Interfacial tension between miscible liquids

Daniel D. Joseph and Howard H. Hu

Department of Aerospace Engineering and Mechanics

University of Minnesota

Minneapolis, MN55455

July 1991

Abstract

We study some basic problems of fluid dynamics of two incompressible miscible liquids modeled as a simple mixture in which the volume of the mixture does not change on mixing. In general, the expansion $\Delta=$div$\mathbf{u}$ in these problems does not vanish. The velocity in such a mixture can be decomposed into a solenoidal and an expansion part. The expansion velocity is induced by diffusion which is proportional to the gradient of the volume fraction in a simple mixture. The expansion can be large at certain times and places. We have carried out an analysis of transient or dynamic interfacial tension for the problem of smoothing of an initial discontinuity of composition across a plane and spherical surface. We find no jump in the mean normal stress across a plane layer but there is a jump proportional to the curvature across the spherical surface. The dynamic tension at the spherical interface decays as $t^{-1/2}$; it has two terms, one term arises from the Korteweg stress and it gives rise to a stress opposing the internal pressure as in the case of equilibrium tension if the Korteweg coefficient has the appropriate sign. The other term arises from the expansion velocity and is proportional to the rate of change of viscosity with volume fraction. This term has the wrong sign for interfacial tension in the case of glycerin and water solutions but has the right sign when the light fluid is more viscous.

1. Introduction

In this paper we study some basic problems of fluid dynamics of two incompressible miscible liquids modeled as a simple mixture in which the density of the mixture is connected to the densities of the two constituents by a linear relation in the volume fraction. Since the density of such a mixture of incompressible liquids is changed by diffusion, the expansion $\Delta=\text{div}\mathbf{u}$ does not vanish in general. The velocity in such a mixture can be decomposed into a solenoidal and an expansion part. The expansion velocity is induced by diffusion which is proportional to the gradient of the volume fraction in a simple mixture. We find that the expansion velocity is always important where the gradients of the volume fraction are sufficiently great, most especially at early times in the mixing layer arising from the smoothing of a initial plane or spherical discontinuity of composition. Another case and place where $\text{div}\mathbf{u}=0$ may be a bad approximation are in driven problems of mixing layer where gradients of composition (or volume fraction) can be maintained in a competition between convection and diffusion.

Dynamical effects can arise in thin mixing layers where the gradients of composition are large. This possibility was already recognized in discussions given by Korteweg [1901] in which he proposes a constitutive equation which includes the stresses induced by gradients of composition which could give rise to effects which mimic surface tension in regions where the gradients are large. The small but interesting history of thought about ersatz interfacial tension in diffusing liquids is given in a paper by Joseph [1990]. The presence of sharp interface in slow diffusion in rising bubbles of water in glycerin is reported there. The shape of such interfaces resemble familiar shapes which can be seen in immiscible liquids. A similar parallel description of drops of miscible and immiscible liquids occurs in the evolution of the falling drops into a vortex ring (Baumann, Joseph, Mohr, Renardy [1991]). Of particular interest is a membrane which

spans the ring and must rupture before a free ring is formed. Such a membrane on a 9/10 glycerin-water ring falling in a 3/2 glycerin -water solution appears in panel e of Fig 1 in the paper by Arecchi, Buah-Bassuah, Francini, Perez-Garcia and Quercioli [1989]. It is hard to explain this membrane without acknowledging some type of interfacial tension. A typical formulation for finding the motion and shapes of miscible drops like the one used by Kojima, Hinch and Acrivos [1984] which uses div**u**=0 in each fluid and classical interface conditions misses out on slow diffusion on the one hand and gradient stresses on the other.

More recently it has been suggested by Barkey and Laporte [1990] that morphological instabilities observed in electrochemical deposition could have their origins in the fields and interfacial dynamics that drive growth with diffusion controlled structure observed on a scale of microns, corresponding to the mass-transfer boundary layer thickness. In another recent study Garik, Hetrick, Orr, Barkey and Ben-Jacob [1991]

" ... reported on the stability of the interface between to miscible fluids of closely matching viscosities when one is driven into the other. For the case where the fluids differ only in solute concentration, we find that spontaneous cellular convective mixing can develop. We suggest that this interfacial patterning is a surface tension effect distinct from viscous fingering; the latter can occur simultaneously. ... On the basis of the above experimental results, we hypothesize that the global morphology of depositional growth, i.e., the number of branches, the stability of the branch tips, and the way it fills space (its "dimension") is determined by the hydrodynamic stability of the interface between the depleted fluid near the growth and the bulk fluid *provided* the gradient is *sufficiently sharp* to provide an effective liquid-liquid interface. Since leading edges grow fastest, hydrodynamic modulation of the liquid-liquid interface à la Hele-Shaw would determine branch position, just as cellular mixing will.
In electrodeposition the existence of a sharp gradient sustained by the growing deposit is experimentally supported."

We have carried out an analysis of transient or dynamic interfacial tension for the problem of smoothing of an initial discontinuity of composition across a plane and spherical surface. The idea is to evaluate the jump in the normal stress across the mixing layer which in this problem reduces to a jump in the mean normal stress (the pressure).

We find no such jump across a plane layer but there is a jump proportional to the curvature across the spherical surface. The dynamic tension at the spherical interface is proportional to $\sqrt{D/t}$ where $D=O(10^{-6}$ cm^2/sec) and t is the time. There are two terms in the expression (7.10) for the interfacial tension; one term arises from the Korteweg stress and it gives rise to a stress opposing the internal pressure as in the case of equilibrium pressure if the Korteweg coefficient has the appropriate sign. A second term arises from the expansion velocity and is proportional to the rate of change of viscosity with volume fraction. This term has the wrong sign for interfacial tension in the case of glycerin and water solutions but has the right sign when the light fluid is more viscous.

2. Mass balance and diffusion

Recently Joseph [1990] has reconsidered the equations of fluid dynamics of two incompressible miscible liquids with gradient stresses. The density of incompressible fluids can vary with concentration ϕ and temperature, but not with pressure. The velocity field $\mathbf{u}$ of such incompressible fluids is not in general solenoidal, div$\mathbf{u}\neq0$. A conservation form of the left hand side of the diffusion equation which differs from the usual substantial derivative of ϕ by the term ϕdiv$\mathbf{u}$, is implied by requiring that the mass per unit total volume of one of the liquids in a material is conserved in the absence of diffusion. Suppose that γ is the density of one liquid per unit total material volume V, $\gamma = m_\gamma/V$ where m_γ is the mass of γ. Then

$$\frac{d}{dt} \int_{V(t)} \gamma \, dV = - \int_{\partial V} \mathbf{q}_\gamma \cdot \mathbf{n} \, dS \,, \tag{2.1}$$

says that the mass of γ in V can change only by diffusion across the boundary of V. In the usual way we find that

$$\frac{d\gamma}{dt} + \gamma \, \text{div}\mathbf{u} = - \, \text{div} \, \mathbf{q}_\gamma \tag{2.2}$$

where $\mathbf{q}_\gamma$ is the flux of γ. Of course, the substantial time derivative of the density $\rho(\gamma)$

$$\frac{d\rho}{dt} = \rho'(\gamma)\frac{d\gamma}{dt} = \rho'(\gamma)\left[\frac{\partial\gamma}{\partial t} + (\mathbf{u}\cdot\nabla)\gamma\right] = -\rho \text{ div } \mathbf{u} \qquad (2.3)$$

is not zero if $\frac{d\gamma}{dt} \neq 0$, and then div$\mathbf{u} \neq 0$. In general $\gamma = \rho_\gamma\phi$ where $\rho_\gamma = m_\gamma/V_\gamma$ is the density of the fluid γ and $\phi = V_\gamma/V$ is the volume fraction. Under isothermal conditions ρ_γ is a constant and we may work with $\rho(\phi)$ and ϕ satisfies (2.2).

Suppose ν is the density of the other liquid per total unit volume. Then $\rho = \nu + \gamma$ and

$$\frac{d\nu}{dt} + \nu \text{ div}\mathbf{u} = -\text{ div } \mathbf{q}_\nu \quad . \qquad (2.4)$$

The continuity equation may be written as

$$\frac{d\nu}{dt} + \frac{d\gamma}{dt} + (\nu+\gamma) \text{ div}\mathbf{u} = 0 \ . \qquad (2.5)$$

Hence, using (2.2) and (2.4) in (2.5), we find that

$$\text{div } (\mathbf{q}_\nu + \mathbf{q}_\gamma) = 0 \ . \qquad (2.6)$$

The sum of the fluxes of the mass of each constituent across the boundary of any material volume V must vanish

$$\int_{\partial V} (\mathbf{q}_\nu + \mathbf{q}_\gamma)\cdot\mathbf{n} \text{ dS} = 0 \qquad (2.7)$$

to conserve the total mass.

If the volume V of a mixture of two liquids does not change on mixing, then $V = V_\gamma + V_\nu$ and the density can be expressed in terms of the volume fraction $\phi = V_\gamma/V$ of one of the constituents by the form

$$\rho(\phi) = \rho_\gamma\,\phi + \rho_\nu\,(1-\phi) \qquad (2.8)$$

where ρ_γ and ρ_ν are the densities of γ and ν, handbook values. Mixtures satisfying (2.8) will be called **simple mixtures**. Equation (2.8) is correct to within 1% for glycerin and water mixtures (see Joseph [1990]). The volume fraction is the natural variable

connecting density and diffusion in simple mixtures. Since $\gamma = \rho_\gamma \phi$ and $v = \rho_v (1-\phi)$ and conserved in the absence of diffusion, it is natural to express the constitutive equation for the fluxes $\mathbf{q}_\gamma$ and $\mathbf{q}_v$ as a nonlinear Ficks' law for each constituent in terms of the volume fraction of one of them

$$\mathbf{q}_\gamma = -D_\gamma(\phi)\nabla(\rho_\gamma\phi) \ ; \ \mathbf{q}_v = -D_v(\phi)\nabla[\rho_v(1-\phi)] \tag{2.9}$$

with different diffusion functions and assume that ρ_γ and ρ_v are constants, as in the isothermal case, then

$$\int_{\partial V} \mathbf{n} \cdot (\mathbf{q}_v + \mathbf{q}_\gamma) \ dS = \int_{\partial V} (D_v\rho_v - D_\gamma\rho_\gamma) \ \mathbf{n} \cdot \nabla\phi \ dS = 0$$

in each and every material volume V, so that either $\mathrm{div}[(D_v\rho_v - D_\gamma\rho_\gamma)\nabla\phi] = 0$ at each and every point in V, or

$$\frac{D_v}{D_\gamma} = \frac{\rho_\gamma}{\rho_v} \tag{2.10}$$

is a constant.

Since the density of a simple mixture of incompressible liquids changes by virtue of diffusion of the volume fraction, the velocity field cannot be solenoidal (cf. (2.3)). However, Galdi, Joseph, Preziosi and Rionero [1991] have shown that if (2.8) holds, then (2.2) and (2.3) imply that,

$$\mathrm{div} \ \mathbf{W} = 0 \ , \tag{2.11}$$

where

$$\mathbf{W} = \mathbf{u} - \frac{(\rho_\gamma - \rho_v)}{\rho_\gamma\rho_v} \ \mathbf{q}_\gamma \ . \tag{2.12}$$

From (2.6), we also get

$$\mathrm{div} \ \hat{\mathbf{W}} = 0 \ ,$$

where

$$\hat{\mathbf{W}} = \mathbf{u} - \frac{(\rho_v - \rho_\gamma)}{\rho_\gamma\rho_v} \ \mathbf{q}_v \ .$$

In this case we may introduce a stream function.

The forgoing development may be carried out for homogeneous fluids with temperature gradients when the Boussinesq approximations are relaxed and the density ρ is related to the temperature T by the special equation

$$\rho = \rho^* (1+\beta T)^{-1}$$

for constant ρ^* and β. Then

$$\mathbf{W} = \mathbf{u} - \beta\kappa\nabla T$$

where κ is the thermo-diffusion coefficient (Pukhnachov,1991).

Landau and Lifshitz [1959] have considered diffusion without explicitly taking up the case of incompressible liquids. They write what might at first glance be thought to be the usual diffusion equation (their(57.3))

$$\rho \frac{dc}{dt} = - \text{div}\mathbf{i} \tag{2.13}$$

where

$$c = m_\gamma/m = \gamma/\rho \tag{2.14}$$

is the mass fraction, m is the total mass and $\mathbf{i}$ is said to be the diffusion flux density, which we shall specify presently, according to our understanding.

Substituting (2.14) into (2.13) using (2.3) we get

$$\rho\frac{d\gamma/\rho}{dt} = \frac{d\gamma}{dt} + \gamma\,\text{div}\mathbf{u} \ . \tag{2.15}$$

This shows that (2.13) is perfectly consistent with mass conservation argument (2.1) provided that

$$\text{div}\mathbf{i} = \text{div}\mathbf{q}_\gamma \tag{2.16}$$

is the divergence of the flux of γ, say the flux of solute.

Landau and Lifshitz develop a coupled thermodynamic theory for **i** and the heat flux under the condition that the concentration gradients are small (which is not the main case of interest here). When temperature and pressure gradients vanish, they find that

$$\mathbf{i} = -\alpha \text{ grad } \hat{\mu} = -\alpha \left(\frac{\partial \hat{\mu}}{\partial c}\right)_{p,T} \text{grad } c = -\rho \, D \text{ grad } c \qquad (2.17)$$

where $\hat{\mu}$ is the chemical potential and D is the diffusion coefficient. For simple mixtures $c = \gamma/\rho = \rho_\gamma \phi/\rho(\phi)$ and

$$\rho \text{ grad } c = \frac{\rho_\gamma \rho_v}{\rho(\phi)} \text{ grad } \phi . \qquad (2.18)$$

After combining (2.15) and (2.16) with (2.13), with constant ρ_γ and ρ_v, we find that

$$\frac{\partial \phi}{\partial t} + \text{div}(\phi \mathbf{u}) = \text{div} \left[D_\gamma(\phi) \nabla \phi \right] \qquad (2.19)$$

where

$$D_\gamma(\phi) = \frac{\rho_v D(\phi)}{\rho_\gamma \phi + \rho_v(1-\phi)} \quad . \qquad (2.20)$$

Many pairs of liquids will give rise to small volume changes upon mixing. These liquids are only approximate simple mixtures. It is probable that nearly all the interesting cases which are not already well described by the theory of perfect incompressible mixtures could be treated as a to-be-developed perturbation of the perfect case.

In areas of applications, problems of mixing liquids (miscible displacements, binary convection, Taylor dispersion, reaction and diffusion, transport of diffusing "passive" scalars like dyes, Marangoni convection, solidification problems, etc), it is assumed that div$\mathbf{u}$=0. In fact, though there are surely many situations in which the assumption that div$\mathbf{u} = 0$ is a good one, there are others in which

$$\text{div}\mathbf{u} = \frac{\rho_\gamma - \rho_v}{\rho_v \rho_\gamma} \text{ div } \mathbf{q}_\gamma = \frac{\rho_v - \rho_\gamma}{\rho_v} \text{ div}[D_\gamma(\phi)\nabla\phi] \qquad (2.30)$$

is large when $\nabla\phi$ is large, as is true when mixing liquids are placed into sudden contact. It is clear already from (2.30) that if gradients are moderate div$\mathbf{u}$ will be small if the prefactor or the diffusion coefficient $D_\gamma(\phi)$ is small. For glycerin $\rho_v = 1.26$ g/cm^3 and water $\rho_\gamma = 1$ g/cm^3, the prefactor 0.26/1.26 is not negligible, but the diffusion coefficient $D_\gamma = O(10^{-6}$ cm^2/sec) is. It follows then that the assumption that div$\mathbf{u}$=0 is a slow diffusion rather that Boussinesq approximation.

3. Momentum balance and Korteweg stresses

To extract the consequences of the balance of momentum it is desirable to frame the theory in term of a material particle, to apply balance laws to a material volume which in the continuous limit is a particle of fluid mass. In the present case we follow Landau and Lifshitz and write the Navier-Stokes equations for the velocity $\mathbf{u}$ of volume of fixed mass. Hence it is the $\mathbf{u}$ in $\mathbf{W}$ which will enter into the balance of momentum.

The possibility that stresses are induced by gradients of concentration and density in diffusing incompressible miscible liquids, as in the theory of Korteweg [1901], can be considered. Such stresses could be important in regions of high gradients giving rise to effects which can mimic surface tension. We have already seen, in (2.30), that it is just the same region of high gradients where the volume changes due to dilution cause the strongest departures from the classical approximation div$\mathbf{u}$=0. We are going to study the superposition of non-classical effects of volume changes div$\mathbf{u}$≠0 due to diffusion and Korteweg stresses.

In the isothermal case, ρ varies with ϕ alone, as in (2.8) and in the notation of Joseph [1990] the Korteweg's expression for the stress due to the combined effects of gradients of ϕ and $\rho(\phi)$ are

$$T_{ij}^{(2)} = \hat{\delta}\, \frac{\partial \phi}{\partial x_i}\frac{\partial \phi}{\partial x_j} + \hat{\gamma}\, \frac{\partial^2 \phi}{\partial x_i \partial x_j} \quad,$$

(3.1)

where

$$\hat{\delta} = (\rho_\gamma - \rho_\nu)^2\, \delta_1 + \delta_2 + 2\nu(\rho_\gamma - \rho_\nu) \,,$$

$$\hat{\gamma} = \gamma_1(\rho_\gamma - \rho_\nu)^2 + \gamma_2 \,.$$

The governing equations are

$$(\rho_\gamma - \rho_\nu)\frac{d\phi}{dt} + \rho\, \mathrm{div}\, \mathbf{u} = 0 \,, \tag{3.2}$$

$$\frac{d\phi}{dt} + \phi\, \mathrm{div}\, \mathbf{u} = \nabla(D_\gamma \nabla \phi) \tag{3.3}$$

and

$$\rho\frac{d\mathbf{u}}{dt} = -\nabla\Pi + \mathrm{div}\, \mathbf{T}^D + \rho\mathbf{g} \,, \tag{3.4}$$

where $\mathbf{T}^D$ is the stress deviator defined by

$$T_{ij}^D = 2\mu\, D_{ij} - \frac{2}{3}\, \delta_{ij}\, \mu\, \mathrm{div}\, \mathbf{u} + \tau_{ij} \quad, \tag{3.5}$$

$$\tau_{ij} = \hat{\delta}\, \frac{\partial \phi}{\partial x_i}\frac{\partial \phi}{\partial x_j} + \hat{\gamma}\, \frac{\partial^2 \phi}{\partial x_i \partial x_j} - \frac{1}{3}\, \delta_{ij}\, \{\, \hat{\delta}\, |\nabla \phi|^2 + \hat{\gamma}\, \nabla^2 \phi\}$$

and Π is the mean normal stress.

The continuity equation (3.2) may be replaced with

$$\mathrm{div}\, \mathbf{W} = 0 \qquad \text{and} \qquad \mathbf{W} = \mathbf{u} - \zeta D_\gamma \nabla \phi \tag{3.6}$$

where

$$\zeta = \frac{(\rho_\nu - \rho_\gamma)}{\rho_\nu} \quad. \tag{3.7}$$

We should be thinking of glycerin ν and water γ, then $\zeta > 0$.

Then, using (3.6), we may eliminate div**u** from (3.5)

$$T^D_{ij} = 2\mu\, D_{ij} - \frac{2}{3}\, \delta_{ij}\, \zeta\mu\, \text{div}(D_\gamma\nabla\phi) + \tau_{ij} \tag{3.8}$$

and rewrite (3.4) as

$$\rho\frac{d\mathbf{u}}{dt} = -\nabla\Big[\, \Pi + Q(\phi)\Big] + \text{div}\Big\{\, 2\mu\, \mathbf{D}[\mathbf{u}] + \hat{\delta}\, \nabla\phi\,\nabla\phi\,\Big\} + \rho\mathbf{g}\,, \tag{3.9}$$

where

$$Q(\phi) = \frac{1}{3}\, \hat{\delta}\, |\nabla\phi|^2 + \frac{2}{3}\, \zeta\mu\, \text{div}(D_\gamma\nabla\phi) - \frac{2}{3}\, \hat{\gamma}\, \nabla^2\phi\,. \tag{3.10}$$

In writing (3.9) we have assumed that $\hat{\gamma}$ is constant. It will be convenient now to also assume that $\hat{\delta}$ is a constant.

We now adopt (3.3), (3.6) and (3.9) as our system of equations governing the evolution of simple mixtures of incompressible liquids. These are five equations for the components of **u** , Π and ϕ. In this preliminary study we shall restrict our attention to some one-dimensional problems for which there is a strong decoupling of equations, but some basic issues can be addressed.

To keep our discussion of basic issues concrete we will use estimates of material parameters for Glycerin-Water systems. One reference for this is the article by Segur [1953]. In figure 1 we have reproduced Segur's experimental data [1953] for the viscosity μ. This can be excellently correlated by the expression

$$\mu = \mu_G\, \exp(\alpha\phi + \beta\phi^2 + \gamma\phi^3)\,, \tag{3.11}$$

where the coefficients α, β and γ depend on temperature T in the way shown in the figure, μ_G is the viscosity of pure glycerin and μ_G=14.99 poise at 20°C. The density of glycerin (G) and water (W) mixtures is given to within 1% by (2.8) with $(\rho_\gamma, \rho_\nu)=(\rho_W, \rho_G)\sim(1, 1.26)$ g/cm^3 at 20°C. Unfortunately we do not have the global dependence of the diffusion coefficient $D(\phi)$. Small gradient theories of diffusion are

inadequate for mixing layers in which ϕ takes on all allowed values from zero to one. A representative value $D(\phi)$ over different concentration, taken from Segur (p.328) is $D_o=5 \times 10^{-6} cm^2/sec$. We will use this representative value in our estimates.
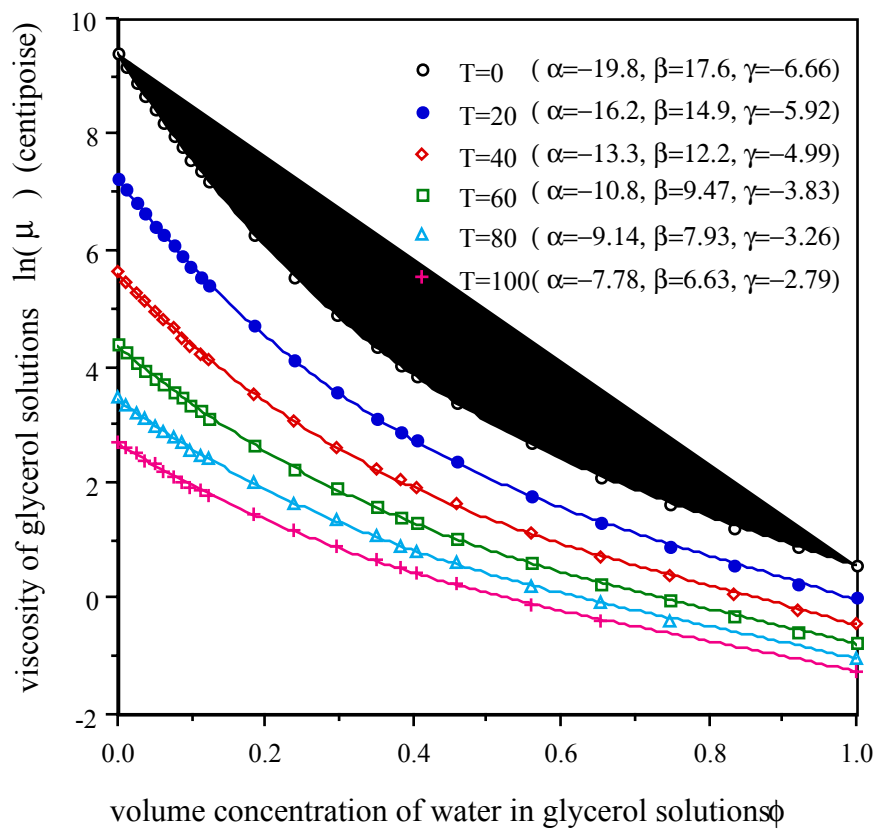
Figure 1. (After Segur [1953]) Viscosity of glycerol solutions at temperature 0−100°C. The expression $\mu = \mu_G \exp(\alpha\phi + \beta\phi^2 + \gamma\phi^3)$ fits the experimental data.

4. One dimensional mixing layer problems

We shall suppose that $\mathbf{u}=u(x,t)\mathbf{e}_x$ where x increases upward against gravity. In this case

$$0 = \text{div } \mathbf{W} = \frac{\partial}{\partial x} \left[u - \zeta D_\gamma \frac{\partial \phi}{\partial x} \right].$$

Hence

$$u = A(t) + u_e (x,t) \tag{4.1}$$

where

$$u_e \overset{\text{def}}{=} \zeta D_\gamma \frac{\partial \phi}{\partial x} \tag{4.2}$$

is the expansion velocity which arises from mixing. In theories in which div$\mathbf{u}$=0 is assumed, u_e=0 and, of course, u_e=0 when the fluids are density matched. Using (4.1) and (4.2) we find that

$$\frac{\partial \phi}{\partial t} + \left[A(t) + \zeta D_\gamma \frac{\partial \phi}{\partial x} \right] \frac{\partial \phi}{\partial x} = (1 - \zeta \phi) \frac{\partial}{\partial x} \left(D_\gamma \frac{\partial \phi}{\partial x} \right) ,$$

or

$$\frac{\partial \phi}{\partial t} + A(t) \frac{\partial \phi}{\partial x} = \frac{\partial}{\partial x} \left[(1 - \zeta \phi) D_\gamma \frac{\partial \phi}{\partial x} \right] .$$

$$\tag{4.3}$$

The momentum equation in one dimension is given by

$$\rho(\phi) \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right] = - \frac{\partial \Pi}{\partial x} + \frac{\partial}{\partial x} \left\{ \frac{4}{3} \mu \frac{\partial u}{\partial x} + \frac{2}{3} \hat{\delta} \left(\frac{\partial \phi}{\partial x} \right)^2 + \frac{2}{3} \hat{\gamma} \frac{\partial^2 \phi}{\partial x^2} \right\}$$

$$+ \rho \, \mathbf{g} \cdot \mathbf{e}_x \tag{4.4}$$

where u is given in terms of A(t) and ϕ by (4.1). We need Π to satisfy (4.4) when, say, u(x,t) and ϕ(x,t) are prescribed at the boundary.

The problem of diffusion is decoupled from (4.4) when A(t)=0. And A(t)=0 if there is a value x such that for all t, u and the diffusion flux $\partial \phi / \partial x$=0. This is the case at

an impermeable wall across which the velocity and the flux of water must vanish. It is also true for mixing problems on unbounded domains for which u and $\partial\phi/\partial x$ vanish at x=±∞. These problems are canonical for the development of mixing layers from initially discontinuous data which are considered below. When A(t)=0

$$u = u_e = \zeta D_\gamma \frac{\partial\phi}{\partial x} \tag{4.5}$$

and (4.3) reduces to

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial x}\left[(1-\zeta\phi)D_\gamma\frac{\partial\phi}{\partial x}\right].$$

If we switch to use the classical diffusion coefficient D(ϕ) given by (2.20), the above diffusion equation then becomes

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial x}\left[D(\phi)\frac{\partial\phi}{\partial x}\right]. \tag{4.6}$$

In the simplest case, we assume that D is independent of ϕ, (4.6) is the classical diffusion equation. With appropriate boundary conditions (4.6) can be solved easily. Then u is given by (4.5), without any considerations from dynamics and the momentum equation (4.4) determine $\Pi(x,t)$ directly. Various issues which arise in the dynamical theory of simple mixtures can be framed in terms of the one-dimensional problems considered below.

5. Dynamic and instantaneous interfacial tension

H. Freundlich in his [1926] 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.

Freundlich [1926] cites the measurements of the dynamic tension by Quinke [1902] of ethyl alcohol in contact with aqueous salt solutions (sulfates 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 and Mason [1981] have reported a maximum value of 1 dyne/cm for the force corresponding to a "transient interfacial tension" between a 2000cs and a 1cs 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, Van den Ven and 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 [1893] and Cahn and Hillard [1954] writing

$$S^* \propto \int_{-x_0}^{x_0} \left(\frac{\partial \phi}{\partial x}\right)^2 dx \tag{5.1}$$

where S^* is the interfacial tension, ϕ is the local composition (the mole fraction of component 1) and x_0 is the "interfacial region". The composition is assumed to satisfy a diffusion equation $\phi_t = D\phi_{xx}$ with diffusion constant D. If at $t=0_+$, $\phi=\phi_+$ for $x>0$ and ϕ_- for $x<0$ and thereafter ϕ is continuous at $x=0$, then

$$\phi(x,t) = \Delta\phi \, f(\eta), \quad f(\eta) = \mathrm{erfc}(\eta), \quad \eta = x/2\sqrt{Dt}$$

where $\Delta\phi = \phi_+ - \phi_-$ and S^* is proportional to

$$\Delta\phi^2 \int_{-x_0}^{x_0} \frac{1}{\pi} \exp(-2\eta^2) \left(\frac{\partial \eta}{\partial x}\right)^2 dx$$

$$= \frac{[\phi_+ - \phi_-]^2}{2\pi\sqrt{Dt}} \int_{-\eta_0}^{\eta_0} \exp(-2\eta^2) \, d\eta$$

At small times the breadth of the diffusion layer scales with $\sqrt{Dt}$. Then the gradient theory leads to a square root singularity for the dynamic tension. Their experiments indicate that $F=S^* \cos\theta$ decays exponentially and does not follow the $t^{-1/2}$ decay that would be required if θ were constant, where θ is the contact angle. It is noteworthy that though the rate of decay of F with time varies between 0.6 to 1.4, the extrapolated value of F 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."

H. Ted Davis [1988] has written an interesting paper, "A theory of tension at a miscible displacement front" in which he supplies a constant of proportionality for the expression (5.1), which he develops independently starting from the Irving-Kirkwood pressure tensor and some simplifying assumptions. He then uses some estimate of constants in his theory to construct a table of values of S* (γ in his notation), given in his table 3.1, varying from about 6.3×10^{-2} dyn/cm for t=1s and D=10^{-9} cm^2/s to 10^{-5} dyn/cm for t=4000s and D=10^{-5} cm^2/s. He notes that "From the entries in this table it follows that the tension of a diffusive mixing zone between miscible fluids, while small, is nevertheless not zero."

The theory used by Smith, et al [1981] and by Davis [1988] evidently requires that one assume wrongly that the density of a mixture of incompressible fluids is constant. Davis restricts his analysis to a two-component regular solution in which the densities of the components 1 and 2 are $n_1 = \widetilde{\phi} n$ and $n_2 = (1-\widetilde{\phi})n$. $\widetilde{\phi}$ is the mole fraction of component 1 and n is the total density, which he says is constant in a regular solution. We shall reinterpret the Davis work for simple mixtures by replacing the mole fraction $\widetilde{\phi}$ with the mass fraction $\hat{\phi} = m_\gamma/m$ of an incompressible liquid (say, water) in a mixture (say, water and glycerin) of total $m = m_\gamma + m_v$ where m_v is the mass fraction of glycerin. Then (n, n_1, n_2) should be replaced by $(m/V, m_\gamma/V_\gamma, m_v/V_v) = (\rho, \rho_\gamma, \rho_v)$ where V is the total material volume and ρ_γ and ρ_v are the ordinary (constant) densities (of water and glycerin) listed in the handbooks. Moreover, if our regular solution keeps its volume after mixing, then

$$n = \rho\widetilde{\phi} + \rho(1-\widetilde{\phi}) = \frac{m}{V}\frac{m_\gamma}{m} + \frac{m}{V}(1 - \frac{m_\gamma}{m})$$

$$= \gamma + v = \rho_\gamma \phi + \rho_v (1-\phi) = \rho(\phi)$$

and the regular solution of Davis is a simple mixture. Obviously, a mixture of incompressible liquids does not have a constant density even though the density of each of its constituents is constant at a fixed temperature.

Davis [1988] expresses well the notion that gradients of composition can lead to anisotropic forces which mimic the effects of interfacial tension:

> When two miscible fluids are placed in contact they will immediately begin to mix diffusively (and convectively if their densities are such as to drive convection) across the concentration front formed at the zone of contact. Although no interface will form at the concentration front, the composition inhomogeneities can give rise to pressure anisotropies and therefore to tension at the mixing zone between the contacted fluids. Diffusive mixing will continuously broaden the mixing zone and reduce the pressure anisotropy and the associated tension. The purpose of this short paper is to examine with the aid of a molecular theory of inhomogeneous fluid the magnitude and rate of reduction of the tension by diffusive mixing of the zone of contact of miscible fluids. The results found here suggest 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 in time.

The calculation in section 6 shows that the dynamic tension does not and should not give rise to a pressure difference across a spreading plane layer. This is a good analogy to interfacial tension which is proportional to curvature and vanishes across plane layers. The calculation of forces over a spherical layer advanced in section 7 does contain curvature terms, but the analogy is not perfect.

May and Maher [1991] have extracted an effective "surface tension" between isobutyne acid and water at near-critical composition (62.1 volume % water) for change of phase from a miscible to immiscible liquid mixture. This binary liquid mixture has an upper critical temperature, $T_c=26.310°C$, below which its two equilibrium phases act as immiscible liquids with an interfacial tension $\sigma=\sigma_o[(T_c-T)/T_c]^{1.23}$. If this system is initially at two phase equilibrium and then has its temperature abruptly raised above T_c but is not mechanically disturbed, the interface will remain visible for many hours as diffusion can only mix the two phases slowly. May and Maher [1991] measured autocorrelation function for light scattered from capillary waves at the interface of two-phase equilibrium and after abruptly raising the temperature to drive the system toward one-phase equilibrium. They used a capillary wave dispersion relation to determine a

decaying transient "surface tension" with a maximum value near 0.01 dyne/cm. They note that " ...This surface tension represents a dynamical integrity of the nonequilibrium interface which may affect pattern formation when the interface is driven.

6. Jump of the normal stress across a plane mixing layer

We shall now examine the problem considered in section 5 without assuming that density is constant and using the one dimensional problem defined by (4.4), (4.5) and (4.6). This is the canonical initial value problem for mixing layers, the smoothing-out of a discontinuity in ϕ at a plane. At t=0, $\phi=\phi_+$ when x>0 and $\phi=\phi_-$ when x<0. Since we are on an infinite domain $\phi=\phi_+$ at x→∞ and $\phi=\phi_-$ as x→ -∞. Without loss of generality we may translate ϕ by $\Delta\phi/2$ where $\Delta\phi=\phi_+ - \phi_- >0$ and suppose that when t=0

$$\phi = \frac{\Delta\phi}{2} \quad \text{for x>0} \qquad \text{and} \qquad \phi = -\frac{\Delta\phi}{2} \quad \text{for x<0} \tag{6.1}$$

and for all t

$$\phi = \frac{\Delta\phi}{2} \quad \text{as x→∞} \qquad \text{and} \qquad \phi = -\frac{\Delta\phi}{2} \quad \text{as x→ -∞} . \tag{6.2}$$

In this situation (4.5) holds and the velocity is proportional to the volume fraction gradient which is infinite at $t=0_+$.

For simplicity we take the diffusion coefficient D to be independent of ϕ and for glycerin-water mixture D is of order 10^{-6} cm^2/sec. Then classical diffusion equation (4.6) has a similarity solution

$$\phi = \frac{\Delta\phi}{\sqrt{\pi}} \int\limits_{-\infty}^{\eta} e^{-\eta^2} d\eta \tag{6.3}$$

with

$$\eta = \frac{x}{2\sqrt{Dt}} . \tag{6.4}$$

Using (6.3) we may express (4.5) as

$$u = u_e = \frac{\zeta \Delta \phi}{2\sqrt{\pi}\,(1\text{-}\zeta\phi)} \sqrt{\frac{D}{t}} \; \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right] . \tag{6.5}$$

The diffusion layer can be defined from the place $-x_o$ where $\psi=\phi\text{-}1/2=\text{-}0.495$ to the place x_o where $\psi=0.495$, or by $-m<\eta<m$ with m about 2. The thickness of the diffusion layer is

$$\Delta x = x_o - (-x_o) = 4m\sqrt{Dt} \tag{6.6}$$

and it tends to zero with t.

Equation (6.5) shows that the expansion velocity which enters into dynamics can be considerable at early times inside the diffusion layer. The gradient of ϕ is the machine which drives the velocity. The velocity decays as $\sqrt{D/t}$.

It is of interest to calculate the jump of the stress across the mixing layer. To find the jump in the stress we integrate (4.4) over the diffusion layer. Outside of this layer the derivatives of ϕ vanish and

$$\int_{-x_o}^{x_o} \rho(\phi)\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x}\right) dx = -[\![\Pi]\!] - g \int_{-x_o}^{x_o} \rho(\phi)\, dx \tag{6.7}$$

where

$$[\![\Pi]\!] = \Pi(x_o, t) - \Pi(-x_o, t) .$$

Equation (6.7) shows that the Korteweg stresses do not enter into the stress jump across the plane mixing layer. This is unlike the calculations of section 5, but like true interfacial tension in which curvature supports a jump in stress. Using the continuity equation it can be easily seen that the contribution due to inertia is always zero

$$\int_{-x_o}^{x_o} \rho(\phi)\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x}\right) dx = \int_{-x_o}^{x_o} \frac{\partial \rho u}{\partial t}\, dx = \rho_v \int_{-x_o}^{x_o} \frac{\partial}{\partial t}\left[D(\phi)\frac{\partial \phi}{\partial x}\right] dx$$

$$= \rho_v \int\limits_{-x_o}^{x_o} \frac{\partial}{\partial x} \left[D(\phi)\frac{\partial \phi}{\partial t} \right] dx = 0,$$

(6.8)

which is also true when $D(\phi)$ depends on ϕ. Therefore

$$[\![\Pi]\!] = - g \int\limits_{-x_o}^{x_o} \rho(\phi)\, dx \ .$$

(6.9)

The jump in normal stress is simply the static pressure difference across the mixing layer.

7. Spreading of a spherical diffusion front and Korteweg stresses

The problem of the spreading of a spherical front with gravity neglected is good for bringing out how Korteweg stresses may enter the normal stress balance when the curvature is not zero. In fact this kind of calculation was carried out for an equilibrium phase change cavitation bubble in the absence of diffusion or motion by Korteweg [1901]. A critical discussion of the Kortewegs' equilibrium calculation can be found in Joseph [1990].

At t=0 a spherical mass of radius r_o of one liquid is inserted into an infinite reservoir of a second liquid. The two liquids are miscible in all proportions. We can imagine a sphere of glycerin in a reservoir of water. The governing equations are (3.3), (3.6) and (3.9) written for spherically symmetric solutions, with one, radial, component of velocity u(r,t) which vanishes at r=0 and r=∞. Under these conditions divW=0 implies that

$$u(r,t) = u_e(r,t) = \zeta D_\gamma \frac{\partial \phi(r,t)}{\partial r} \ .$$

(7.1)

The diffusion equation (3.3) may then be written as

$$\frac{\partial \phi}{\partial t} = D \frac{\partial}{\partial r}\left(\frac{\partial \phi}{\partial r}\right) + \frac{2D}{r}\frac{\partial \phi}{\partial r}$$

(7.2)

where the water fraction $\phi(r,t)=1$ when $r>r_o$, $t=0$ and $\phi(r,t)=0$ when $r<r_o$, $t=0$. When the thickness of the mixing layer at $r=r_o$ is small, it is locally like a plane and the 2nd term on the right side of (7.2) may be neglected. This reduces our problem to the one considered in section 6 centered on $r=r_o$ and it has the same self similar solution with

$$\eta = \frac{r-r_o}{2\sqrt{Dt}} \, , \tag{7.3}$$

when $2\eta\sqrt{Dt} \ll r_o$.

The momentum equation (3.9) may be written as

$$\rho(\phi) \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} \right] = - \frac{\partial}{\partial r} \left[\Pi + Q(\phi) \right] + 2 \frac{\partial}{\partial r} \left(\mu \frac{\partial u}{\partial r} \right) + \frac{4\mu}{r} \frac{\partial u}{\partial r}$$

$$- 4\mu \frac{u}{r^2} + \frac{\partial}{\partial r} \left[\hat{\delta} \left(\frac{\partial \phi}{\partial r} \right)^2 \right] + \frac{2\hat{\delta}}{r} \left(\frac{\partial \phi}{\partial r} \right)^2 \tag{7.4}$$

where $\rho(\phi)$ is given by (2.8) and $\mu(\phi)$ by (3.11). After integrating over the mixing layer from $r_1 = r_o - 2m\sqrt{Dt}$ to $r_2 = r_o + 2m\sqrt{Dt}$, we find that

$$\int_{r_1}^{r_2} \left\{ \rho(\phi) \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} \right) - 4\mu \frac{\partial u/r}{\partial r} - \frac{2\hat{\delta}}{r} \left(\frac{\partial \phi}{\partial r} \right)^2 \right\} dr =$$

$$\left[- \Pi - Q(\phi) + 2\mu \frac{\partial u}{\partial r} + \hat{\delta} \left(\frac{\partial \phi}{\partial r} \right)^2 \right]_{r_1}^{r_2} \tag{7.5}$$

Outside the mixing layer $(r_1(t),r_2(t))$, ϕ is essentially constant and u is essentially zero. The contribution due to the inertia at the left hand side of (7.5) is again found to be zero as in the case of the plane layer. After writing

$$\int_{r_1}^{r_2} \mu \frac{\partial u/r}{\partial r} \, dr = \left[\mu \frac{u}{r} \right]_{r_1}^{r_2} - \int_{r_1}^{r_2} \mu'(\phi) \frac{u}{r} \frac{\partial \phi}{\partial r} \, dr \tag{7.6}$$

and putting terms outside the mixing layer to zero we get

$$\int_{r_1}^{r_2} \{4 \mu'(\phi) \frac{u}{r} \frac{\partial \phi}{\partial r} - \frac{2\hat{\delta}}{r} (\frac{\partial \phi}{\partial r})^2\} \, dr = - \left[\Pi \right]_{r_1}^{r_2} . \tag{7.7}$$

Now we evaluate (7.7) at very early times, when the mixing layer is very thin, $r_2 - r_1 = 4m\sqrt{Dt}$ and $r \approx r_0$. Using the same approximations with $r \approx r_0$ in the two terms of the integral of (7.7), we find that

$$\frac{2}{r_0} \int_{r_1}^{r_2} \{2 \mu'(\phi) u \frac{\partial \phi}{\partial r} - \hat{\delta} (\frac{\partial \phi}{\partial r})^2\} \, dr = \frac{2}{r_0} \int_{r_1}^{r_2} \{2 \frac{\mu'(\phi)\zeta D}{1-\zeta\phi} - \hat{\delta} \} (\frac{\partial \phi}{\partial r})^2 \, dr$$

$$= \frac{1}{r_0} \sqrt{\frac{D}{t}} \int_{-m}^{m} \{2 \frac{\mu'(\phi)\zeta}{1-\zeta\phi} - \frac{\hat{\delta}}{D} \} \phi'^2 \, d\eta .$$

Finally,

$$\Pi(r_1,t) - \Pi(r_2,t) = \frac{2}{r_0} T(t) \tag{7.8}$$

where the "transient surface tension" is given by

$$T(t) = \sqrt{\frac{D}{t}} \int_{-m}^{m} \{ \frac{\mu'(\phi)\zeta}{1-\zeta\phi} - 0.5 \frac{\hat{\delta}}{D} \} \phi'^2 \, d\eta . \tag{7.9}$$

For glycerin and water solutions at 20°C we may evaluate (7.9) using values for μ' and ζ near to (3.11) as

$$T(t) = \sqrt{\frac{D}{t}} \left[164.5 \frac{-\hat{\delta}}{D} - 428.7 \right] \tag{7.10}$$

with D about 7.5×10^{-6} cm^2/sec, but we do not have any knowledge about the value of Korteweg stress coefficient $\hat{\delta}$. There are two terms in the expression for the dynamic interfacial tension; one term arises from the Korteweg stress and it gives rise to a stress opposing the internal pressure as in the case of equilibrium pressure if the Korteweg

coefficient $\hat{\delta}$ has a negative sign. A second term arises from the expansion velocity and is proportional to the rate of change of viscosity with volume fraction. This term has the wrong sign for interfacial tension in the case of glycerin and water solutions but has the right sign when the light fluid is more viscous.

In general $D(\phi)$ is not a constant and the error function solution (6.3) is not valid. However even in this case (4.6) admits a similarity solution with

$$\phi = f(\eta), \qquad \eta = \frac{x}{2\sqrt{D_o t}} \quad, \tag{7.11}$$

where D_o is representive value of $D(\phi)$ and

$$\frac{d}{d\eta} \left(\frac{D(f)}{D_o} \frac{df}{d\eta} \right) + 2\eta \frac{df}{d\eta} = 0 \tag{7.12}$$

where

$$f = \frac{\Delta\phi}{2} \quad \text{for } \eta = 0_+ \qquad \text{and} \qquad f = -\frac{\Delta\phi}{2} \quad \text{for } \eta = 0_-$$

and

$$f = \frac{\Delta\phi}{2} \quad \text{as } \eta \to \infty \qquad \text{and} \qquad f = -\frac{\Delta\phi}{2} \quad \text{as } \eta \to -\infty \ .$$

Following now the derivation leading to (7.9) we find again with

$$T(t) = \sqrt{\frac{D_o}{t}} \int\limits_{-\eta_1}^{\eta_2} \left\{ \frac{\mu'(\phi)\zeta}{1-\zeta\phi} \frac{D(\phi)}{D_o} - 0.5 \frac{\hat{\delta}}{D_o} \right\} \phi'^2 \, d\eta \tag{7.13}$$

where η_1 and η_2 mark the effective end of the diffusion layer replacing m in (7.9). In general $\phi(\eta)$ will not be antisymmetric if $D(\phi)$ is not an even function.

8. Conclusions and discussion

1. A theory of motion and mixing of two incompressible liquids ν and γ can be developed based on the equation of state for the density

$$\rho(\phi) = \rho_\gamma \, \phi + \rho_v \, (1-\phi) = \rho_v \, (1-\zeta\phi)$$

of a simple mixture. The natural variable connecting composition to density is the volume fraction ϕ say of γ with constant densities ρ_v and ρ_γ under isothermal conditions.

2. The velocity **u** is not solenoidal because the density $\rho(\phi)$ changes due to diffusion. For simple mixtures the vector

$$\mathbf{W} = \mathbf{u} - \frac{\zeta D}{1-\zeta\phi} \, \nabla\phi$$

is solenoidal div**W**=0. The velocity **u** can be decomposed into a solenoidal part $\mathbf{u}_s$, div$\mathbf{u}_s$=0, and an expansion part $\mathbf{u}_e$ where

$$\mathrm{div}\,\mathbf{u}_e = \Delta = \zeta \, \mathrm{div}\, [\frac{D}{1-\zeta\phi} \, \nabla\phi\,]$$

is the expansion and $D(\phi)$ is a diffusion function of ϕ, a quantity of order 10^{-6} cm^2/sec in many liquids. $D(\phi)$ is assumed to be constant in standard theories of Fick's law (but it varies in experiments). The expansion velocity is driven by gradients of the volume fraction.

3. In one dimensional problems with one component of velocity $u(x,t)$ perpendicular to the mixing layer we have

$$u(x,t) = A(t) + u_e(x,t)$$

where $A(t)$ is the solenoidal part of the velocity, an identical formula holds for spherically symmetric one dimensional problems with r the radius replacing x and

$$u_e(r,t) = \frac{\zeta D}{1-\zeta\phi} \frac{\partial\phi}{\partial r}(r,t) \quad .$$

4. The problem of dynamic interfacial tension due to effects of the expansion velocity and Korteweg stresses are analyzed by evaluating the jump of the normal stress across plane and spherical mixing layers which smooth an initial discontinuity of composition. We find no jump across a plane layer but there is a jump proportional to the curvature across

the spherical surface. The dynamic tension at the spherical interface decays as $\sqrt{D/t}$. There are two terms in the expression (7.10) for the interfacial tension; one term arises from the Korteweg stress and it gives rise to stress opposing the internal pressure as in the case of equilibrium pressure if the Korteweg coefficient has the appropriate sign. A second term arises from the expansion velocity and is proportional to the rate of change of viscosity with volume fraction. This term has the wrong sign for interfacial tension in the case of glycerin and water solution but has the right sign when light fluid is more viscous.

Acknowledgment

References

Arecchi, F.T., Buah-Bassuah, P.K., Francini, F., Perez-Garcia, C. & Quercioli, F., 1989, An experimental investigation of the break-up of a liquid drop falling in a miscible fluid, *Europhys. Lett.*, **9** (4), 333-338 .

Barkey, D.P. & Laporte, P.D., 1990, J. Electrochem. Soc., **137**, 1655 .

Baumann, N., Joseph, D.D., Mohr, P. & Renardy, Y., 1991, Vortex rings of one fluid in another in free fall, Phys. Fluids (to appear)

Cahn, J. & Hilliard, J., 1958, Free Energy of s Nonuniform System I: Interfacial free Energy, *J. Chem. Phys.*, 28, 258-267.

Davis, H.T., 1988, A theory of tension at a miscible displacement front, in *Numerical Simulation and Oil Recovery*, Ed. Wheeler, M., IMA, **2**.

Freundlich, H., 1926, *Colloid and Capillary Chemistry*, London, Mathuen & Co. Ltd.

Galdi, P., Joseph, D.D., Preziosi, L. & Rionero, S., 1991, Mathematical problems for miscible incompressible fluids with Korteweg stresses. *European J. Mech. B/Fluids* .

Garik, P., Hetrick, J., Orr, B., Barkey, D. & Ben-Jacob, E., 1991, Interfacial cellular mixing and a conjecture on global deposit morphology, *Physical Review Letters.* **66**(12),1606-1609.

Joseph, D.D., 1990, Fluid dynamics of two miscible liquids with slow diffusion and Korteweg stresses. *European J. Mech. B/Fluids*, **9**, n° 6, 565-596.

Kojima, M., Hinch, E.J. & Acrivos, A., 1984, The formation and expansion of a toroidal drop moving in a quiescent fluid., *Phy. Fluids*, **1**, (8), 1309-1313

Korteweg, D., 1901, Sur la forme que prennant les e quations du mouvement des fluides si l'on tient compte des forces capillaires cause es par des variations de densite . *Arch. Ne erl. Sciences Exactes et Naturelles, Series II*, **6**,1-24.

Landau, L.D. & Lifshitz, E.M. 1959, Fluid Mechanics, Pergamon Press, Addison-Wesley Publishing Co. Chap.VI.

May, S.E. and Maher, J.V., 1991, Capillary wave relaxation for a meniscus between miscible liquids (submitted to Phys. Rev. Letters)

Quinke, G., 1902, Die oberfä chenspannung an der Grenge von Alkohol mit wä sserigen Salzlö sungen, *Ann. Phys.*, **9**, (4).

Pukhnachov,V.V.,1991, Mathematical model of natural convection under low gravity, Institute for Mathematics and its Applications, Preprint #796, Univ. of Minnesota.

Segur, J.B., 1953, Physical properties of glycerol and its solutions, in *Glycerol* (eds. C.S. Miner, and N.N. Dalton), Reinhold.

Smith, P.G., Van Den Ven M. & Mason, S.G., 1981, The transient interfacial tension between two miscible fluids, *J. Colloid Interface Sci.*, **80**, (1), 302-303

Van der Waals, M., 1895, Theorie thermodynamique de la capillaritė dans l'hypothė se d'une variation de densitė , *Arch. Neerl. Sci. Ex. Nat.*, **28**, 121-201