f*) a second molasses drop is monitored. In (*e*) the tail of the drop is breaking. It may break the reform In (*f*) a small "capillary bubble" forms on the molasses thread.

miscible liquids that mix, but mix so slowly that essentially no mixing has taken place over the time of an experiment, or even a lifetime?

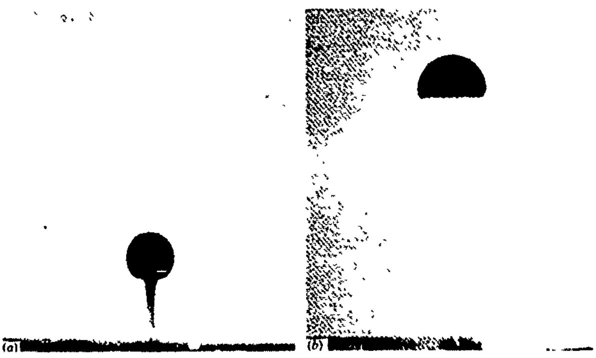


FIGURE 5. Photographs of a thermal in 'Hyvis 30' (silhouetted against a bright background) with $Ra = 312$, $V_0 = 20.5\,\mathrm{cm}^3$. $\Delta T_0 = 48.7°\mathrm{C}$, $\mu_0/\mu_\infty = 0.024$. The initial Reynolds number is $2.8 \times 10^{-5}$. Photographs were taken (*a*) 3 min 30 s and (*b*) 26 min 33 s after injection.

Fig. 4. – Thermal plume of dyed liquid (Griffiths, [1986*a*] © Cambridge University Press) Similar pictures of thermal plumes which resemble those shown in Figure 2 can be found in Griffiths' [1986*b*]. He considers, but rejects, the idea that interfacial tension might play a role in the 22% discrepancy between the observed rise velocity and the velocity predicted by Stokes' law.

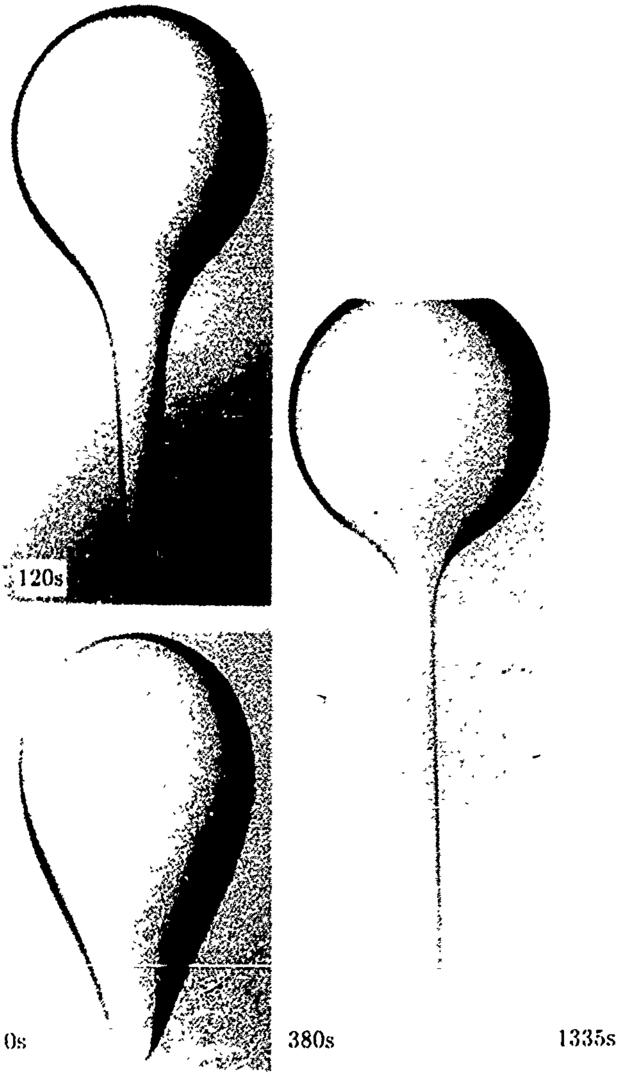


Fig. 5. – (After Koh&Leal [1990] © American Institute of Physics). Unstable spherical drop of 10,000 cs Dow silicone oil ($\mu = 101$ P, $\rho = 0.972\ \mathrm{gm/cm^3}$) in Pale 1,000 oil (oxidized castor oil, $\mu = 391$ P, $\rho = 1.021$)

In Figure 4 we show some photographs of a dyed thermal plume taken by Griffiths [1986].

The first question is to what extent can these drops, bubbles and plumes be described as free surface problems with zero interfacial tension, and no diffusion. The second question is if there are forces due to gradients of density and composition which are active in producing the shape of the interfaces we observe and if there are such forces, how they may be modeled. The third question is when and how should diffusion be entered into the dynamical description.

In Figure 5 we show photographs of Koh & Leal [1990] of an unstable spherical drop of 10,000 cs Dow silicone oil in Pale 1,000 oil.

## 2. History

The idea that there are capillary forces at work in the layer between miscible liquids goes back at least to an 1871 report of J. Bosscha, cited in a paper of Korteweg [1901], and reproduced here. Korteweg, in a footnote on the second page of his famous paper, notes that

1. M. J. Bosscha, in particular, has published, in the proceedings of the 30th of September and the 25th of November 1871 of the Academy of Sciences of Amsterdam 1871/72, #3 and 5, some observations on the very slow motion of a solution in water or in a less concentrated solution; they seem to him to find their most natural explanation in the existence of appreciable capillary forces in the layer between the two liquids, miscible in all proportions.

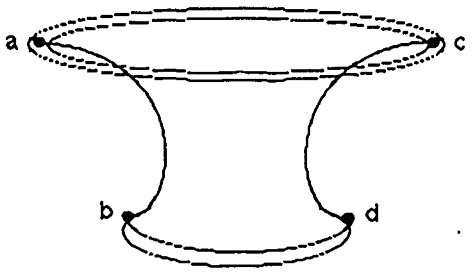
Messieurs J. J. Thomson and H. F. Newall on the contrary attribute to other causes similar phenomena that they have observed (*see* pages 430 and 431 of their article "On the formation of vortex rings by drops falling into liquids and allied phenomena" *Proc. R. Soc.* **39**, 1885, p. 417).

Since the question does not seem to us to be resolved, we believe it useful to publish an appendix to this paper of the French translation of some extracts of the proceedings cited above and of an unedited letter of M. Bosscha treating the same subject. As the particular conditions in which the volume of these "Archives" were published have forbidden us from asking M. Bosscha permission to publish these extracts, we have communicated them without his knowledge at our own respondibility, hoping as well that M. Bosscha will excuse this indiscretion.

## APPENDIX

### Extract of a communication made by M. Bosscha at the Academy of Sciences of Amsterdam, in the session of 30 September 1871

« A test tube, of which the bottom is stretched into a funnel with a fine opening, is partly immersed in water which fills a large cylindrical vessel. When the water in the tube reaches the same height as in the water, one injects a crystal of a soluble substance in the water. The liquid contained in the tube then becomes specifically heavier than the surrounding water and begins to flow in a thin thread. This liquid thread exhibits all the details of a jet of ordinary water, except that the flow is much slower so that one has no need for any artifice to observe directly all the phenomena which accompany it. Some distance from the opening, one sees bulges form themselves which more and more take the form of drops, all of them linked by very thin liquid threads. Soon these threads break and are pulled into the drops which henceforth fall freely. Because of the great resistance which they meet in their fall the small drops thus formed flatten, at the center they form themselves into skull caps, concave on the bottom, which terminate by breaking in their turn, in such a way that each drop is transformed into a ring which enlarges itself more and more and disperses itself slowly, as much by the motion of the liquid as by diffusion. It sometimes happens that a tight ring falls through the already enlarged ring which preceded it; in these conditions a liquid film is carried from the interior boundary of the last large ring (ac), which looks like a known capillary surface, but which contracts itself until at the end the two rings have formed only one.



According to the observations of the author, one can do this experiment with any salt. The experiment works even when one lets flow a less concentrated solution, as long as the difference in the birefringent powers permits one to distinguish between them. If one makes use of a tube of which the bottom is pulled into a fine point toward the interior, one can, by suitably regulating the hydrostatic pressure, make a vertical jet of the liquid from the cylindrical vessel climb in the tube; under these conditions one can also observe separation into small drops, but it is sometimes necessary to tap slightly against the glass to produce the effect.

From a theoretical point of view it seems important to do these experiments with some liquids which combine themselves with a considerable release of heat. I have been able to verify that sulphuric acid and water, or a solution of caustic potash in dilute sulphuric acid tends thus to assume a surface as small as possible. from this it results then that capillary attractions are of an altogether different nature than chemical attraction. »

### Extracts from a letter of M. Bosscha from 22 May, 1901

« The phenomena which I have observed related to the slow flow of one liquid into another, however slow the flow, remain nevertheless phenomena of motion, and the states I have observed are always states of motion. It is only by way of approximation that one can think of thems as states of equilibrium.

> This is why I have always tried to claim some deep scruples that capillary forces *only* produce the clearly defined forms which are taken by the flowing liquid.
>
> But each time that I have repeated the experiment, in other respects very simple, and that I saw the liquid thread give rise to local bulges, as in an ordinary jet of water, and resolve themselves then into small drops which finally becomme rings, my conviction became stronger that capillary action must even play here an important role. What strikes me especially was to see how of the two consecutive rings the higher, smaller one falls through the lower, larger one, and carries clearly in its motion a portion of interior rim of the other, so that between the larger ac and smaller bd a film forms a surface of revolution from it, of which a meridional can very well be the link of a chain.
>
> I returned to this subject later in a discussion relative to the agglutination of particles suspended in liquids. When this question became the subject of one of the sessions of the Academy, I recall that while I was occupying myself with the preceding experiments, I took note of the remarkable experiments of M. Vogelsang on globulites (microscopic drops suspended in a mixture of baum of Canada and carbon sulphide; these drops consist of a supersaturated solution of dissolved sulphur in carbon sulphide).
>
> M. Vogelsang has described (*Arch. Néerl.*, (1), **5**, 166, etc.) the motion of these drops in the liquids, motions such that they approach one another until contact. An attractive action of these drops at appreciable distance cannot be attributed to molecular attraction of the drops themselves. In my opinion one is rather forced to search for a motive force in the liquid. It is thus that I thought to myself that each drop is a center of concentration of sulphur, depleting sulphur from the liquid environment, so that each drop will be surrounded by concentric layers in which the percentage of sulphur poor hydrospheres of neighboring drops come into contact, if there exists in reality a surface tension at the boundary of the two layers of unequal concentrations, it is necessary that the tendency of this surface of separation to become a minimum, brings about the fusion of the layers; this will be caused because some new layers of more packed drops come into contact until at the end the drops touch themselves.
>
> I have thought that there is here a means to explain in an analogous fashion the tendency to agglutination that one can observe with small solid particles suspended in a liquid. These solid particles can more particularly concentrate around themselves certain elements of the liquid in which they are suspended. »

The notion that capillary forces are responsible for the phenomena observed by Bosscha is not shared by Thomson and Newall [1885] who appear to suggest that such phenomena, which they observed independently and apparently without knowledge of Bosscha's work, are associated with instabilities of motion, and not with capillarity. It is refreshing to see the pictures which they draw to represent what they observe, at a time before the taking of photographs of these things was a common practice. Their sketched pictures are art in science, emphasizing the scientifically relevant details, suppressing the others.

J. J. Thomson and H. F. Newall, On the formation of vortex rings by drops falling into liquids, and some allied phenomena, *Proc. R. Soc.* (London) **39**, (1885).

> « If a tube be drawn out into a fine capillary and be filled with sulphuric acid, and held so that its capillary end is just beneath the surface of a column of water, a fine stream of acid flows down; and on it marked beadings appear. Each bead gives rise to a vortex ring, and the rings so formed behave in characteristic manner (*Fig.* 9). Here there seems strong

evidence of a tension between the acid and the water, but the appearances are to be explained by differences of velocity in the stream, brought about by motion in the column of water, or by vibrations communicated to the capillary tube. If the experiment be made with all care to avoid vibration, the stream falls unbroken through a column of 8 inches of water: whilst if a tap be given to the acid tube a break occurs in the stream, in consequence of a momentary stop in the flow of acid, a small bead is formed, and from it a ring. If no care is taken to avoid vibration the beads will follow one another very rapidly. It may be objected that if there existed a surface tension, it would only be when disturbances were communicated that beading would appear. But in such a case, the resolution into drops would be complete, and small spherules would be formed between the larger drops. In fact, however, the connexions between the beadings are fine filaments of acid, so that the beadings are never really separated from one another. We have, moreover, convinced ourselves of the correctness of this explanation, by allowing a stream of cold water with lycopodium powder to flow from a fine tube into a column of slightly warm water; similar cessations in flow and formations of beadings may be observed; the rings are not well formed, but this is to be expected, for the conditions are not nearly so favourable. »

Fig. 6. – (their figure 9)
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In fact the citation does not really tell us what might be the real cause of the capillary-like phenomena seen in their sketch. A theory in which stresses due to gradients of concentration and density are allowed, say the Korteweg's theory, could conceivably give rise both to the capillary phenomena and the deviations from classical capillarity which are observed. Perhaps it is just this thought which motivated Korteweg to remark that "... the question does not seem to us to be resolved ...".

## 3. Dynamic and instantaneous interfacial tension

Freudlich [1926] in his treatise on colloid and capillary chemistry in discussing the methods of measuring interfacial tension between immiscible liquids and the theory of the phenomenon, notes that

> « .., there is little new to be said.... We have only to remember here we are in the end always dealing with solutions. For the one liquid will always be soluble in the other to some degree, however small. Hence the *dynamic* tension of liquids, when first brought into contact, is to be distinguished from the *static* tension, when the two liquids are mutually saturated. Not only do liquids which are not miscible in all proportions have a mutual surface tension; even two completely miscible liquids, before they have united to form one phase, exhibit a dynamic interfacial tension. For we get by careful overlaying of any two liquids a definite meniscus, a jet of one liquid may be generated in another, and so on The tension decreases rapidly during the process of solution, and becomes zero as soon as the two liquids have mixed completely. »

Freudlich [1926] cites the measurements of the dynamic tension by Quinke [1902] of ethyl alcohol in contact with aqueous salt solutions (sulphates of zinc, copper, etc). These two liquids are miscible in all proportions. Quinke used the method of drop weight to make his measurements. In these liquids the drop, as it emerges, does not pass into streaks, but keeps at first its shape. He found values between 0.8 and 3 dyne/cm.

Smith, Van den Ven & Mason [1981] have reported a maximum value of 1 dyne/cm for the force corresponding to a "transient interfacial tension" between a 2,000 cs and a 1 cs silicone oil. According to the authors, these are two mutually soluble liquids whose interdiffusion is sufficiently slow to enable this measurement to be made. They note that

> « In principle there exists between any two separated fluid phases which have a chemical potential difference, an instantaneous interfacial tension which may or may not persist with time. We are unaware of reports in the literature of measurements of interfacial tension between two miscible liquids. »

It is clear that in the case of two liquids miscible in all proportions we are not dealing with an equilibrium situation, there is no equilibrium tension. Rather, we are looking at stress effects due to differences in density and composition and possibly even temperature which influence the positions occupied by interdiffusing fluids. One could imagine that when the gradients of composition are large, as in the boundary layer between two regions of different composition suddenly put into contact, that these stresses give rise to an effect which might be called "transient interfacial tension."

Smith, et al used the Wilhelmy plate method to measure the tension as a function of time, which decreases with time because of diffusion. A solid sample experiences a capillary force P due to the deformed interface which is given by

$$P = 2(l+d)\,S^*\cos\theta \tag{1}$$

where $l$ is the length of the plate, $d$ its thickness, $S^*$ is interfacial tension and $\theta$ the apparent contact angle. Their experimental result is summarized in their Figure 1, reproduced below in Figure 7.

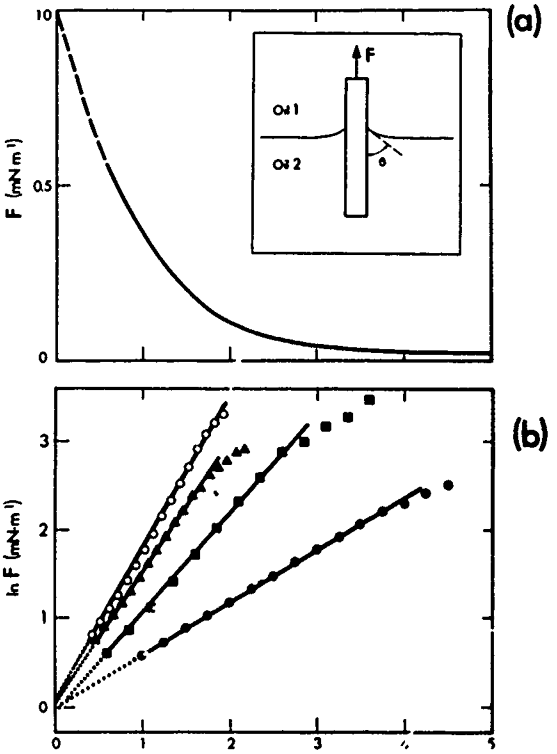

FIG 1. (*a*) Typical decay of capillary force on a Wilhelmy plate for two mutually miscible silicone oils (schematic details of experiment are shown in the inset); (*b*) Logarithm of $F$ vs time, for various experimental runs. The extrapolated force at zero time yields in all cases, $F_0 = 1.0$ mN/m.

Fig. 7. — (after Smith *et al.*)
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They note that a theoretical description of the capillary force per unit length $F = P/2(l+d)$ is possible only if the variation of $S^*$ and $\theta$ with time are known. They measure $F(t)$ in their figure 1, but $S^*(t)$ and $\theta(t)$ are unknown.

Smith, Van den Ven & Mason [1981] present an expression for the chemical potential based on expressions for the free energy in a nonuniform system given by van der Waals [1983], Cahn & Hilliard [1954] writing

$$S^* \propto \int_{-x_0}^{x_0} \left(\frac{\partial\varphi}{\partial x}\right)^2 dx \tag{2}$$

where $S^*$ is the interfacial tension, $\varphi$ is the local composition and $x_0$ is the "interfacial region." The composition is assumed to satisfy a diffusion equation $\varphi_t = D\varphi_{xx}$ with diffusion constant D. If at $t=0_+$, $\varphi=\varphi_+$ for $x>0$ and $\varphi_-$ for $x<0$ and thereafter $\varphi$ is continuous at $x=0$, then

$$\varphi(x,t)=[\varphi_+-\varphi_-]f(\eta), \qquad f(\eta)=\operatorname{erfc}\eta, \qquad \eta=x/2\sqrt{Dt}$$

and S* is proportional to

$$(3) \qquad [\varphi_+-\varphi_-]^2\int_{-x_0}^{x_0}\frac{4}{\pi}\exp(-2\eta^2)\left(\frac{\partial\eta}{\partial x}\right)^2 dx=\frac{2[\varphi_+-\varphi_-]^2}{\pi\sqrt{Dt}}\int_{-\eta_0}^{\eta_0}\exp(-2\eta^2)\,d\eta.$$

At small times the breadth of the diffusion layer scales with $\sqrt{Dt}$. Then the gradient theory (2) leads to a square root singularity for the dynamic tension. A finite tension as $t\to 0$ then implies $\theta\to\pi/2$. Figure 7(*b*) shows that F decays exponentially and does not follow the $t^{-1/2}$ decay that would be required by $F=S^*\cos\theta$ if $\theta$ were constant. It is noteworthy that though the slopes in Figure 7(*b*) vary between 0.6 to 1.4, the extrapolation to zero time does not vary and leads reproducibly to a force of ~1 dyn/cm. They conclude that "... present experiments do indeed confirm that an instantaneous interfacial tension exists between mutually miscible liquids."

The measurements of Quinke [1902] using the drop weight method and those of Smith et al appear to be the only ones so far reported. Smith et al remarked that the Wilhelmy technique appears to be the most sensitive and that other surface tension measuring techniques such as the pendant drop method were found to be unsuitable due to the small magnitude and transient nature of the force involved. I looked at pendant drops of some pairs of miscible liquids. They give rise at early times to shapes similar to, but not the same as, pendant drops of immiscible liquids; compare Figures 8 and 9.

## 4. Generalized incompressibility and Korteweg's theory

It can be argued that the measurement of interfacial tension between miscible liquids is not a viable proposition since there is no such thing as an equilibrium interfacial tension between miscible liquids. The concepts of a dynamical and instantaneous interfacial tension are certainly more useful but they are not fundamental. What is fundamental is the study of the way in which differences of density, composition, and temperature enter into the stress tensor in a fluid mixture. The parameters we shall need to measure are ultimately to be defined by a theory giving the precise nature of general forces that give rise to capillary like phenomena in particular situations. Korteweg's theory, discussed below, is perhaps an example of how such a theory might look. Certainly, the expression (2) is far too special to be useful in a fundamental treatment.

### 4.1. COMPRESSIBLE FLUIDS

Korteweg was motivated on the one hand by the work of van der Waals [1894] who

> « ...has shown by theoretical considerations of great importance that it is very probable that the hypothesis that the discontinuity at the surface of liquid and its vapor is only

Fig. 8a

Fig. 8b

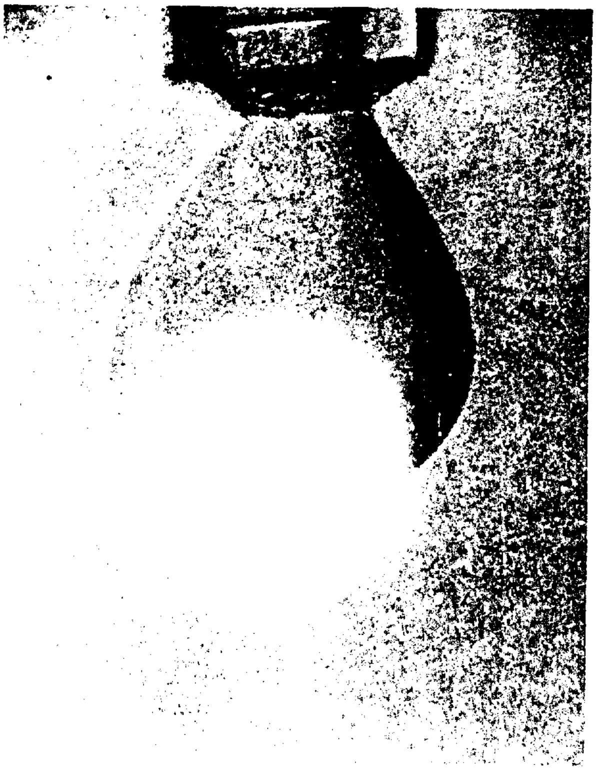

Fig. 8c

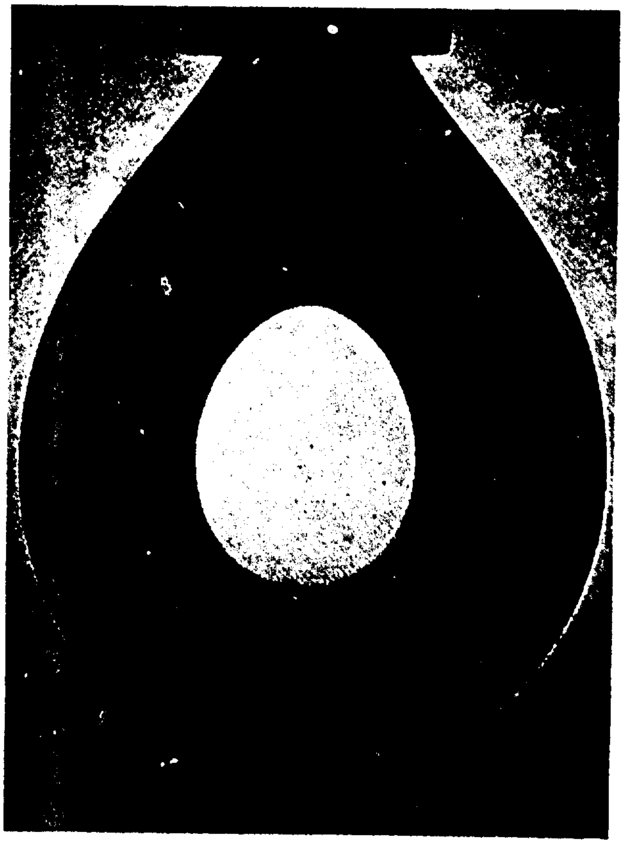

Fig. 9. Profile of a Benzene-water pendant drop

Fig. 8. Mobil 1 synthetic motor oil (0.83 g/cc at 22°C) in mineral oil (0.82 g/cc at 22°C). This looks like a pendant drop due to surface tension (see Fig. 6). The three frames were photographed at four-second intervals. We think that the side drift of the drop is due to convection and other temperature effects induced by the hot lights used for illumination.

> apparent and that there is a layer of transition, very thin to be sure, but of a thickness much larger in ordinary conditions than the radius of the sphere of action of the molecules, and which can even grow indefinitely as one approaches the critical temperature. »

For this problem, Korteweg proposed a continuum approach with a compressible fluid model with a stress $\mathbf{T}^{(1)}$ of the usual Navier-Stokes type plus a part $\mathbf{T}^{(2)}$ depending on density derivatives alone:

$$T_{ij}^{(1)} = -p\,\delta_{ij} + \mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) + \lambda \frac{\partial u_l}{\partial x_l}\delta_{ij} \tag{4}$$

and

$$T_{ij}^{(2)} = (\alpha\nabla^2\rho + \beta\nabla\rho\,.\,\nabla\rho)\,\delta_{ij} + \delta\frac{\partial\rho}{\partial x_i}\frac{\partial\rho}{\partial x_j} + \gamma\frac{\partial^2\rho}{\partial x_i\,\partial x_j} \tag{5}$$

where $p$ and the coefficients $\alpha$, $\beta$, $\delta$, $\gamma$, $\mu$ and $\lambda$ are functions say of the density $\rho$ and temperature $\theta$.

Korteweg showed how his theory reduced to the classical theory of capillarity. He looked at the layer between two smooth surfaces of equal and different density and he calculated the difference in the normal stresses. He found that this difference is proportional to the mean curvature, but only in a certain special sense. For example, the equations of motion using (4) and (5) are satisfied when the velocity is zero and body forces, density and pressure depend only on the radius in spherical coordinates. He finds that the jump of $T_{rr} = \mathbf{e}_r\,.\,\mathbf{T}\,.\,\mathbf{e}_r$ across the layer $r = r_1$ and $r = r_2$ is

$$T_{rr}\Big|_{r_1}^{r_2} = -\int_{r_1}^{r_2}\rho\,b_r\,dr - \frac{2\gamma\rho'}{r}\Big|_{r_1}^{r_2} + 2\int_{r_1}^{r_2}\frac{-\delta + (d\gamma/d\rho)}{r}\rho'^2\,dr \tag{6}$$

where $b_r$ is the radial component of the body force, $b_\theta = b_\varphi = 0$ and $\rho' = d\rho/dr$. According to Truesdell [1965].

> « If we suppose that the shell is a layer of transition between two homogeneous fluids, so that $\rho' = 0$ when $r \leqq r_1$ and when $r \geqq r_2$, the second term on the right-hand side vanishes. To obtain results appropriate to a thin shell of transition, we calculate the limit as $r_1 \to r_0$ and $r_2 \to r_0$. The first integral on the right side vanishes. Under suitable assumptions of smoothness, the remaining integral yields a term proportional to $2S^*/r_0$ (where $S^*$ is the surface tension) as expected from the classical theory of capillarity. »

Actually, to get the classical theory we need to assume a lack of smoothness, that is,

$$\left(-\delta + \frac{d\gamma}{d\rho}\right)\rho'^2 \to \delta(r - r_0) \tag{7}$$

where $\delta(r - r_0)$ is Dirac's delta function. One defect of this derivation of capillarity is that the equations motion, even at equilibrium will not allow the compact support required to put $\rho'\Big|_{r_r}^{r_2}=0$; this is a very small defect. Another problem is that we evidently need to say that $\rho'$ goes to a singularity which looks like the square root of a Dirac measure. I don't know of any physical principle which would lead to such a strong result. A third defect is that the relation of the density gradient theory to the usual molecular interpretation of surface tension, based on the action of cohesive forces at a surface, which are in equilibrium in the bulk, do not seem to have been worked out. Certainly this theory could not apply to the surface tension which exists between density matched immiscible liquids, nor was it meant to do so.

There are a number of interesting papers on Korteweg-type theories for compressible fluids (*see*, for example, Dunn [1986]). These theories rely strongly on thermodynamic arguments for compressible fluids which evidently do not apply to the incompressible fluids under discussion here.

### 4.2. GENERALIZED INCOMPRESSIBLE FLUIDS

On the other hand, Korteweg also thought that his theory might apply to the processes of slow diffusion of miscible incompressible liquids such as were already described in the previously cited account of the experiments of J. Bosscha. He says that

> « Let us suppose ... that one must deal with two liquids miscible in all proportions, or indeed, a solution with variable concentration. In this case it cannot be a question of equilibrium, correctly speaking, before the concentration has by diffusion become equal everywhere. Moreover, in considering diffusion as a very slow process, one can deal with provisional equilibrium, where Eqs. {our (4) and (5) with $u=0$ and $\rho$ replaced by $\varphi$} are satisfied momentarily. In such equilibria, all possible distributions of concentration, satisfying these equations, could rigorously occur, since the distribution at a given moment depends on the initial distribution and the laws of diffusion. »

Provisional equilibrium of drops and bubbles require at least that the density of the mixture be independent of the concentration. Otherwise the density will vary and buoyancy will produce motion.

We did several bubble injection experiments like those described in Figure 1 but with two fluids of matched density. In one case, we added just enough sugar to water to match the density of glycerin. The density-matched sugar solution has a much higher viscosity than glycerin. When injected into the glycerin, the sugar solution sometimes appears to pull into a sphere; more often after a short time it splits into two segments: one rises and one falls. These two segments then take a more pronounced spherical shape. Perhaps this suggests that the spherical shape is more easily obtained by a drop and bubble in motion than by capillary forces at the surface. Glycerin injected into a sugar solution did not pull into a sphere but maintained the thread-like shape it had in the capillary tube. Evidence for capillary type phenomena here was that capillary-like bulges developed on the thread before it lost its identity to diffusion.

We were never completely successful in matching the density and it may be impossible to do so. The problem is that the volume of a mixture of two constituents need not be the same as the sum of the volumes of the two constituents before mixing. For example, small changes of the total volume $V_T$ of a mixture of glycerin and water at 20°C, with a maximum change of 1.1% for a mixture of 60% glycerin by weight, are observed and reported by Segur [1953] in the data shown in figure 10. Suppose that before mixing the volume of water is given by $V_w = m_w/\rho_w$ where $m_w$ is the mass and $V_w$ the volume of water and similarly, for glycerin $V_G = m_G/\rho_G$. After mixing, the density of the mixture is

$$\rho = \frac{m}{V_T} = \frac{m_w + m_G}{V_T} \overset{\text{def}}{=} \gamma_w + \gamma_G = \rho_w \frac{V_w}{V_T} + \rho_G \frac{V_G}{V_T}.$$

Now, if we ignore the small volume change, then

$$(8)_1 \qquad V_T = V_w + V_G$$

and

$$(8)_2 \qquad \rho = \varphi \rho_w + (1 - \varphi) \rho_G.$$

where $\varphi = V_w/V_T$. Equations $(8)_1$ and $(8)_2$ define a simple mixture, linear in the water fraction. This is a good approximation of the actual mixture density with errors of less than 1% over the entire range of concentration $0 \leqq \varphi \leqq 1$. The fact that simple mixtures arise only as an approximation means that the mixture of liquids with the same density will not retain this density after mixing, because of the volume change. Therefore, the density in a diffusion layer may vary from point to point, even though the density on either side of the layer is the same.

There are other measures of composition and concentration. The mass fraction say of liquid A in liquid B, $\hat{\varphi} = m_A/m$ where $m = m_A + m_B$, is a second measure and the mole fraction $\tilde{\varphi} = n_A/n$, $n = n_A + n_B$, where $n_A$ is the number of moles of A, is a third measure.

The relation between these three different volume measures is nonlinear. For example,

$$\hat{\varphi} = \frac{m_A}{m_A + m_B} = \frac{\rho_A V_A}{\rho_A V_A + \rho_B V_B} = \frac{\rho_A \varphi}{\rho_A \varphi + \rho_B (1 - \varphi)}$$

and

$$\hat{\varphi} = \frac{n_A M_A}{n_A M_A + n_B M_B} = \frac{M_A \tilde{\varphi}}{M_A \tilde{\varphi} + M_B (1 - \tilde{\varphi})}$$

where $M_A$ and $M_B$ denote the masses of one mole of constituents A, B respectively.

To allow for the possibility that composition gradients and density gradients can both induce stress, we may generalize Korteweg's formula, writing

$$(9) \quad T_{ij}^{(2)} = \delta_1 \frac{\partial \rho}{\partial x_i} \frac{\partial \rho}{\partial x_j} + \delta_2 \frac{\partial \varphi}{\partial x_i} \frac{\partial \varphi}{\partial x_j} + \gamma_1 \frac{\partial^2 \rho}{\partial x_i \partial x_j} + \gamma_2 \frac{\partial^2 \varphi}{\partial x_i \partial x_j} + \nu \left\{ \frac{\partial \rho}{\partial x_i} \frac{\partial \varphi}{\partial x_j} + \frac{\partial \rho}{\partial x_j} \frac{\partial \varphi}{\partial x_i} \right\}$$

This is an isotropic expression, invariant to a change in the sign of the axis of reference. In fact, it is the most general second order tensor composition of the first and second

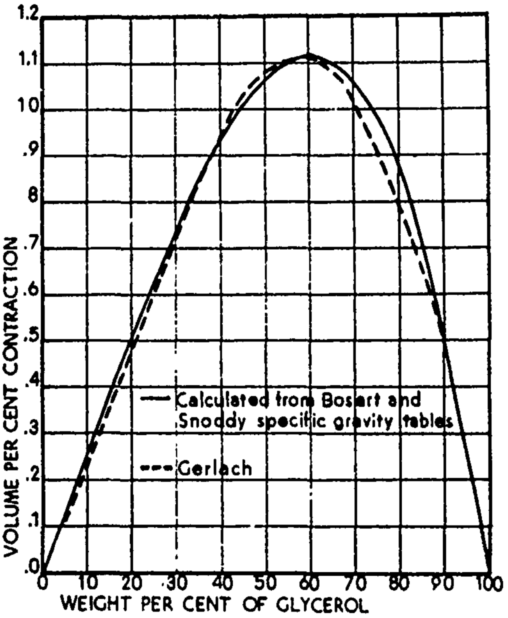

**Figure 7-4.** Contraction of glycerol and water when mixed

TABLE 7-12. VOLUMETRIC CONTRACTION OF GLYCEROL AND WATER WHEN MIXED AT 20°C

Calc. from sp. gr. Data of Bosart and Snoddy

| Parts or % by Wt | | Parts by Vol | | % by Vol | | Sp. Gr. 20/20°C of Soln. Bosart and Snoddy | Vol of 100 g of Soln. at 20°C | % Contraction in Vol |
|---|---|---|---|---|---|---|---|---|
| Glyc. | Water | Glyc. | Water | Glyc. | Water | | | |
| 100 | 0 | 79.278 | 0.0 | 100.00 | 0 | 1.26362 | 79.278 | 0.000 |
| 90 | 10 | 71.350 | 10.018 | 87.69 | 12.31 | 1.23755 | 80.948 | 0.516 |
| 80 | 20 | 63.423 | 20.035 | 75.99 | 24.01 | 1.21090 | 82.730 | 0.872 |
| 75 | 25 | 59.459 | 25.044 | 70.36 | 29.64 | 1.19720 | 83.676 | 0.979 |
| 70 | 30 | 55.495 | 30.053 | 64.87 | 35.13 | 1.18355 | 84.641 | 1.059 |
| 65 | 35 | 51.531 | 35.062 | 59.51 | [illegible].49 | 1.16980 | 85.636 | 1.105 |
| 62 | 38 | 49.153 | 38.067 | 56.36 | 43.64 | 1.16155 | 86.245 | 1.118 |
| 60 | 40 | 47.567 | 40.071 | 54.28 | 45.72 | 1.15605 | 86.655 | 1.122 |
| 59 | 41 | 46.774 | 41.073 | 53.24 | 46.76 | 1.15325 | 86.865 | 1.118 |
| 58 | 42 | 45.981 | 42.074 | 52.22 | 47.78 | 1.15050 | 87.073 | 1.115 |
| 56 | 44 | 44.396 | 44.078 | 50.18 | 49.82 | 1.14500 | 87.491 | 1.111 |
| 54 | 46 | 42.810 | 46.082 | 48.16 | 51.84 | 1.13945 | 87.917 | 1.097 |
| 52 | 48 | 41.225 | 48.085 | 46.16 | 53.84 | 1.13395 | 88.344 | 1.082 |
| 50 | 50 | 39.639 | 50.089 | 44.18 | 55.82 | 1.12845 | 88.774 | 1.063 |
| 40 | 60 | 31.711 | 60.106 | 34.54 | 65.46 | 1.10135 | 90.959 | 0.934 |
| 30 | 70 | 23.783 | 70.124 | 25.33 | 74.67 | 1.07470 | 93.214 | 0.738 |
| 20 | 80 | 15.856 | 80.142 | 16.52 | 83.48 | 1.04880 | 95.516 | 0.502 |
| 10 | 90 | 7.929 | 90.160 | 8.08 | 91.92 | 1.02395 | 97.834 | 0.260 |
| 0 | 100 | 0.0 | 100.177 | 0.00 | 100.00 | 1.00000 | 100.177 | 0.000 |

Calculations: Density of water at 20°C = 0.99823.

Density of 100% glycerol at 20°C = 1.26138.

$$\text{Volume of liquid} = \text{Wt/Density} = \frac{\text{Wt} \div \text{Density of water}}{\text{Sp. gr. of liquid.}}.$$

Fig. 10. – (After Segur [1953] © Glycerol, Reinhold). Volume contraction of glycerin and water The graph of figure 7.4 and the 6th column of table 7.12 show that the simple mixture Eq. (8) holds to within an accuracy of about one percent.

gradients of $\rho$ and $\varphi$. We allow $\delta_1$, $\delta_2$, $\gamma_1$, $\gamma_2$, $\nu$ to depend on $\rho$, $\varphi$ and the temperature $\theta$.

It is necessary to emphasize and to explain what we mean when we say that we are here operating in the frame of incompressible fluids. We do not mean that the density is a constant. In fact we like to assume that there is an equation of state

$$\rho=\rho(\varphi, \theta) \tag{10}$$

so that the density depends on composition and temperature, which may vary with position and time. By an incompressible fluid we lean that the density cannot be changed by pressure; the pressure does not have an equation of state. The pressure is determined by the motion; in a system of equations with $n-1$ unknowns, it is the $n$-th unknown.

The equation of state (10) implies that even though the fluid is incompressible to squeezing, the velocity field is not divergence free. Indeed

$$\frac{d\rho}{dt}=\rho_\theta\frac{d\theta}{dt}+\rho_\varphi\frac{d\varphi}{dt}=-\rho\,\mathrm{div}\,\mathbf{u}. \tag{11}$$

where

$$\frac{d}{dt}=\frac{\partial}{\partial t}+\mathbf{u}.\nabla, \qquad \rho_\theta=\frac{\partial\rho}{\partial\theta}, \qquad \rho_\varphi=\frac{\partial\rho}{\partial\varphi}.$$

We have in general seven unknowns ($\mathbf{u}$, $p$, $\rho$, $\theta$, $\varphi$) and seven equations counted as follows: Equations (10) and (11) are two equations. The conservation of momentum gives three more equations

$$\rho\frac{d\mathbf{u}}{dt}=-\nabla p+2\,\mathrm{div}(\mu\,\mathbf{D}[\mathbf{u}])+\nabla\lambda\,\mathrm{div}\,\mathbf{u}+\mathrm{div}\,\mathbf{T}^{(2)}+\rho\,\mathbf{g}. \tag{12}$$

where $\mu$ and $\lambda$ depend on $\theta$ and $\varphi$ and $\mathrm{div}\,\mathbf{T}^{(2)}$ is a composition of derivatives of $\rho$ and $\varphi$. Two more equations can be found in diffusion equations for $\theta$ and $\varphi$:

$$\frac{d\theta}{dt}=\mathrm{div}(\kappa\nabla\theta)+\Phi, \tag{13}$$

where $\kappa$ is the thermal diffusivity and $\Phi$ is proportional to the dissipation function $(T^{(1)}_{ij}+T^{(2)}_{ij})\,u_{i,j}$ and

$$\frac{d\varphi}{dt}=\mathrm{div}(D\nabla\varphi), \tag{14}$$

where D is a diffusion coefficient.

Yih [1965] has given an interesting discussion of the effects of diffusivities on gravitational instability in our frame of incompressibility in which $\mathrm{div}\,\mathbf{u}\neq 0$ is allowed. [I changed Yih's notation (C, T) for solute density and temperature, to ($\gamma$, $\theta$)]. He was interested in dilute solutions, say salt water, and worked with $\gamma=m_A/V_T$, where $m_A$ is the mass of solute, a small fraction of the total mass, and $m_B = m - m_A$ is the mass of the solvent and $V_T$ the volume of the mixture. Of course, there were no Korteweg-like terms in his analysis. Without giving any derivation he writes that

$$\frac{d\theta}{dt} + \theta \operatorname{div} \mathbf{u} = \operatorname{div}(\kappa \nabla \theta) + \Phi \tag{15}$$

but neglects $\Phi$, and

$$\frac{d\gamma}{dt} + \gamma \operatorname{div} \mathbf{u} = \operatorname{div}(\kappa' \nabla \gamma). \tag{16}$$

He writes two forms for the continuity Eq. (11) and

$$\frac{d\rho}{dt} + \rho \operatorname{div} \mathbf{u} = \operatorname{div}(\kappa' \nabla \gamma) \tag{17}$$

this last form again without derivation. He argues, I think incorrectly, that if (11) is adopted $\operatorname{div} \mathbf{u}$ is not the volume expansion, and he proceeds to work with (17), eventually putting $\operatorname{div} \mathbf{u} = 0$ as an approximation.

Eq. (11) is certainly a correct statement which follows rigorously from the transport theorem and the statement that the total mass in a material volume $\Omega$ across which no mass passes is conserved. The same argument, which requires that we differentiate the Jacobian of the transformation of volumes, shows that $\operatorname{div} \mathbf{u}$ is the volume expansion. If we now state, for example, that $\gamma$ is also conserved if there is no flux of solute across the boundary of $\Omega$, then

$$\frac{d}{dt} \int_{\Omega} \gamma \, d\Omega = - \int_{\partial\Omega} \mathbf{q}_{\gamma} \cdot \mathbf{n} \, ds \tag{18}$$

where $\mathbf{q}_{\gamma}$ is the flux of $\gamma$ and if we let it be given by Fick's law $\mathbf{q}_{\gamma} = -\kappa' \nabla \gamma$, then (16) follows by the usual arguments. The total mass of solute plus solvent is conserved in $\Omega$, but solute and solvent diffuse in and out of $\Omega$.

I can make sense of (17) if I imagine that $\mathbf{u}$ is the solvent velocity and $\Omega$ a "material" volume of solvent in which the total mass is not conserved. Since I wish to use the $\mathbf{u}(\mathbf{x}, t)$ which I may actually measure, I will not use (17).

The Eq. (15) for $\theta$ also follows from a conservation argument in which we suppose, without justification, that the temperature is conserved in the absence of heat conduction and frictional heating:

$$\frac{d}{dt} \int_{\Omega} \theta \, d\Omega = \int_{\Omega} \Phi \, d\Omega - \int_{\partial\Omega} \mathbf{q}_{\theta} \cdot \mathbf{n} \, ds \tag{19}$$

where $\mathbf{q}_{\theta} = -\kappa \nabla \theta$. This statement of conservation is not a physical principle and it seems to be in conflict with the balance of energy. The energy equation for incompressible mixtures in which the pressure is a dynamical variable has not yet been worked out.

We may work with the volume fraction $\varphi = V_A/V_T$ which is related to $\gamma = m_A/V_T = \rho_A \varphi$. We have useful simplifications under isothermal conditions in which we may suppose $\rho = \rho(\varphi) = \rho_A \varphi + \rho_B(1-\varphi)$ to a good approximation, with constant values for $\rho_A$ and $\rho_B$.

Then equation (16) reduces to

$$\frac{d\varphi}{dt} + \varphi \operatorname{div} \mathbf{u} = \operatorname{div}(\mathrm{D}\, \nabla\varphi) \tag{20}$$

replacing (14). And

$$\mathbf{T}^{(2)}_{ij} = \hat{\delta} \frac{\partial\varphi}{\partial x_i} \frac{\partial\varphi}{\partial x_j} + \hat{\gamma} \frac{\partial^2 \varphi}{\partial x_i \partial x_j} \tag{21}$$

$$\hat{\delta} = \delta_1 \rho_\varphi^2 + \delta_2 + 2\nu\rho_\varphi + \gamma_1 \rho_{\varphi\varphi} \quad \text{and} \quad \hat{\gamma} = \gamma_1 \rho_\varphi + \gamma_2. \tag{22}$$

The governing equations are

$$\rho_\varphi \frac{d\varphi}{dt} + \rho \operatorname{div} \mathbf{u} = 0, \tag{23}$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p + 2 \operatorname{div}(\mu \mathbf{D}[\mathbf{u}]) + \nabla\lambda \operatorname{div} \mathbf{u} + \operatorname{div} \mathbf{T}^{(2)} + \rho \mathbf{g} \tag{24}$$

with $\mathbf{T}^{(2)}$ given by (21), and (20) governs diffusion. If we suppose that $\rho$ is a known function of $\varphi$, say a simple mixture (8), then (23), (24) and (20) are five equations for $\mathbf{u}$, $\varphi$, $p$.

Another diffusion equation for the volume fraction $\varepsilon = 1 - \varphi = V_B/V_T$ follows from the same argument $d\varepsilon/dt + \varepsilon \operatorname{div} \mathbf{u} = \operatorname{div}(\mathrm{D}' \nabla\varepsilon)$, relating D and D'. Of course, generally $\mathrm{D}' \neq \mathrm{D}$, glycerin does not diffuse into water at the same rate that water diffuses into glycerin.

## 5. Motionless solutions and steady solutions

Motionless solutions with $\mathbf{u} = 0$ can persist only when $\operatorname{curl}(d\mathbf{u}/dt) = 0$. We can form an expression for this by taking the curl of (12). This leads to the vorticity equations for the incompressible Korteweg equation. If, for simplicity, $\delta_1$, $\delta_2$, $\gamma_1$, $\gamma_2$ and $\nu$ in (9) are assumed to be constants, then

$$\begin{aligned} \nabla\rho \wedge \frac{d\mathbf{u}}{dt} - \rho \operatorname{curl} \frac{d\mathbf{u}}{dt} - 2 \operatorname{curl}(\mu \mathbf{D}[\mathbf{u}]) + \mathbf{g} \wedge \nabla\rho \\ + \delta_1 \nabla\rho \wedge \nabla(\nabla^2 \rho) + \delta_2 \nabla\varphi \wedge \nabla(\nabla^2 \varphi) + \nu[\nabla\rho \wedge \nabla(\nabla^2 \varphi) + \nabla\varphi \wedge \nabla(\nabla^2 \rho)] = 0. \end{aligned} \tag{25}$$

In general motionless solutions require $\mathbf{g} \wedge \nabla\rho = 0$ so that $\nabla\rho$ is parallel to gravity or is zero due to density matching. In the first case $\rho = \rho(z, t)$ and if $\rho = \rho(\varphi)$ is a function $\varphi$ alone, then $\varphi = \varphi(z, t)$ is determined by the diffusion equation. We can imagine that $\rho(\varphi)$ is given by (8). Then $\nabla\rho = [\![\rho]\!] \nabla\varphi$ where $[\![\rho]\!] = \rho_A - \rho_B$. Given this simple mixture equation, the reader can return to (25) with $\varphi=\varphi(z, t)$ and find a nonlinear equation for $\rho(z, t)$ in a static stratification.

If we imagine that density matching is possible, that $\rho(\varphi)=\rho_c=\varphi\rho_A+(1-\varphi)\rho_B$, with $\rho_A=\rho_B$, then motionless solutions exist only if

$$\nabla\varphi \wedge \nabla(\nabla^2\varphi)=0. \tag{26}$$

This works for vertical stratification $\varphi=\varphi(z, t)$ and for radial stratification in spherical polar coordinates.

Steady solutions of (20), (21), (23) and (24) can be expected whenever the boundary data is steady and suitable. For exemple, we could find the steady solution for plane Couette flow between parallel plates when the bottom plate is stationary and constant $\varphi$ is prescribed there, and the top plate moves parallel to itself with constant speed and $\varphi$ is another constant there. The stability problem for a motionless solution with $\rho(\varphi)$ greater below (Korteweg-Benard problem) has some interesting features. A general elementary mathematical formulation of the aforementioned problems can be found in the forthcoming paper by Galdi, Joseph, Preziosi & Rionero [1991].

## 6. Falling drops, rising bubbles and plumes

A basic and basically unsolved problem of fluid dynamics is to determine the evolution of rising bubbles and falling drops of one miscible liquid in another. This problem is unsteady as long as diffusion operates. An important question is whether it is necessary to introduce a stress depending on gradients of concentration, temperature and density in our equations to get results which agree with experiments like those shown in Figures 1, 2, 3, 4, 6, 7.

One method for doing such problems is to imagine that diffusion is so slow that it can be neglected. Then the problem is treated as a free interface problem, using the usual jump conditions at the interface, except that the interfacial tension is put to zero. This is the method followed by Kojima, *et al.* [1984], Koh & Leal [1989] and Pozrikidis [1990]. However, if the interface was really that sharp, the gradients of composition, density and temperature might be expected to induce strong capillary-like stress effects across the interface. One question is whether it is necessary to introduce such gradient stresses to explain the shape of drops, bubbles and plumes shown here and elsewhere. Another question, already framed, is how and when to take into account the effects of diffusion.

One can argue about all this using the water bubble in glycerin shown in Figure 1 as an example. We dont't know what the streamline pattern around the water bubble might be, but perhaps it is like the Hadamard-Rybczynski bubble with a tail.

As the bubble rises, its leading edge is pushed into fresh glycerin. This, together with the circulation inside the bubble which brings fresh water up to the leading edge, generates the sharpest gradients there with weaker gradients at the trailing edge. Whether or not the Korteweg terms are actually important in sustaining the spherical shape we see at

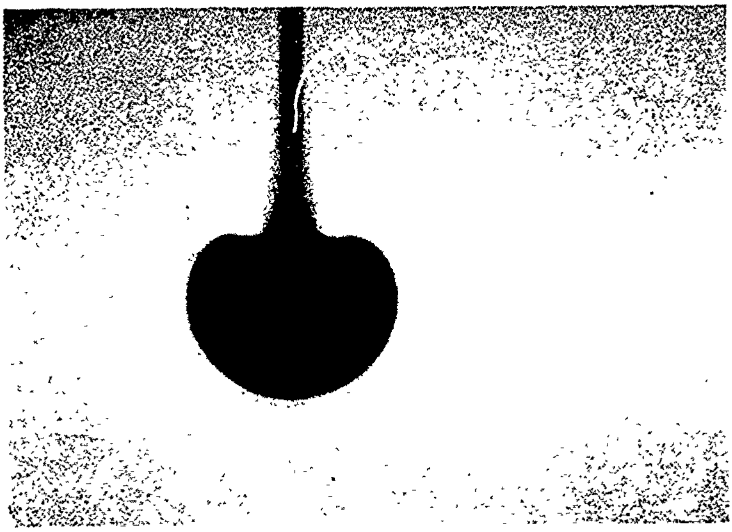

Fig. 11 *a*

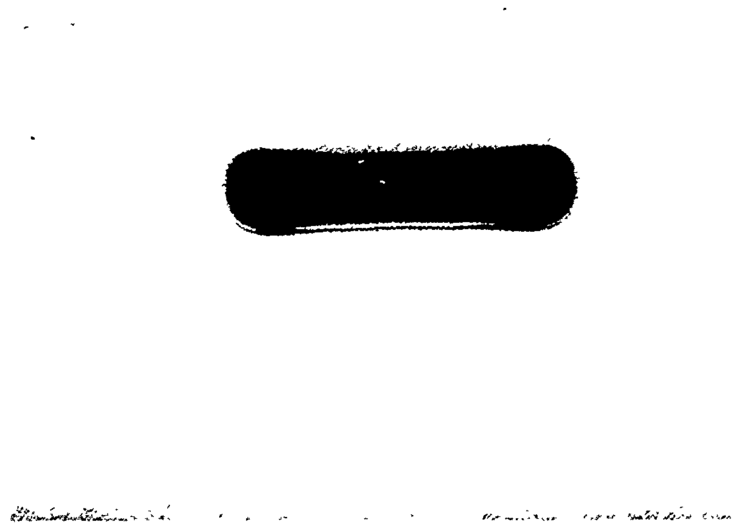

Fig. 11 *b*

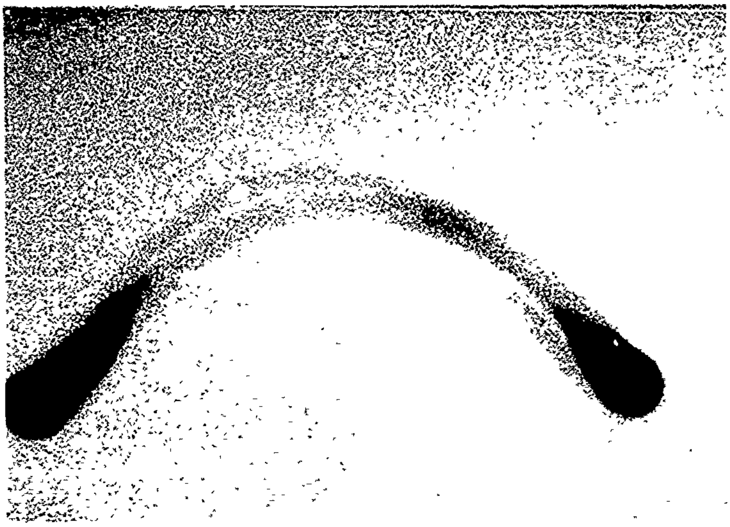

Fig. 11 *c*

Fig. 11 *d*

Fig. 11 – (After Kojima, Hinch&Acrivos, [1984] © American Institute of Physics) Falling drops of aqueous corn syrup of density 1.329 g/cm$^3$ and viscosity 3.9. Poise into aqueous corn syrup of density 1.264 g/cm$^3$ and viscosity 0.51 Poise. (*a*) A depression forms at the rear stagnation point, (*b*) a vortex ring forms, (*c*) the ring is unstable. (*d*) (after Joseph, Renardy, Baumann&Mohr [1991]). An unstable vortex ring of silicone oil falling in safflower oil. The interfacial tension is 1.68 dyn/cm.

the leading edge of the water bubble through the whole 48 seconds of its rise is something I would like to know.

Kojima *et al.* [1984] presented data for falling drops of miscible liquids, *see* Figure 11 (*a*), (*b*) and (*c*), and they carried out an analysis of the problem at vanishing Reynolds numbers. They say that

> « ... Under the assumptions of zero interfacial tension and creeping flow, the theory provides a qualitative description for the initial stages of the drop evolution ... but is unable to account for the observed drop expansion during latter stages of deformation ... On the other hand, if small inertial effects are retained in the analysis, the theory predicts that a slender open fluid torus possessing an arbitrary cross-sectional geometry will expand without change of shape to first order in Reynolds number. Quantitative comparisons of theoretically predicted rates of expansion with experimental measurements suggest the possible existence of a small, time-dependent interfacial tension across the drop interface. »

The reader may compare the unstable miscible vortex ring shown in Figure 11 (*c*) with the unstable immiscible vortex ring shown in Figure 11 (*d*).

The argument just given could conceivably be applied to thermal plumes; as a plume rises its leading edge pushes always into a freshly cold part of the liquid. The circulations in the plume could act to bring hot liquid to the leading edge giving rise to sharp gradients of temperature and density there. Thermals, like buoyant miscible bubbles, take on shapes which may be influenced by stresses associated with thermally induced density gradients (see *Figs.* 4, 12 and 13).

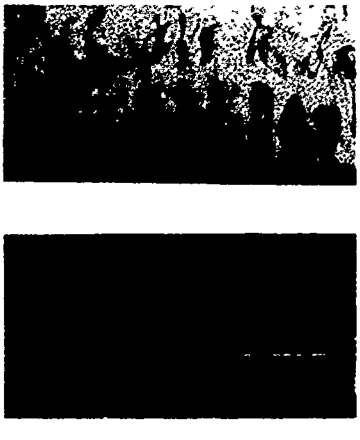

Fig. 12. – Thermal plumes in water (Sparrow, Husar&Goldstein [1970])

Fig. 13. -- (After Kojima, Hinc&Acrivos,1984).
Cold drop initially – 7°C falls into the same liquid initially at 21°C

A thermal drop (*Fig.* 13) was created by Kojima, Hinch and Acrivos [1984].

> « ... by using the same fluid for the drop as for the bulk medium but at a sufficiently low temperature such that the density difference was large enough for the drop to fall in the continuum under the force of gravity. Under these conditions, the effect of the interfacial tension should be negligible, since the authors are unaware of reports in the literature which suggests that a time dependent interfacial tension exists between two identical fluids having different temperature. »

A comparison of thermal plumes and drops shows a similar structure. The plume shown in Figure 4 has a less diffuse structure.

Thermally induced density gradients will be sharper in relatively viscous drops and plumes which are poor head conductors and have large coefficients $d\rho/d\theta$ of thermal expansion. I do not know of any reason to reject the possible action of thermally induced gradient stresses in some of these fluids.

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*Note added in proof.* – An interesting calculation similar to the one by Smith *et al.* [1981], has come to my attention (T. Davis, A theory of tension at a miscible displacement front, *in* Numerical Simulation and Oil Recovery, M. Wheeler Ed., *I.M.A.*, **2**, Springer-Verlag, 1988). Davis calculates the magnitude and rate of reduction of the tension by diffusive mixing of the zone of contact of miscible liquids He suggests that instabilities in miscible frontal displacement may be similar to those in ultralow tension immiscible frontal displacement, with the added caveat that in the miscible process the tension decreases continuously with time

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