

Non-solenoidal Velocity Effects and Korteweg Stresses in Simple Mixtures of Incompressible Liquids

Daniel D. Joseph[‡], Adam Huang, and Howard Hu
Department of Aerospace Engineering and Mechanics
University of Minnesota, Minneapolis, MN 55455

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 $\Delta = \text{div} \mathbf{u}$ 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. 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. In the context of the new theory, we derive a new and elementary solution which describes diffusion of binary species along a pipe. An analysis of this solution to small disturbances leads to a nonseparable problem which is solved by a finite element method. The numerical study indicates stability under all circumstances.

[‡]At a time 30 years ago when I was trying to prove theorems Fritz showed me by example how applied math ought to apply. He had an enormous impact on my development as an empirical scientist. I admire him greatly and treasure our years of friendship.

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Acknowledgment

References

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.

In all the previous studies of incompressible mixing liquids known to us (miscible displacements, binary convection, Taylor dispersion, reaction and diffusion, transport of diffusing dyes, Marangoni convection, diffusion controlled solidification, etc), it is universally and incorrectly assumed that $\text{div} \mathbf{u} = 0$. One aim of our study is to find the situations in which $\text{div} \mathbf{u} = 0$ is a good approximation. In fact $\text{div} \mathbf{u} = 0$ is exact when the difference of density of the two constituents is zero and when there is no diffusion. It is a good approximation in some situations when the density difference is small, as in a Boussinesq approximation and when the diffusion is slow. However, even in the Boussinesq or slow diffusion approximation there are problems in which $\text{div} \mathbf{u}$ is large at certain times and places. 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 $\text{div} \mathbf{u} = 0$ is 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 $\text{div} \mathbf{u} = 0$ 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 two 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 $D = O(10^{-6} \text{ cm}^2/\text{sec})$ 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, $\text{div}\mathbf{u} \neq 0$. A conservation form of the left-hand side of the diffusion equation which differs from the usual substantial derivative of ϕ by the term $\phi \text{div}\mathbf{u}$, 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

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

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

$$\frac{d\gamma}{dt} + \gamma \text{div}\mathbf{u} = -\text{div}\mathbf{q}_\gamma \quad (2.2)$$

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

$$\frac{d\rho}{dt} = \rho'(\gamma) \frac{d\gamma}{dt} \quad (2.3)$$

is not zero when

$$\frac{d\gamma}{dt} = \frac{\partial\gamma}{\partial t} + (\mathbf{u} \cdot \nabla)\gamma \neq 0, \quad (2.4)$$

that is, in the usual case. Hence, the continuity equation gives

$$\operatorname{div}\mathbf{u} = -\frac{1}{\rho} \frac{d\rho}{dt} \neq 0. \quad (2.5)$$

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

$$\frac{d\nu}{dt} + \nu \operatorname{div}\mathbf{u} = -\operatorname{div}\mathbf{q}_\nu. \quad (2.6)$$

The continuity equation may be written as

$$\frac{d\nu}{dt} + \frac{d\gamma}{dt} + (\nu + \gamma) \operatorname{div}\mathbf{u} = 0. \quad (2.7)$$

Hence, using (2.2) and (2.6) in (2.7), we find that

$$\operatorname{div}(\mathbf{q}_\nu + \mathbf{q}_\gamma) = 0. \quad (2.8)$$

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

$$\int_{\partial V} (\mathbf{q}_\nu + \mathbf{q}_\gamma) \cdot \mathbf{n} dS = 0. \quad (2.9)$$

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

$$\rho(\phi) = \rho_\gamma \phi + \rho_\nu(1 - \phi) \quad (2.10)$$

where ρ_γ and ρ_ν are the densities of γ and ν , handbook values. Mixtures satisfying (2.10) will be called **simple mixtures**. Equation (2.10) 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 $\nu = \rho_\nu(1 - \phi)$ and conserved in the absence of diffusion, it is natural to express the constitutive equation for the fluxes \mathbf{q}_γ and \mathbf{q}_ν as a nonlinear Ficks' law for each constituent in terms of the volume fraction of one of them

$$\mathbf{q}_\gamma = -D_\gamma(\phi)\nabla(\rho_\gamma\phi); \quad \mathbf{q}_\nu = -D_\nu(\phi)\nabla[\rho_\nu(1 - \phi)] \quad (2.11)$$

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

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

in each and every material volume V , so that the ratio of diffusion functions

$$\frac{D_\nu}{D_\gamma} = \frac{\rho_\gamma}{\rho_\nu} \quad (2.12)$$

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. (2.5)). However, Galdi, Joseph, Preziosi and Rionero [1991] have shown that if (2.10) holds, then (2.2) and (2.5) imply that

$$\operatorname{div} \mathbf{w} = 0, \quad (2.13)$$

where

$$\mathbf{w} = \mathbf{u} - \frac{(\rho_\gamma - \rho_\nu)}{\rho_\gamma \rho_\nu} \mathbf{q}_\gamma. \quad (2.14)$$

From (2.8), we also get

$$\operatorname{div} \hat{\mathbf{w}} = 0,$$

where

$$\hat{\mathbf{w}} = \mathbf{u} - \frac{(\rho_\gamma - \rho_\nu)}{\rho_\gamma \rho_\nu} \mathbf{q}_\nu.$$

In this case we may introduce a streamfunction.

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))

$$\rho \frac{dc}{dt} = -\operatorname{div} \mathbf{i} \quad (2.15)$$

where

$$c = m_\gamma / m = \gamma / \rho \quad (2.16)$$

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 (2.16) into (2.15) using (2.5) we get

$$\rho \frac{d\gamma/\rho}{dt} = \frac{d\gamma}{dt} + \gamma \operatorname{div} \mathbf{u}. \quad (2.17)$$

This shows that (2.15) is perfectly consistent with mass conservation argument (2.1) provided that

$$\operatorname{div} \mathbf{i} = \operatorname{div} \mathbf{q}_\gamma \quad (2.18)$$

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

Landau and Lifshitz develop a coupled thermodynamic theory for \mathbf{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

$$\mathbf{i} = -\alpha \text{grad} \hat{\mu} = -\alpha \left(\frac{\partial \hat{\mu}}{\partial c} \right)_{p,T} \text{grad} c = -\rho D \text{grad} c \quad (2.19)$$

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

$$\rho \text{grad} c = \frac{\rho_\gamma \rho_\nu}{\rho(\phi)} \text{grad} \phi \quad (2.20)$$

After combining (2.17) and (2.18) with (2.15), with constant ρ_γ and ρ_ν , we find that

$$\frac{\partial \phi}{\partial t} + \text{div}(\phi \mathbf{u}) = \text{div}[D_\gamma(\phi) \nabla \phi] \quad (2.21)$$

where

$$D_\gamma(\phi) = \frac{\rho_\nu D(\phi)}{\rho_\gamma \phi + \rho_\nu (1 - \phi)}. \quad (2.22)$$

Chemical engineers learn how to deal with diffusion from Bird, Stewart and Lightfoot [1958] who use a mixture theory and based on a number averaged velocity \mathbf{u}_i of species i , a mass averaged velocity $\mathbf{u} = \sum_{i=1}^N \rho_i \mathbf{u}_i / \rho$ where $\rho_i = N_i m_i / V$ is the density of the species i , m_i is the mass of one of them, N_i is the number of them in V and $\rho = \sum_{i=1}^N \rho_i$. Diffusion equations are defined from mass conservation consideration by introducing the relative flux

$$\mathbf{j}_i \stackrel{\text{def}}{=} \rho_i (\mathbf{u}_i - \mathbf{u}), \quad \sum_{i=1}^N \mathbf{j}_i = 0. \quad (2.23)$$

Then, the mass balance equations

$$\frac{\partial \rho}{\partial t} + \text{div} \rho \mathbf{u} = 0, \quad (2.24)$$

$$\frac{\partial \rho}{\partial t} + \text{div} \rho_i \mathbf{u}_i = 0, \quad (2.25)$$

may be combined into diffusion equations

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \rho_i \mathbf{u} = -\operatorname{div} \mathbf{j}_i \quad (2.26)$$

Mixture theories assume interpenetrating continua where molecules of different species, say glycerin and water, occupy the same point but move with different velocities. Short range forces which glue liquids of different type together and force cooperative motions are ignored

Bird, et al. do not explicitly consider simple mixture of incompressible liquids where the volume fraction is the nature variable of composition. However, John Brady has shown us how this kind of theory can be extracted from the mixture theory of Bird, et al. The volume fraction ϕ of the i th species is given by

$$\phi_i = \rho V_i / M_i, \quad \sum_{i=1}^N \phi_i = 1 \quad (2.27)$$

where M_i is the mass per mole and V_i is the volume of the i th species in one mole. In binary mixtures $N = 2$, $\phi_1 = \phi$, $\phi_2 = 1 - \phi$ and

$$\rho = \rho_1 + \rho_2 = \frac{M_1}{V_1} \phi + \frac{M_2}{V_2} (1 - \phi) \quad (2.28)$$

which is always true whether or not there is a volume change of mixing. When there is no volume change V_1 and V_2 are constants and we may compare (2.10) and (2.28) to show that $(\gamma, \nu, \rho_\gamma, \rho_\nu) = (\rho_1, \rho_2, M_1/V_1, M_2/V_2)$. Moreover, when V_1 is constant, we may write

$$\rho_\gamma \left(\frac{\partial \phi}{\partial t} + \operatorname{div} \phi \mathbf{u} \right) = -\operatorname{div} \mathbf{j}_1. \quad (2.29)$$

The relative flux can be identified with \mathbf{q}_γ when \mathbf{q}_γ is expressed as in (2.11). The relation $\operatorname{div}(\mathbf{q}_\gamma + \mathbf{q}_\nu) = 0$ which holds in general is satisfied identically for simple mixture satisfying (2.11) and (2.12) because in this case $\mathbf{q}_\gamma + \mathbf{q}_\nu = \mathbf{j}_1 + \mathbf{j}_2 = 0$. Bird, et al. model diffusion, their \mathbf{j}_i , in the same manner as

Landau and Lifshitz, \mathbf{j}_1 replaces \mathbf{i} in (2.19), so that all authors will arrive at the same results when the consequences of incompressibility are modeled by simple mixtures (2.10).

We have investigated the consequences for mass balance and diffusion of the assumption that the volumes of incompressible constituent do not change on mixing. This is expressed by (2.10) which shows that the density of such a mixture may change by dilution and that the volume fraction is the material variable connecting mass and diffusion. It follows from our theory that the velocity \mathbf{u} is not solenoidal but that a linear combination \mathbf{w} (or $\hat{\mathbf{w}}$) of the velocity and a species flux are solenoidal. These effects could also be obtained from equations contained in the theories presented by Landau and Lifshitz [1959] and by Bird, et al. [1958], but they seem not to have been explored.

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 universally and incorrectly assumed that $\text{div}\mathbf{u} = 0$. Presumably the practitioners of these arts know what they are doing and recognize that they are making an approximation, like the Boussinesq approximation. In fact, though there are surely many situations in which the assumption that $\text{div}\mathbf{u} = 0$ is a good one, there are others in which

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

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 $\text{div} \mathbf{u}$ will be small if the prefactor or the diffusion coefficient $D_\gamma(\phi)$ is small. For glycerin $\rho_\nu = 1.26g/cm^3$ and water $\rho_\gamma = 1g/cm^3$, 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 $\text{div} \mathbf{u} = 0$ is a slow diffusion rather than 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. A natural method for this is to apply balance laws to a material volume which in the continuous limit is a particle of fluid mass. The same perception is behind the use of a mass averaged velocity in mixture theories. In both cases we defer to the statement that the laws of dynamics are framed relative to the velocity \mathbf{u} of a 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 $\text{div} \mathbf{u} = 0$. We are going to study the superposition of non-classical effects of volume changes $\text{div} \mathbf{u} \neq 0$ due to diffusion and Korteweg stresses.

In the isothermal case, ρ varies with ϕ alone, as in (2.10) 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

$$\begin{aligned} \hat{\delta} &= (\rho_\gamma - \rho_\nu)^2 \delta_1 + \delta_2 + 2\nu (\rho_\gamma - \rho_\nu), \\ \hat{\gamma} &= \gamma_1 (\rho_\gamma - \rho_\nu)^2 + \gamma_2. \end{aligned}$$

The governing equations are

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

$$\frac{d\phi}{dt} + \phi \operatorname{div} \mathbf{u} = \nabla(D_\gamma \nabla \phi) \quad (3.3)$$

and

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \Pi + \operatorname{div} \mathbf{T}^D + \rho \mathbf{g}, \quad (3.4)$$

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

$$\begin{aligned} T_{ij}^D &= 2\mu D_{ij} - \frac{2}{3} \delta_{ij} \mu \operatorname{div} \mathbf{u} + \tau_{ij}, \\ \tau_{ij} &= \hat{\delta} \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} + \hat{\gamma} \frac{\partial^2 \phi}{\partial x_i \partial x_j} - \frac{1}{3} \delta_{ij} \left\{ \hat{\delta} |\nabla \phi|^2 + \hat{\gamma} \nabla^2 \phi \right\} \end{aligned} \quad (3.5)$$

and Π is the mean normal stress.

The continuity equation (3.2) may be replaced with

$$\operatorname{div} \mathbf{w} = 0 \quad \text{and} \quad \mathbf{w} = \mathbf{u} - \zeta D_\gamma \nabla \phi \quad (3.6)$$

where

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

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

Then, using (3.6), we may eliminate $\operatorname{div} \mathbf{u}$ from (3.5)

$$T_{ij}^D = 2\mu D_{ij} - \frac{2}{3} \delta_{ij} \zeta \mu \operatorname{div} (D_\gamma \nabla \phi) + \tau_{ij} \quad (3.8)$$

and rewrite (3.4) as

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

where

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

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 \mathbf{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

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

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 $\mu_G = 14.99$ *poise* at $20^\circ C$. The density of glycerin (G) and water (W) mixtures is given to within 1% by (2.10) with $(\rho_\gamma, \rho_\nu) = (\rho_W, \rho_G) \sim (1, 1.26) g/cm^3$ at $20^\circ C$. Unfortunately we do not have the global dependence of the diffusion coefficient $D_\gamma(\phi)$. 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 $D = 5 \times 10^{-6} cm^2/sec$. We will use this representative value in our estimates.

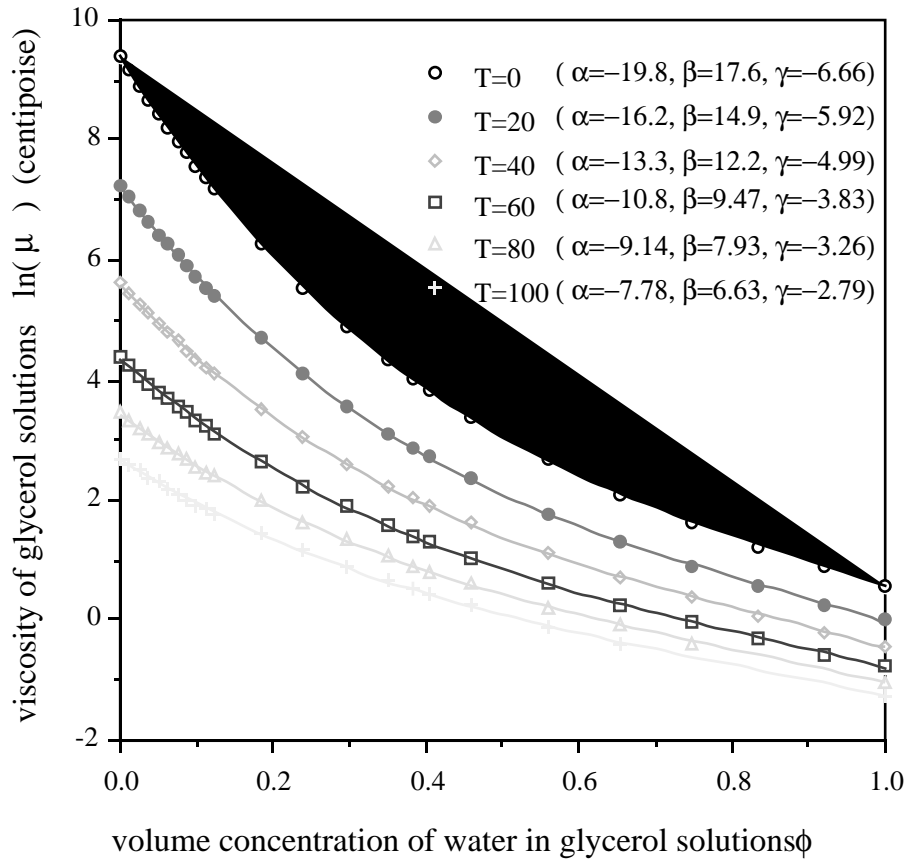


Figure 1: (After Segur [1953]) Viscosity of glycerol solutions at temperature $0 - 100^{\circ}\text{C}$. The expression $\mu = \mu_G \exp(\alpha\phi + \beta\phi^2 + \gamma\phi^3)$ fits the experimental data.

4 One dimensional mixing layer problems

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

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

Hence

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

where

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

is the expansion velocity which arises from mixing. In theories in which $\operatorname{div}\mathbf{u} = 0$ 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 $\phi(x, t)$ 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 $x = \pm\infty$. These problems are canonical for the development of mixing layers from initially discontinuous data which are considered below. When $A(t) = 0$,

$$u = u_e = \zeta D_\gamma \frac{\partial\phi}{\partial x} \quad (4.5)$$

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 $D(\phi)$ given by (2.22), the above diffusion equation then becomes

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

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 2000 *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, 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

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

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

$$\phi(x, t) = [\phi_+ - \phi_-] f(\eta), \quad f(\eta) = \operatorname{erfc}(\eta), \quad \eta = x/2\sqrt{Dt}$$

and S^* is proportional to

$$[\phi_+ - \phi_-]^2 \int_{-x_0}^{x_0} \frac{1}{\pi} \exp(-2\eta^2) \left(\frac{\partial \eta}{\partial x} \right)^2 dx = \frac{[\phi_+ - \phi_-]^2}{2\pi\sqrt{Dt}} \int_{-\eta_0}^{\eta_0} \exp(-2\eta^2) d\eta$$

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 *dyne/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 $6.3 \times 10^{-2} \text{dyne/cm}$ for $t = 1s$ and $D = 10^{-9} \text{cm}^2/s$ to 10^{-5}dyne/cm for $t = 4000s$ and $D = 10^{-5} \text{cm}^2/s$. 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 $n_1 = \tilde{\phi}n$ and $n_2 = (1 - \tilde{\phi})n$. $\tilde{\phi}$ 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 $\tilde{\phi}$ with the mass fraction $\hat{\phi} = m_\gamma/m$ of an incompressible liquid (say, water) in a mixture (say, water and glycerin) of total $m = m_\gamma + m_\nu$ where m_ν is the mass fraction of glycerin. Then (n, n_1, n_2) should be replaced by $(m/V, m_\gamma/V_\gamma, m_\nu/V_\nu) = (\rho, \rho_\gamma, \rho_\nu)$, where V is the total material volume and ρ_γ and ρ_ν are the ordinary (constant) densities (of water and glycerin) listed in the handbooks. Moreover, if our regular solution keeps its volume after mixing, then

$$n = \rho\tilde{\phi} + \rho(1 - \tilde{\phi}) = \frac{m}{V} \frac{M_\gamma}{m} + \frac{m}{V} \left(1 - \frac{m_\gamma}{m}\right) = \gamma + \nu = \rho_\gamma\hat{\phi} + \rho_\nu(1 - \hat{\phi}) = \rho(\hat{\phi})$$

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 type of calculation of dynamic tension given above, as well as the calculation to be carried out in section 6 given rise to a pressure difference across a spreading plane layer. This is not a good analogy to interfacial tension which gives rise to a pressure difference 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 far reaching, even in the spherically symmetric case.

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 $t = 0$, water lies above glycerin

$$\phi = 1 \text{ for } x > 0, \quad \phi = 0 \text{ for } x < 0 \quad (6.1)$$

where ϕ is the water fraction. We are on an infinite domain and

$$\phi = 1 \text{ for } x \rightarrow \infty, \quad \phi = 0 \text{ for } x \rightarrow -\infty \quad (6.2)$$

for all $t > 0$. 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 $10^{-6} \text{ cm}^2/\text{sec}$. Then classical diffusion equation (4.6) has a similarity solution

$$\phi = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\eta} e^{-\eta^2} d\eta \quad (6.3)$$

with

$$\eta = \frac{x}{2\sqrt{(Dt)}}. \quad (6.4)$$

Using (6.3) we may express (4.5) as

$$\begin{aligned} u = u_e &= \frac{\zeta}{2(1-\zeta\phi)} \sqrt{\frac{D}{t}} \phi' \left(\frac{x}{2\sqrt{Dt}} \right) \\ &= \frac{\zeta}{2\sqrt{\pi}(1-\zeta\phi)} \sqrt{\frac{D}{t}} \exp \left[- \left(\frac{x}{2\sqrt{Dt}} \right)^2 \right]. \end{aligned} \quad (6.5)$$

The diffusion layer can be defined from the place $-x_o$ where $\psi = \phi - 1/2 = -0.495$ 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

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

and it tends to ∞ 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

$$\int_{-x_0}^{x_0} \rho(\phi) \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right) dx = -[\Pi] - g \int_{-x_0}^{x_0} \rho(\phi) dx \quad (6.7)$$

where

$$[\Pi] = \Pi(x_0, t) - \Pi(-x_0, t).$$

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

$$\int_{-x_0}^{x_0} \rho(\phi) \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \right) dx = \int_{-x_0}^{x_0} \frac{\partial \rho u}{\partial t} dx = D \rho_\nu \int_{-x_0}^{x_0} \frac{\partial}{\partial t} \left(\frac{\partial \phi}{\partial x} \right) dx = 0, \quad (6.8)$$

which is also true for general diffusion coefficient $D(\phi)$. Therefore

$$[\Pi] = -g \int_{-x_0}^{x_0} \rho(\phi) dx. \quad (6.9)$$

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_0 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 $r = \infty$. Under these conditions $\text{div}\mathbf{w} = 0$ implies that

$$u(r, t) = u_e(r, t) = \zeta D_\gamma \frac{\partial \phi(r, t)}{\partial r}. \quad (7.1)$$

The diffusion equation (3.3) may then be written as

$$\frac{\partial \phi}{\partial t} = D \frac{\partial}{\partial r} \left(\frac{\partial \phi}{\partial r} \right) + \frac{2D}{r} \frac{\partial \phi}{\partial r} \quad (7.2)$$

where the water fraction $\phi(r, t) = 1$ when $r > r_0$, $t = 0$ and $\phi(r, t) = 0$ when $r < r_0$, $t=0$. When the thickness of the mixing layer at $r = r_0$ 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 $r = r_0$ and it has the same self similar solution with

$$\eta = \frac{r - r_0}{2\sqrt{Dt}}, \quad (7.3)$$

when $2\eta\sqrt{Dt} \ll r_0$.

The momentum equation (3.9) may be written as

$$\rho(\phi) \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} \right] = -\frac{\partial}{\partial r} \left[\Pi + Q(\phi) \right] + 2 \frac{\partial}{\partial r} \left(\mu \frac{\partial u}{\partial r} \right) + \frac{4\mu}{r} \frac{\partial u}{\partial r} - 4\mu \frac{u}{r^2} + \frac{\partial}{\partial r} \left[\hat{\delta} \left(\frac{\partial \phi}{\partial r} \right)^2 \right] + \frac{2\hat{\delta}}{r} \left(\frac{\partial \phi}{\partial r} \right)^2 \quad (7.4)$$

where $\rho(\phi)$ is given by (2.10) and $\mu(\phi)$ by (3.11). After integrating over the mixing layer from $r_1 = r_0 - 2m\sqrt{Dt}$ to $r_2 = r_0 + 2m\sqrt{Dt}$, we find that

$$\int_{r_1}^{r_2} \left\{ \rho(\phi) \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} \right) - 4\mu \frac{\partial u/r}{\partial r} - \frac{2\hat{\delta}}{r} \left(\frac{\partial \phi}{\partial r} \right)^2 \right\} dr = \left[-\Pi - Q(\phi) + 2\mu \frac{\partial u}{\partial r} + \hat{\delta} \left(\frac{\partial \phi}{\partial r} \right)^2 \right]_{r_1}^{r_2} \quad (7.5)$$

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

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

and putting terms outside the mixing layer to zero we get

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

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

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

$$\frac{1}{r_0} \sqrt{\frac{D}{t}} \int_{-m}^m \left\{ 2 \frac{\mu'(\phi)\zeta}{1-\zeta\phi} - \frac{\hat{\delta}}{D} \right\} \phi^2 d\eta. \quad (7.8)$$

Finally,

$$\Pi(r_2, t) - \Pi(r_1, t) = \frac{2}{r_0} \sqrt{\frac{D}{t}} \int_{-m}^m \left\{ \frac{\mu'(\phi)\zeta}{1-\zeta\phi} - 0.5 \frac{\hat{\delta}}{D} \right\} \phi^2 d\eta. \quad (7.9)$$

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

$$\Pi(r_1, t) - \Pi(r_2, t) = \frac{2}{r_0} \sqrt{\frac{D}{t}} \left[164.5 \frac{-\hat{\delta}}{D} - 428.7 \right] \quad (7.10)$$

with D about $7.5 \times 10^{-6} cm^2/sec$, but we do not have any knowledge about the value of Korteweg stress coefficient $\hat{\delta}$. Equation (7.10) reminds one of interfacial tension with a time dependent tension $T(t)$ whose values are given by comparing the right-hand side of (7.10) with $2T(t)/r_0$. 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.

8 The effects of convection on diffusion

In section 5 and 6 we studied problems in which velocity and stresses are induced by gradients of the volume fraction in simple mixtures. In these problems the gradients of ϕ are the engine which drives motion and the

motion is important only at early times. In other cases the motion is driven externally and the distribution of ϕ is driven by a balance of diffusion and convection. In this case, as in the other, the assumption that $\text{div} \mathbf{u} = 0$ can lead to large errors. The effects of expansion due to mixing on the distribution of velocity can be assumed by elementary analysis of steady flow. In the steady case, equations (4.1) to (4.4) reduce to

$$u = A + u_e, \quad (8.1)$$

$$u_e = \frac{\zeta D}{1 - \zeta \phi} \frac{d\phi}{dx}, \quad (8.2)$$

$$A \frac{d\phi}{dx} = D \frac{d^2 \phi}{dx^2}, \quad (8.3)$$

$$\frac{\rho(\phi)}{2} \frac{du^2}{dx} = -\frac{d}{dx} [\Pi + Q(\phi)] + \frac{d}{dx} \left[2\mu \frac{du}{dx} + \delta \hat{\left(\frac{d\phi}{dx} \right)^2} \right] + \rho(\phi) \mathbf{g} \cdot \mathbf{e}_x. \quad (8.4)$$

From (8.3) we find that

$$\phi = C_1 + C_2 \exp(Ax/D) \quad (8.5)$$

and from (8.2) and (8.1) we get

$$u_e = \frac{\zeta C_2}{1 - \zeta \phi} A \exp\left(\frac{Ax}{D}\right) \quad (8.6)$$

and

$$u = A \left[1 + \frac{\zeta C_2}{1 - \zeta \phi} \exp\left(\frac{Ax}{D}\right) \right] \quad (8.7)$$

where C_1 , C_2 and A are to be determined from the boundary conditions. The variation of effective pressure $\Pi(x)$ is determined by C_1 , C_2 and A , after putting (8.5) and (8.6) into (8.4). If, for example, we set Dirichlet conditions by prescribing $\phi(0) = \phi_0$ and $\phi(L) = \phi_L$, then

$$\phi(0) = \phi_0 + (\phi_L - \phi_0) \frac{\exp(Ax/D) - 1}{\exp(AL/D) - 1}. \quad (8.8)$$

The distribution of ϕ between 0 and L depends on the balance between diffusion and convection. We may define a diffusion length

$$\ell = D/A, \quad (8.9)$$

or an effective diffusion parameter

$$S = \frac{D}{LA} = \frac{\text{molecular diffusion}}{\text{convective diffusion}} = \frac{\text{diffusion velocity}}{\text{convective velocity}}. \quad (8.10)$$

Then the distribution of concentration is

$$\phi = \phi_0 + (\phi_L - \phi_0) \frac{\exp(\frac{x}{SL}) - 1}{\exp(\frac{1}{S}) - 1}, \quad (8.11)$$

and the expansion velocity in (8.2) can be evaluated

$$u_e(x) = \frac{A\zeta(\phi_L - \phi_0) \exp(\frac{x}{SL})}{\exp(\frac{1}{S}) - 1 - \zeta [\phi_0(\exp(\frac{1}{S}) - 1) + (\phi_L - \phi_0)(\exp(\frac{x}{SL}) - 1)]}. \quad (8.12)$$

If S is very small, then $\phi = \phi_0$ for most values of x , with a narrow mixing layer of thickness of order of ℓ near $x = L$. And the expansion velocity u_e , neglected in analysis which assume $\text{div} \mathbf{u} = 0$, will be important inside this layer. We may estimate that

$$u_e(0) \approx 0, \quad u_e(L) \approx A \frac{\zeta(\phi_L - \phi_0)}{1 - \zeta\phi_L} \quad (8.13)$$

when S is small. The effects of the expansion velocity are confined to the narrow mixing layer and the assumption that $\text{div} \mathbf{u} = 0$ is valid outside the mixing layer. Equation (8.13) also indicates that the expansion velocity inside the mixing layer is of the same order as the constant convection velocity A if the density ratio ζ is not too small. If S is not small, and this is a realizable possibility in many situations, then the expansion velocity will not be small and will not be confined to boundary layer. The velocity A can be determined from considerations involving momentum in the Hele Shaw example to be considered in the next section.

9 Two- and three-dimensional problems

In this section we will formulate initial-boundary value problems for simple incompressible binary mixtures which are miscible in all proportions. We will leave away the Korteweg stresses and emphasize non-classical effects arising from the observation that $\operatorname{div} \mathbf{u} \neq 0$ in general for such mixtures. We have found that

$$\mathbf{u} = \mathbf{w} + \mathbf{u}_e, \quad (9.1)$$

$$\mathbf{u}_e = \frac{\zeta D}{1 - \zeta \phi} \nabla \phi = \nabla h(\phi), \quad (9.2)$$

$$\operatorname{curl} \mathbf{u} = \operatorname{curl} \mathbf{w}, \quad (9.3)$$

$$\operatorname{div} \mathbf{u} = \operatorname{div} \mathbf{u}_e = \nabla^2 h. \quad (9.4)$$

The governing equations expressing the balance of mass, diffusion of species and momentum are

$$\operatorname{div} \mathbf{w} = \operatorname{div}(\mathbf{u} - \mathbf{u}_e) = 0, \quad (9.5)$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \phi \mathbf{w} = \operatorname{div}(D \operatorname{grad} \phi) \quad (9.6)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla \left(p + \frac{2}{3} \mu \operatorname{div} \mathbf{u} \right) + \operatorname{div} \left[\mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \right] \quad (9.7)$$

where $\rho = 1 - \zeta \phi$ and $\mu = \mu(\phi)$ depends on ϕ ; usually $\mu(\phi)$ is a rapidly varying function. We should think of ϕ as the water fraction of the glycerin-water mixture. The diffusion (9.6) show that the water fraction is advected with the solenoidal velocity \mathbf{w} . When written in terms of the mass average velocity, (9.6) becomes

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi + \phi \operatorname{div} \mathbf{u} = \operatorname{div} \left(\frac{\zeta D}{1 - \zeta \phi} \nabla \phi \right) \quad (9.8)$$

The weight difference $\zeta = (\rho_G - \rho_W)/\rho_G$ between the two species of our binary mixture, e.g., glycerin and water is a primary parameter which measures the extent of non-solenoidality. The expansion velocity is proportional to ζ and is zero for two species with the same density.

Turning next to boundary conditions at a solid wall, we note that the diffusive flux of any species across an impermeable, bounding surface vanishes. If \mathbf{n} is the outward normal at such a surface (from the fluid to solid), we have

$$\mathbf{n} \cdot \nabla \phi = 0 \tag{9.9}$$

This implies that

$$\mathbf{u}_e \cdot \mathbf{n} = 0 \tag{9.10}$$

at an impermeable boundary. There is no reason to suppress the slip velocity of each of the two species of our binary, but for several reasons, it seems appropriate to enforce a no-slip boundary condition for the mass-averaged velocity \mathbf{u} . If the velocity of a solid wall is prescribed as \mathbf{U} , then at the wall

$$\mathbf{u} = \mathbf{U}. \tag{9.11}$$

Of course, \mathbf{u} vanishes at a stationary wall. The paper by Mo and Rosenburger [1991] on molecular-dynamic simulations of flow with binary diffusion in a two-dimensional channel with atomically-rough walls establishes the no-slip condition via the mutual cancellation of the nonvanishing, opposing slip velocities of the components.

Suppose that the velocity of \mathbf{U} of the solid wall is prescribed, \mathbf{n} is the normal and \mathbf{t} is any tangent vector on the wall, $\mathbf{n} \cdot \mathbf{t} = 0$. Then since $\mathbf{u}_e \cdot \mathbf{n} = \mathbf{n} \cdot \nabla \phi = 0$ and $\mathbf{u} = \mathbf{U}$ on the wall, we get

$$\mathbf{w} \cdot \mathbf{n} = \mathbf{U} \cdot \mathbf{n}, \tag{9.12}$$

$$\mathbf{w} \cdot \mathbf{t} = \mathbf{U} \cdot \mathbf{t} - \mathbf{u}_e \cdot \mathbf{t}. \quad (9.13)$$

We can think that ϕ is determined by the diffusion equation and that $\mathbf{n} \cdot \nabla \phi = 0$. Then $\mathbf{u}_e \cdot \mathbf{t}$ can be thought as given and (9.12) and (9.13) look like prescribed, non-classical conditions for \mathbf{w} . Of course, in practice everything is coupled, but the description just given is good for sorting it out.

10 Basic solution for diffusion in a pipe

The problem being taken up here is in a three-dimensional domain with walls, but the solution is one dimensional. We don't think that the problem or its solution has been given before. Consider a pipe of arbitrary but constant cross section and length. The entrance to the pipe is at $x = 0$ and the exit at $x = L$. The pressure is taken to be the same at $x = 0$ and $x = L$ so pressure does not drive flow, and $\phi_0 \neq \phi_L$ are prescribed water fractions at the entrance and exit. We satisfy the condition that $\mathbf{u} = 0$ on the wall by taking $\mathbf{u} = \mathbf{u}_e + \mathbf{w} = 0$ everywhere. The diffusion equation (9.8) than reduces to

$$\frac{d}{dx} \left(\frac{D}{1 - \zeta \phi} \frac{d\phi}{dx} \right) = 0. \quad (10.1)$$

The solution $\phi = \Phi(x)$ of (10.1), which satisfies the prescribed conditions

$$\Phi(0) = \phi_0, \quad \Phi(L) = \phi_L \quad (10.2)$$

is given by

$$\Phi(x) = \frac{1}{\zeta} \left\{ 1 - (1 - \zeta \phi_0)^{1-x/L} (1 - \zeta \phi_L)^{x/L} \right\} \quad (10.3)$$

It is easy to verify from (10.3) and follows directly from (10.1) that

$$\frac{\zeta D}{1 - \zeta \Phi} \frac{d\Phi}{dx} = u_e = \text{const.} \quad (10.4)$$

where the expansion velocity is given by $u_e = \mathbf{e}_x u_e$. This velocity is balanced by a volume-averaged velocity $\mathbf{w} = \mathbf{e}_x w_{ox}$ where

$$w_{ox} = -u_e. \quad (10.5)$$

11 Stability of the basic solution for diffusion in a pipe

Let us consider the stability of the basic solution

$$\phi = \Phi(x), \quad \mathbf{u} = \mathbf{u}_e + w_{ox} \mathbf{e}_x = 0, \quad (11.1)$$

where $w_{ox} = D \ln \frac{1-\zeta\phi_0}{1-\zeta\phi_1}$ and $\Phi(x)$ is given by (10.3), \mathbf{u}_e by (9.2). Following the standard procedure of linear stability analysis, we introduce small perturbations to above solution, linearize the equations, and use L and $\rho_w L^2 / \mu_w$ as length and time scale to normalize the equations. We then introduce the temporal mode $e^{\sigma t}$. The resulting dimensionless linearized equations governing the perturbations are

$$\frac{\partial w_x}{\partial x} + \frac{\partial w_y}{\partial y} = 0 \quad (11.2)$$

$$\sigma\phi + w_{ox} \frac{\partial\phi}{\partial x} + w_x \frac{d\Phi}{dx} = \frac{\partial}{\partial x} \left(\tau \frac{\partial\phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\tau \frac{\partial\phi}{\partial y} \right) \quad (11.3)$$

$$\rho_0 \sigma u = -\frac{\partial\psi}{\partial x} + \frac{\partial}{\partial x} \left[2\mu_0 \frac{\partial u}{\partial x} \right] + \frac{\partial}{\partial y} \left[\mu_0 \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right] \quad (11.4)$$

$$\rho_0 \sigma v = -\frac{\partial\psi}{\partial y} + \frac{\partial}{\partial x} \left[\mu_0 \left(\frac{\partial v}{\partial y} + \frac{\partial u}{\partial x} \right) \right] + \frac{\partial}{\partial y} \left[2\mu_0 \frac{\partial v}{\partial y} \right] \quad (11.5)$$

$$u = w_x + \frac{\zeta\tau}{1-\zeta\Phi} \frac{\partial\phi}{\partial x} - w_{ox} \frac{\zeta\phi}{1-\zeta\Phi} \quad (11.6)$$

$$v = w_y + \frac{\zeta\tau}{1 - \zeta\Phi} \frac{\partial\phi}{\partial y} \quad (11.7)$$

where w_x, w_y are x, y components of \mathbf{w} , respectively, $\psi = p + \frac{2}{3}\mu_0\text{div}\mathbf{u}$, and $\tau = \frac{\rho_G D}{\mu_G}$, $\mu_0 = \frac{\mu_W}{\mu_G} e^{\Phi(x)}$. Using equations (11.6) and (11.7) we can eliminate \mathbf{w} from the continuity and diffusion equations

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} - \frac{\partial}{\partial x} \left(\tau a(x) \frac{\partial\phi}{\partial x} - a(x) w_{ox} \phi \right) - \tau a(x) \frac{\partial^2 \phi}{\partial y^2} = 0 \quad (11.8)$$

$$\sigma\phi = \tau\Delta\phi - \frac{d\Phi}{dx} \left(u + w_{ox} a(x)\phi - \tau a(x) \frac{\partial\phi}{\partial x} \right) + w_{ox} \frac{\partial\phi}{\partial x} \quad (11.9)$$

where Δ is the two dimensional Laplacian, and $a(x) = \zeta/(1 - \zeta\Phi(x))$. Equation (11.4), (11.5), (11.8) and (11.9) are four equations for u, v, ϕ and ψ .

The boundary conditions we take for this system are $v = p = \phi = 0$ at $x = 0$ and $x = 1$, $u = v = \frac{\partial\phi}{\partial x} = 0$ at $y = 0$ and $y = r$, with r being the width of the channel. Admittedly these conditions are rather artificial, but it is very difficult to specify simple, realistic boundary conditions for the physical process we are trying to model here. We could imagine that the two ends of the channel are porous plates which help maintain the concentration of water, while the no-slip condition forces the tangential velocity v to vanish on these plates.

The system of partial differential equations we just derived have variable coefficients depending on x . We can reduce it into a system of ordinary differential equations if we leave away the boundaries in the y direction. We shall first consider this case.

As we said before when ζ is zero, the problem degenerates to the classical diffusion problem. The basic concentration distribution becomes a linear function of x , and the stability problem is reduced to that of the usual one-

dimensional diffusion equation, while the velocity field is not involved. The eigenvalues are then given by

$$\sigma_0 = -\tau(n\pi)^2, n = 1, 2, \dots \quad (11.10)$$

When ζ is small but not zero, we can perturb this problem by expanding the unknowns as well as the eigenvalues into series of ζ , for example,

$$\sigma = \sigma_0 + \sigma_1\zeta + \sigma_2\zeta^2 + O(\zeta^3), \quad (11.11)$$

with the zeroth order solution given by the conventional diffusion problem. Carrying out this procedure to first order, we found that σ_1 is zero. However, it is not possible to carry on this perturbation beyond first order analytically. For general cases like glycerin and water, of which ζ is about 0.21, which is not too small, we solved the system of differential equations numerically by the finite element method. More about the numerical method is said later. Results of this case are shown in figure 2, in which the difference between the first eigenvalue and σ_0 is presented as functions of ζ for different values of ϕ_1 and ϕ_0 . In this one-dimensional case, we found $\sigma - \sigma_0$ is positive. This means that non-solenoidality is a destabilizing factor, although the influence is rather small. We also note that for the cases we calculated σ is nearly proportional to τ and the viscosity ratio $m = \frac{\mu_W}{\mu_G}$ is not a parameter.

In two dimensions, the problem is not separable in general. However, we can get an explicit solution if we look at waves which are so short that the variable coefficients in the linearized equations are essentially constant over the length of one wave. We may then freeze these coefficients at each and every point (x_0, y_0) and seek stability locally to disturbances of the form

$$e^{\sigma t} e^{i\alpha(x-x_0)} e^{i\beta(y-y_0)} \quad (11.12)$$

where $\alpha^2 + \beta^2 \rightarrow \infty$ for short waves. We find that

$$\alpha u + \beta v + \tau(\alpha^2 + \beta^2)a\phi + i\alpha a w_{ox}\phi = 0, \quad (11.13)$$

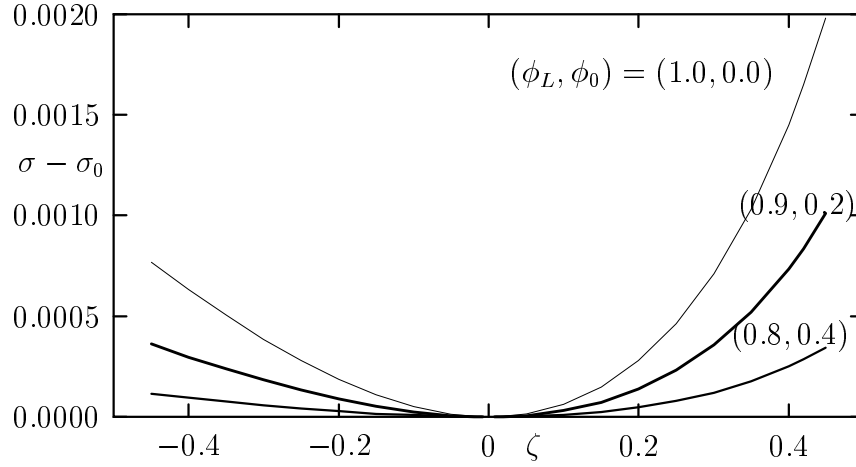


Figure 2: $\sigma - \sigma_0$ as functions of ζ , in one-dimensional case, $\tau = 0.01$, $\sigma_0 = -0.098696$.

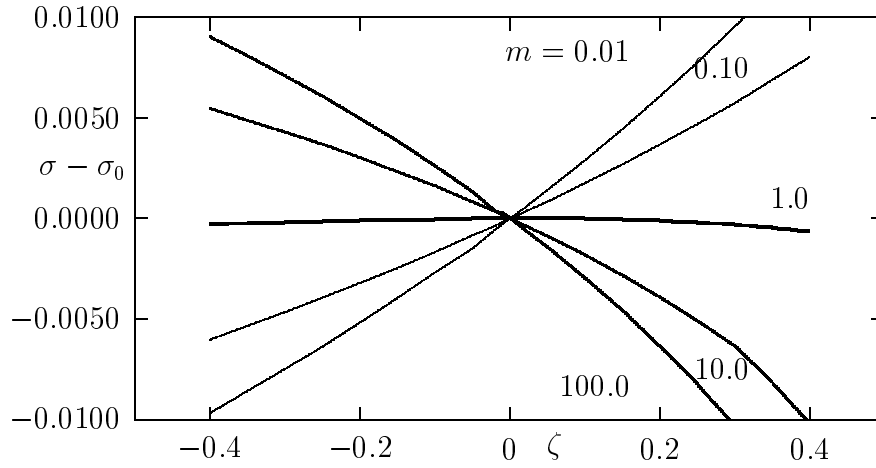


Figure 3: $\sigma - \sigma_0$ as functions of ζ , wall effect included. $\tau = 0.01$ and $r = 0.1$. $m = \frac{\mu_w}{\mu_G}$ is the viscosity ratio. σ_0 is as in figure 2.

$$\left[\sigma + i\alpha w_{ox} + \tau(\alpha^2 + \beta^2)\right] \phi + \Phi' (u + \alpha w_{ox} \phi - i\alpha \tau \phi) = 0, \quad (11.14)$$

$$\rho_0 \sigma u = -i\alpha \psi - 2\alpha^2 \mu_0 u + 2i\alpha \mu_0' u - \beta \mu_0 (\beta u + \alpha v), \quad (11.15)$$

$$\rho_0 \sigma v = -i\beta \psi + [i\mu_0' - \alpha \mu_0] (\beta u + \alpha v) - 2\beta^2 \mu_0 v. \quad (11.16)$$

After eliminating ψ , we find that

$$\left[\rho_0 \sigma + \mu_0(\alpha^2 + \beta^2) + i\mu_0' \alpha\right] (\beta u - \alpha v) = 0. \quad (11.17)$$

Equation (11.17) determines two eigenvalues,

$$\sigma_1 = -\frac{\mu_0}{\rho_0}(\alpha^2 + \beta^2) + i\frac{\mu_0'}{\rho_0}\alpha \quad (11.18)$$

and

$$\sigma_2 = -\tau(\alpha^2 + \beta^2) - i\alpha w_{ox} + \frac{\tau\beta^2\alpha^2}{\alpha^2 + \beta^2}\Phi'^2. \quad (11.19)$$

The first term of σ_2 is negative, which arises from the conventional diffusion equation. The last term of (11.19) is destabilizing. However, this term is dominated by $(\alpha^2 + \beta^2)$ in the limit of large $\alpha^2 + \beta^2$. Hence the effect of non-solenoidality of the velocity field on the growth rate is minimal for very short waves.

We next consider the wall effects by restricting the mixture to a rectangular domain. We take a slim channel with a width of 0.1 length for our calculation. In this case the conventional diffusion solution still exists because in which the velocity can be taken zero everywhere. The perturbation of ζ works only when the two constituents have the same viscosity. In more general cases, the system has to be solved numerically. We have developed a general code to solve eigenvalue problems of systems of PDE's. The finite element method is used to approximate the equations. However, this leads to very large matrices, which defies the use of common direct eigenroutines. We use a modified Arnoldi iterative method developed by Saad [1989] to find

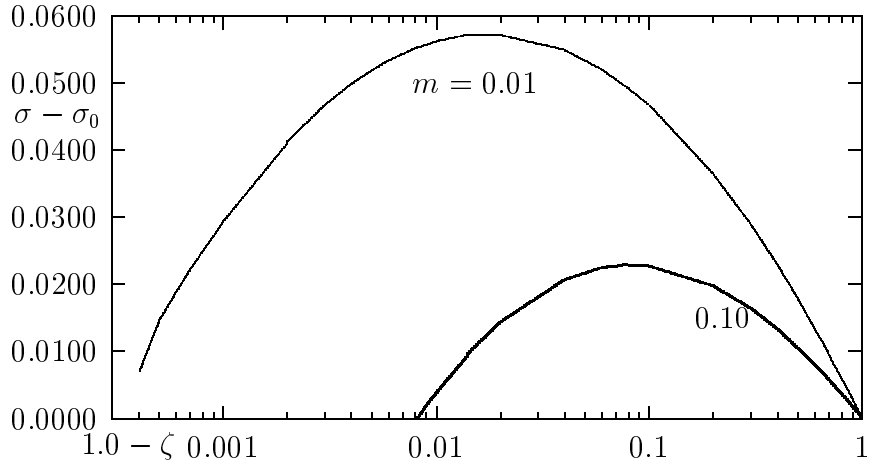


Figure 4: $\sigma - \sigma_0$ as functions of ζ as ζ is close to 1.0. Other parameters are the same as in figure 3.

the eigenvalue with the largest real (or imaginary) part. For more details of the numerical method and the related eigenvalue problem for large matrices, see Hu & Joseph [1989], Huang & Joseph [1994] and Saad [1980,1989]. Applying our numerical code to this 2-dimensional problem, we found when the lighter component is less viscous, non-solenoidality of the velocity field has a destabilizing effect, while if the lighter fluid is more viscous, it is stabilizing, as shown in figure 3, in which a special case, $\phi_1 = 1.0$, $\phi_0 = 0.0$ is presented. There is a cross symmetry between parameters m and ζ , i.e. a positive ζ and a larger than one m are equivalent to a negative ζ and a less than one m . This is due to the fact that the two fluids are complement to each other, if one is lighter, the other is heavier, and ζ can be defined the other way around for the same physical process.

Figure 3 shows that the growth rate increases with ζ when m is less than

one. However, when ζ gets close to one, the growth rate decreases, as shown in figure 4, so instability is not realized for this steady solution.

12 Conclusion and Discussion

A new solution describing the diffusion of species along a pipe driven by prescribed concentration difference with no net mass flux across any phase perpendicular to the walls of the pipe is derived. In this solution, $\mathbf{w} + \mathbf{u}_e = 0$, so that the volume-averaged velocity balances the expansion velocity everywhere. An analysis of stability indicates that the effect of the non-solenoidality of the velocity field on the stability is rather small for small density difference, nevertheless, when wall effect is included, there exists a cross symmetry between the viscosity ratio and the density difference, in that the non-solenoidality can be either stabilizing or destabilizing, depending on the physical properties of the two constituents in a fashion as described above.

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