NON-SOLENOIDAL VELOCITY EFFECTS AND KORTEWEG STRESSES IN SIMPLE MIXTURES OF INCOMPRESSIBLE LIQUIDS

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

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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. 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.
Contents

1. Introduction
2. Mass balance and diffusion
3. Momentum balance and Korteweg Stresses
4. One dimensional mixing layer problems
5. Dynamic and instantaneous interfacial tension
6. Jump of the normal stress across a plane mixing layer
7. Spreading of a spherical diffusion front and Korteweg stresses
8. The effects of convection and diffusion
9. Miscible displacement in a Hele Shaw cell
10. Conclusions and discussion

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 $\nabla=\text{div}\mathbf{u}$ 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-Bassuh, 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 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 $\phi$ 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 \( \phi \) 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 \( \gamma \) is the density of one liquid per unit total material volume \( V \), \( \gamma = m_\gamma V \) where \( m_\gamma \) is the mass of \( \gamma \). Then

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

(2.1)
says that the mass of \( \gamma \) in \( V \) can change only by diffusion across the boundary of \( V \). In the usual way we find that

\[
\frac{d\gamma}{dt} + \gamma \text{div} \mathbf{u} = - \text{div} \mathbf{q}_\gamma
\]

(2.2)
where \( \mathbf{q}_\gamma \) is the flux of \( \gamma \). Of course, the substantial time derivative of the density \( \rho(\gamma) \)

\[
\frac{d\rho}{dt} = \rho'(\gamma) \frac{d\gamma}{dt}
\]

(2.3)
is not zero when

\[
\frac{d\gamma}{dt} = \frac{\partial \gamma}{\partial t} + (\mathbf{u} \cdot \nabla) \gamma \neq 0
\]

(2.4)
that is, in the usual case. Hence, the continuity equation gives

\[
\text{div} \mathbf{u} = - \frac{1}{\rho} \frac{d\rho}{dt} \neq 0
\]

(2.5)
In general \( \gamma = \rho_\gamma \phi \) where \( \rho_\gamma = m_\gamma V_\gamma \) is the density of the fluid \( \gamma \) and \( \phi = V_\gamma V \) is the volume fraction. Under isothermal conditions \( \rho_\gamma \) is a constant and we may work with \( \rho(\phi) \) and \( \phi \) satisfies (2.2).

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

\[
\frac{d\nu}{dt} + \nu \text{div} \mathbf{u} = - \text{div} \mathbf{q}_\nu
\]

(2.6)
The continuity equation may be written as
\[
\frac{dv}{dt} + \frac{d\gamma}{dt} + (v+\gamma) \text{div} u = 0 .
\]
(2.7)

Hence, using (2.2) and (2.6) in (2.7), we find that
\[
\text{div} (q_v + q_\gamma) = 0 .
\]
(2.8)

The sum of the fluxes of the mass of each constituent across the boundary of any material volume V must vanish
\[
\int_{\partial V} (q_v + q_\gamma) \cdot n \ dS = 0
\]
(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
\[
\rho(\phi) = \rho_\gamma \phi + \rho_\nu (1-\phi)
\]
(2.10)

where $\rho_\gamma$ and $\rho_\nu$ are the densities of $\gamma$ and $\nu$, handbook values. Mixtures satisfying (2.10) will be called \textit{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 $q_\gamma$ and $q_\nu$ as a nonlinear Ficks' law for each constituent in terms of the volume fraction of one of them
\[
q_\gamma = -D_\gamma(\phi) \nabla (\rho_\gamma \phi) ; \ q_\nu = -D_\nu(\phi) \nabla [\rho_\nu(1-\phi)]
\]
(2.11)

with different diffusion functions and assume that $\rho_\gamma$ and $\rho_\nu$ are constants, as in the isothermal case, then
\[ \int_{\partial V} \mathbf{n} \cdot \mathbf{q} \, dS = \int_{\partial V} (D_\nu \rho_\nu - D_\gamma \rho_\gamma) \mathbf{n} \cdot \nabla \phi \, dS = 0 \]

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

\[ \frac{D_\nu}{D_\gamma} = \frac{\rho_\gamma}{\rho_\nu} \]  

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,

\[ \text{div } \mathbf{W} = 0 \]  

(2.13)

where

\[ \mathbf{W} = \mathbf{u} - \frac{(\rho_\gamma - \rho_\nu)}{\rho_\gamma \rho_\nu} \mathbf{q}_\gamma \]  

(2.14)

From (2.8), we also get

\[ \text{div } \hat{\mathbf{W}} = 0 \]  

where

\[ \hat{\mathbf{W}} = \mathbf{u} - \frac{(\rho_\nu - \rho_\gamma)}{\rho_\gamma \rho_\nu} \mathbf{q}_\nu \]  

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))

\[ \rho \frac{dc}{dt} = - \text{div } \mathbf{i} \]  

(2.15)
where

\[ c = \frac{m}{m} = \frac{\gamma}{\rho} \quad (2.16) \]

is the mass fraction, \( m \) is the total mass and \( i \) 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

\[ \rho \frac{d\gamma/\rho}{dt} = \frac{d\gamma}{dt} + \gamma \text{div} \mathbf{u} \quad . \quad (2.17) \]

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

\[ \text{div} i = \text{div} q_{\gamma} \quad (2.18) \]

is the divergence of the flux of \( \gamma \), 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

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

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 \( \rho_{\gamma} \) and \( \rho_{\nu} \), we find that

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

where

\[ D_{\gamma}(\phi) = \frac{\rho_{\nu} D(\phi)}{\rho_{\gamma} \phi + \rho_{\nu}(1-\phi)} \quad . \quad (2.22) \]
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 \( u_i \) of species \( i \), a mass averaged velocity \( \bar{u} = \frac{\sum_i N_i m_i}{\rho} \) where \( \rho = \sum_i N_i \rho_i \).

Diffusion equations are defined from mass conservation consideration by introducing the relative flux

\[
\begin{align*}
\mathbf{j}_i & \overset{\text{def}}{=} \rho_i \left( \mathbf{u}_i - \mathbf{u} \right), \\
\sum_i N_i \mathbf{j}_i & = 0 .
\end{align*}
\]

Then, the mass balance equations

\[
\begin{align*}
\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{u}_i &= 0 , \\
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} &= 0 ,
\end{align*}
\]

may be combined into diffusion equations

\[
\begin{align*}
\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{u}_i &= - \nabla \cdot \mathbf{j}_i .
\end{align*}
\]

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 \( \phi_i \) of the \( i \)th species is given by

\[
\begin{align*}
\phi_i &= \frac{\rho V_i}{M_i} , \\
\sum_i N \phi_i &= 1
\end{align*}
\]
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

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

The relative flux can be identified with $\mathbf{q}_\gamma$ when $\mathbf{q}_\gamma$ is expressed as in (2.11). The relation $\text{div} (\mathbf{q}_\gamma + \mathbf{q}_\nu) = 0$ 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

$$\text{div} \mathbf{u} = \frac{\rho_f \rho_v}{\rho_v \rho_g} \text{div} \mathbf{q}_g = \frac{\rho_f \rho_g}{\rho_v} \text{div} [D_g(\phi) \nabla \phi]$$

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 $D_g(\phi)$ is small. For glycerin $\rho_v = 1.26 \text{ g/cm}^3$ and water $\rho_g = 1 \text{ g/cm}^3$, the prefactor $0.26/1.26$ is not negligible, but the diffusion coefficient $D_g = O(10^{-6} \text{ cm}^2/\text{sec})$ 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 $u$ in $W$ 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 $\text{div} u = 0$. We are going to study the superposition of non-classical effects of volume changes $\text{div} u \neq 0$ due to diffusion and Korteweg stresses.

In the isothermal case, $\rho$ varies with $\phi$ 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 $\phi$ and $\rho(\phi)$ are

$$T^{(2)}_{ij} = \hat{\delta} \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} + \hat{\gamma} \frac{\partial^2 \phi}{\partial x_i \partial x_j}, \quad (3.1)$$

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

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

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

and

$$\rho \frac{du}{dt} = -\nabla \Pi + \text{div} T^D + \rho g, \quad (3.4)$$
where \( T^D \) is the stress deviator defined by

\[
T^D_{ij} = 2\mu D_{ij} - \frac{2}{3} \delta_{ij} \mu \text{div} \ u + \tau_{ij},
\]

and \( \Pi \) is the mean normal stress.

The continuity equation (3.2) may be replaced with

\[
\text{div} \ W = 0 \quad \text{and} \quad W = u - \zeta D\gamma \nabla \phi\]

where

\[
\zeta = \frac{(\rho_v - \rho_\gamma)}{\rho_v}.\]

We should be thinking of glycerin \( v \) and water \( \gamma \), then \( \zeta > 0 \).

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

\[
T^D_{ij} = 2\mu D_{ij} - \frac{2}{3} \delta_{ij} \zeta \mu \text{div}(D\gamma \nabla \phi) + \tau_{ij}
\]

and rewrite (3.4) as

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

where

\[
Q(\phi) = \frac{1}{3} \hat{\delta} |\nabla \phi|^2 + \frac{2}{3} \zeta \mu \text{div}(D\gamma \nabla \phi) - \frac{2}{3} \hat{\gamma} \ \nabla^2 \phi.
\]

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 \( \mathbf{u} \), \( \Pi \) and \( \phi \). 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 \( \mu \). This can be excellently correlated by the expression

\[
\mu = \mu_G \exp(\alpha \phi + \beta \phi^2 + \gamma \phi^3),
\]  

(3.11)

where the coefficients \( \alpha \), \( \beta \) and \( \gamma \) depend on temperature \( T \) in the way shown in the figure, \( \mu_G \) is the viscosity of pure glycerin and \( \mu_G = 14.99 \) poise at 20°C. The density of glycerin (G) and water (W) mixtures is given to within 1% by (2.10) with \((\rho_G, \rho_W)\sim(1,1.26)\) g/cm\(^3\) at 20°C. Unfortunately we do not have the global dependence of the diffusion coefficient \( D_\phi(\phi) \). Small gradient theories of diffusion are inadequate for mixing layers in which \( \phi \) takes on all allowed values from zero to one. A representative value \( D(\phi) \) over different concentration, taken from Segur (p.328) is \( D=5\times10^{-6}\text{cm}^2/\text{sec} \). We will use this representative value in our estimates.
The expression $\mu = \mu_G \exp(\alpha \phi + \beta \phi^2 + \gamma \phi^3)$ fits the experimental data.

Figure 1. (After Segur [1953]) Viscosity of glycerol solutions at temperature 0–100°C.
4. One dimensional mixing layer problems

We shall suppose that $u = u(x,t) = x$ where $x$ increases upward against gravity. In this case

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

Hence

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

(4.1)

where

$$u_e \overset{\text{def}}{=} \zeta D \frac{\partial \phi}{\partial x}$$

(4.2)

is the expansion velocity which arises from mixing. In theories in which $\text{div } u = 0$ 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

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

or

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

(4.3)

The momentum equation in one dimension is given by

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

(4.4)

where $u$ is given in terms of $A(t)$ and $\phi$ by (4.1). We need $\Pi$ 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 \( A(t)=0 \)

\[
u = u_e = \zeta D \frac{\partial \phi}{\partial x} \tag{4.5}
\]

and (4.3) reduces to

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

If we switch to use the classical diffusion coefficient \( D(\phi) \) given by (2.22), the above diffusion equation then becomes

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

In the simplest case, we assume that \( D \) is independent of \( \phi \), (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

\[ S^* \propto \int_{-x_0}^{x_0} \left( \frac{\partial \phi}{\partial x} \right)^2 \, dx \]  \hspace{1cm} (5.1)

where \( S^* \) is the interfacial tension, \( \phi \) 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 \( \phi_- \) for \( x<0 \) and thereafter \( \phi \) is continuous at \( x=0 \), then

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

and \( S^* \) is proportional to

\[ [\phi_+ - \phi_-]^2 \int_{-x_0}^{x_0} \frac{1}{\pi} \exp(-2\eta^2) \left( \frac{\partial \eta}{\partial x} \right)^2 \, dx \]

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

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 \( \theta \) were constant, where \( \theta \) 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 $S^*$ ($\gamma$ in his notation), given in his table 3.1, varying from about 6.3x10^{-2} dyn/cm for $t=1$s and $D=10^{-9}$ cm$^2$/s to 10^{-5} dyn/cm for $t=4000$s 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 $n_1=\phi_1 n$ and $n_2=(1-\phi_1)n$. $\phi_1$ 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 $\phi_1$ 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 $m_\nu$ is the mass fraction of glycerin. Then $(n,n_1,n_2)$ should be replaced by $(m/V,m_\gamma V/m_\gamma,m_\nu V/m_\nu)=(\rho,\rho_\gamma,\rho_\nu)$ where $V$ is the total material volume and $\rho_\gamma$ and $\rho_\nu$ are the ordinary (constant) densities (of water and glycerin) listed in the handbooks. Moreover, if our regular solution keeps its volume after mixing, then

$$n = \rho \hat{\phi} + \rho (1-\hat{\phi}) = \frac{m_\gamma}{V} \frac{m}{m} + \frac{m_\nu}{V} \left(1 - \frac{m_\gamma}{m}\right) = \gamma + \nu = \rho_\gamma \phi + \rho_\nu (1-\phi) = \rho(\phi)$$
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 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 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 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 $\phi$ at a plane. At $t=0$, water lies above glycerin
\[ \phi = 1 \text{ for } x > 0, \quad \phi = 0 \text{ for } x < 0 \]  \tag{6.1}

where \( \phi \) is the water fraction. We are on an infinite domain and

\[ \phi = 1 \text{ for } x \infty, \quad \phi = 0 \text{ for } x \not\infty \]  \tag{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 \( \phi \) 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

\[ \phi = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\eta} e^{-\eta^2} \, d\eta \]  \tag{6.3}

with

\[ \eta = \frac{x}{2\sqrt{Dt}} \]  \tag{6.4}

Using (6.3) we may express (4.5) as

\[ u = u_e = \frac{\zeta}{2(1-\zeta \phi)} \sqrt{\frac{D}{t}} \, \phi'\left( \frac{x}{2\sqrt{Dt}} \right) \]

\[ = \frac{\zeta}{2\sqrt{\pi} (1-\zeta \phi)} \sqrt{\frac{D}{t}} \exp\left[ -\left( \frac{x}{2\sqrt{Dt}} \right)^2 \right] \]  \tag{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

\[ \Delta x = x_o - (-x_o) = 4m\sqrt{Dt} \]  \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 $\phi$ 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 $\phi$ vanish and

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

(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

$$\int_{-x_0}^{x_0} \frac{\partial \rho \nu}{\partial x} \, dx = 0, \quad (6.8)$$

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

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

(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 \( r=\infty \). 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 \( r>r_o, t=0 \) 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

\[
\eta = \frac{r-r_o}{2\sqrt{Dt}}, \quad (7.3)
\]

when \( 2\eta\sqrt{Dt} \ll r_o \).

The momentum equation (3.9) may be written as

\[
\rho(\phi) \left[ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} \right] = - \frac{\partial}{\partial r} \left[ \Pi + Q(\phi) \right] + 2 \frac{\partial}{\partial r} \left( \mu \frac{\partial u}{\partial r} \right) + \frac{4\mu}{r} \frac{\partial u}{\partial r} - 4\mu \frac{u}{r^2} + \frac{\partial}{\partial r} \left[ \delta \left( \frac{\partial \phi}{\partial r} \right)^2 \right] + \frac{2\delta}{r} \left( \frac{\partial \phi}{\partial r} \right)^2 \quad (7.4)
\]
where ρ(φ) is given by (2.10) and μ(φ) 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

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

Outside the mixing layer \((r_1(t), r_2(t))\), \(\phi\) 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

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

and putting terms outside the mixing layer to zero we get

\[
\int_{r_1}^{r_2} \left\{ 4 \mu'(\phi) \frac{u}{r} \frac{\partial \phi}{\partial r} - \frac{2\delta}{r} \left( \frac{\partial \phi}{\partial t} \right)^2 \right\} \, dr = - \left[ \Pi \right]_{r_1}^{r_2} \tag{7.7}
\]

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

\[
\frac{2}{r_0} \int_{r_1}^{r_2} \left\{ 2 \mu'(\phi) u \frac{\partial \phi}{\partial r} - \hat{\delta} \left( \frac{\partial \phi}{\partial t} \right)^2 \right\} \, dr = \frac{2}{r_0} \int_{r_1}^{r_2} \left\{ 2 \mu'(\phi) \frac{\zeta D}{1-\zeta \phi} - \hat{\delta} \right\} \left( \frac{\partial \phi}{\partial t} \right)^2 \, dr
\]

\[
= \frac{1}{r_0} \sqrt{\frac{D}{t}} \int_{-m}^{m} \{ 2 \mu'(\phi) \frac{\zeta}{1-\zeta \phi} - \hat{\delta} \} \phi^2 \, d\eta. \tag{7.8}
\]

Finally,
For glycerin and water solutions at 20°C we may evaluate (7.9) using values for \( \mu' \) and \( \zeta \) near to (3.11) as

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

(7.9)

with \( D \) about 7.5x10^{-6} \text{ cm}^2/\text{sec}, but we do not have any knowledge about the value of Korteweg stress coefficient \( \hat{\delta} \). (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 \( \phi \) 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 \( \phi \) 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

\[ u = A + u_e , \quad (8.1) \]

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

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

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

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

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

The distribution of \( \phi \) between 0 and \( L \) depends on the balance between diffusion and convection. We may define a diffusion length
or an effective diffusion parameter

\[
S = \frac{D}{LA} = \frac{\text{molecular diffusion}}{\text{convective diffusion}} = \frac{\text{diffusion velocity}}{\text{convective velocity}}. \tag{8.10}
\]

Then the distribution of concentration is

\[
\phi = \phi_0 + (\phi_L - \phi_0) \frac{\exp(xS) - 1}{\exp(S) - 1}, \tag{8.11}
\]

and the expansion velocity in (8.2) can be evaluated

\[
ue(x) = A \zeta (\phi_L - \phi_0) \frac{\exp(xS)}{\exp(S) - 1 - \zeta [\phi_0(\exp(S) - 1) + (\phi_L - \phi_0)(\exp(xS) - 1)]}. \tag{8.12}
\]

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 \( \text{div} u = 0 \), will be important inside this layer. We may estimate that

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

when \( S \) is small. The effects of the expansion velocity are confined to the narrow mixing layer and the assumption that \( \text{div} u = 0 \) is valid outside the mixing layer. (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 \( \zeta \) 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. Miscible displacement in a Hele-Shaw cell
In this final section we are going to formulate a theory of miscible displacement in a Hele Shaw cell. The problem of miscible displacement in oil bearing sands is an important one for applications. It is well known that the equations which govern the flow of a single viscous incompressible liquid between the closely spaced parallel plates defining Hele Shaw cell are in the form of Darcy's equations with the averaged velocity proportional to the two dimensional gradient of piezometric pressure. From this springs an analogy between flow in a porous media and the more easily visualized flow in a Hele Shaw cell. This analogy has been pursued for the case of incompressible mixing liquids under the assumption of zero expansion \( \text{div} \mathbf{u} = 0 \), by many authors (see Homsy [1987] for a recent review). It was suggested already by Davis [1988] that the kind instability leading to fingering and tip-splitting observed in the miscible displacement experiments in a Hele-Shaw cell could be associated with an ersatz surface tension due to sharp gradient in composition. His idea of transient interfacial tension was discussed in section 5.

It is therefore of interest to see if a reasonable Hele Shaw theory with expansion velocity and Korteweg stresses included can be formulated to guide the interpretation of experiments. The theory given below is presumably valid under the usual assumptions resulting from small gap which lead to low Reynolds number viscously dominated flows in which the derivatives of the velocity normal to the walls are much larger than derivatives in the plane of the motion. Obviously this assumption cannot hold for small diffusion layer at early times in which the velocity and the derivatives of the volume fraction are effectively infinite. So we start our discussion of the theory with the remark that it may indeed fail at early times when fresh liquids of different composition are neighbors. After this we hope that lubrication approximations which are usually made for miscible displacement in a Hele Shaw cell (see Homsy [1987]) are valid.
Consider the flow in a Hele-Shaw cell, the geometry of which is shown in figure 2. The top of the cell is connected to a reservoir of glycerin and the bottom of the cell is flush with a reservoir of water, both reservoirs are open to atmosphere. The flow is falling freely under gravity in a small gap of thickness $b$, and there is a second macroscopic dimension $L$, with $b/L = \varepsilon << 1$. The reader should visualize this by imagining a razor like slit protruding into a vast reservoir of fresh stirred liquid. The equations (3.2), (3.3) and (3.4) can be simplified by averaging over the thin gap in this situation.
Figure 2. Geometry of a Hele-Shaw Cell. The top of the cell is connected to a reservoir of fluid 1 (glycerin) and the bottom of the cell is flush with a reservoir of fluid 2 (water).
Since $\varepsilon = b/L << 1$, the diffusion equation (3.3) requires that the variation of the volume concentration $\phi$ across the gap to be small, of the order of $\varepsilon^2$. Moreover, since there is no flux of water across such a wall, $\partial \phi / \partial z = 0$, there. Thus it is reasonable to assume that $\phi$ is independent of $z$; this means that the density and viscosity are also independent of $z$. Let the velocity $\mathbf{u} = (u_x, u_y, u_z)$, and $(x, y, z)$ be the coordinate system shown in figure 2. Unlike $\phi$, physics requires that $\mathbf{u} = 0$ on the walls and we are thinking of flow driven by gravity, so that $\mathbf{u}$ depends on $z$. When equations (3.2) and (3.3) are averaged over the gap, they become

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial y} (\rho v) = 0,$$

(9.1)

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial x} (\phi u) + \frac{\partial}{\partial y} (\phi v) = \frac{\partial}{\partial x} \left( D \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial \phi}{\partial y} \right),$$

(9.2)

where $u$ and $v$ are simple averages of the velocities $u_x$ and $u_y$ over the gap. In the momentum equation (3.9), since the flow is slow, or the Reynolds number based on gap size is small, we can neglect the inertial terms at the left hand of the equation. Obviously this last idea is erroneous at early times in the problem of plane mixing layers. An order of magnitude (lubrication) analysis yields that pressure $\Pi$ is independent of $z$ and

$$-\frac{\partial \Pi}{\partial x} + \rho g + \delta \left[ \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial x} \right)^2 + \frac{\partial}{\partial y} \left( \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} \right) \right] - \frac{\partial Q(\phi)}{\partial x} = 0,$$

(9.3)

$$-\frac{\partial \Pi}{\partial y} + \delta \left[ \frac{\partial}{\partial z} \left( \frac{\partial u_x}{\partial z} \right) + \frac{\partial}{\partial y} \left( \frac{\partial \phi}{\partial y} \frac{\partial \phi}{\partial z} \right) + \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} \right)^2 \right] - \frac{\partial Q(\phi)}{\partial y} = 0.$$

(9.4)

(9.3) and (9.4) can be integrated over $z$ twice, leading directly to the expressions for $u_x$ and $u_y$. Then the averaged velocities $u$ and $v$ can be obtained easily as

$$u = \frac{b^2}{12\mu} \left\{ -\frac{\partial \Pi}{\partial x} + \rho g + \delta \left[ \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial x} \right)^2 + \frac{\partial}{\partial y} \left( \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} \right) \right] - \frac{\partial Q(\phi)}{\partial x} \right\}.$$
\[
v = \frac{b^2}{12\mu} \left\{ \frac{\partial \Pi}{\partial y} + \delta \left[ \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial y} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\partial \phi}{\partial x} \right)^2 \right] - \frac{\partial Q(\phi)}{\partial y} \right\}. \tag{9.6}
\]

Now we further assume that the flow is uniform in \(y\)-direction, and the velocity in \(y\)-direction \(v\) is zero. In this unidirectional flow, we get the simplified equations (4.2), (4.3)

\[
u = A(t) + \frac{\zeta D}{1-\zeta \phi} \frac{\partial \phi}{\partial x}, \tag{9.7}
\]

\[
\frac{\partial \phi}{\partial t} + A(t) \frac{\partial \phi}{\partial x} = D \frac{\partial^2 \phi}{\partial x^2}, \tag{9.8}
\]

\[
\frac{\partial \Pi}{\partial x} = \rho g - \frac{12\mu}{b^2} u + \delta \left[ \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial x} \right)^2 \right] - \frac{\partial Q(\phi)}{\partial x}. \tag{9.9}
\]

Equation (9.7) and (9.8) are the same as the exact equation (4.1) and (4.3) for one dimensional flow but (9.9) is different than (4.4) because inertia effects which are important at the initial stage of mixing have been suppressed. We shall confine our attention to the evolution to the steady state, after the transients, which may be poorly represented in this formulation, have decayed. In this stage \(\partial \phi / \partial x\) is not too large and we imagine that \(A(t)\) is generated from free fall in which terms containing derivatives of \(\phi\) in (9.9) are small relative to gravity term. Inclusion of the neglected terms would not change the qualitative features of the analysis to follow.

Under the aforementioned approximation we may formulate a one-dimensional miscible displacement problem for simple mixtures of incompressible liquids in a Hele-Shaw cell as an initial value, free fall problem satisfying the following set of dimensionless equations

\[
u = U(t) + \frac{\zeta S}{1-\zeta \phi} \frac{\partial \phi}{\partial x}, \tag{9.10}
\]

\[
\frac{\partial \phi}{\partial t} + U(t) \frac{\partial \phi}{\partial x} = S \frac{\partial^2 \phi}{\partial x^2}, \tag{9.11}
\]
\[ \frac{\partial \Pi}{\partial x} = \rho - \mu \cdot u \] (9.12)

where

\[ \mu(\phi) = \exp(\alpha \phi + \beta \phi^2 + \gamma \phi^3) \] (9.13)

and

\[ S = \frac{D}{L}, \quad V = \rho_g b^2/12 \mu_G \] (9.14)

is the effective diffusion parameter (8.10). Dimensionless variables \((x,t,u,U,\Pi)\) are related dimensional parameter \((x,t,u,A,\Pi)\) by scaling

\[ (x,t,u,U,\Pi) = \left( \frac{x}{L}, \frac{V}{L}, \frac{u}{V}, \frac{A}{\rho_g L} \right) \]

Dirichlet boundary conditions for the problem of free fall are

\[ \phi(0,t) = 0, \quad \phi(1,t) = 1, \quad \Pi(0,t) = \Pi(1,t) = \Pi_a \] (9.15)

where the constant \(\Pi_a\) corresponds to atmospheric pressure. We shall assume that somehow the liquids are initially arranged so that

\[ \phi = 0 \text{ for } x < 1/2; \text{ and } \phi = 1 \text{ for } x > 1/2 . \] (9.16)

This is a common assumption for problems of immiscible and miscible displacement. \(U(t)\) here is a function of time only, which can be determined by integrating the pressure equation (9.12) over the cell \(x=(0,1)\) and applying the pressure conditions at the end of (9.15). Thus

\[ U(t) = \left\{ \int_0^1 \rho(\phi) \, dx - \zeta S \int_0^1 \frac{\mu(\phi)}{1 - \zeta \phi} \, d\phi \right\} / \int_0^1 \mu(\phi) \, dx . \] (9.17)

Therefore the flow in a Hele-Shaw cell is governed by the unsteady nonlinear transport equation (9.11), with \(U(t)\) given by (9.17). The problem is solved numerically.

Figure 3 shows the distribution of the volume concentration \(\phi\) in the cell at different times for three cases. At the initial time, \(\phi\) is a step function at \(x=1/2\). As time
evolves, diffusion smooths out the front and back of the step, and convection washes the step downwards. The curves for \( t=\infty \) correspond to the steady equilibrium state given in (8.11). For small \( S \), the diffusion is confined within a narrow layer. Changing the density ratio \( \zeta \) only affects the \( U(t) \) in (9.17) and does not greatly influence the evolution of the diffusion profile as shown in the figure.

Again the velocity \( u \) in (9.10) can be decomposed into a solenoidal and an expansion part. The variation of the expansion velocity \( u_e = \frac{\zeta S \frac{\partial \phi}{\partial x}}{1-\zeta \phi} \) is plotted in figure 4 (a) and (b). When \( S \) is not small, as in figure 4(a), and this is a realizable possibility in many situations, then the expansion velocity will not be small and will not be confined to the mixing layer. When \( S \) is small, in figure 4(b), the expansion velocity is confined within the narrow mixing layer, and it is almost zero outside this layer thus the assumption that \( \text{div} u = 0 \) is valid outside the mixing layer.

10. Conclusions and discussion

1. A theory of motion and mixing of two incompressible liquids \( \nu \) and \( \gamma \) can be developed based on the equation of state for the density

\[
\rho(\phi) = \rho_\gamma \phi + \rho_\nu (1-\phi) = \rho_\nu (1-\zeta \phi)
\]

of a simple mixture. The natural variable connecting composition to density is the volume fraction \( \phi \) say of \( \gamma \) with constant densities \( \rho_\nu \) and \( \rho_\gamma \) under isothermal conditions.

2. The velocity \( u \) is not solenoidal because the density \( \rho(\phi) \) changes due to diffusion. For simple mixtures the vector
Figure 3. Distribution of volume concentration $\phi$ at different times for three cases. (1) Solid lines, $S=1$, $\zeta=0$. (2) Short dashed lines, $S=1$, $\zeta=0.2$. And (3) Long dashed lines, $S=0.01$, $\zeta=0.2$. 
expansion velocity $u_e$

(a)
Figure 4. Variation of the expansion velocity \( u_e \) in the cell at different times. For very small \( S \), the expansion velocity is confined to a narrow mixing layer. (a) \( S=1, \, \zeta=0.2 \). (b) \( S=0.01, \, \zeta=0.2 \).
\[ \mathbf{W} = \mathbf{u} - \frac{\zeta D}{1 - \zeta \phi} \nabla \phi \]

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

\[ \text{div}\mathbf{u}_e = \Delta = \zeta \text{div} \left[ \frac{D}{1 - \zeta \phi} \nabla \phi \right] \]

is the expansion and \( D(\phi) \) is a diffusion function of \( \phi \), 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. It is nearly universally but incorrectly assumed that \( \text{div}\mathbf{u} = 0 \) when treating problems involving the diffusion of incompressible liquids. This assumption is a good approximation near to two conditions where it is exact: (1) \( \zeta = 0 \), small \( |\zeta| = |\rho_v - \rho_f|/\rho_v \) is a nearly density matched situation which is a kind of Boussinesq approximation. There are problems, however, like the problem of the smoothing-out of a discontinuity at a plane or spherical front in which the expansion is infinite at the initial instant, and of large values for small times, not matter how small \( |\zeta| > 0 \) might be. (2) \( D = 0 \) there is no diffusion and we might imagine two homogeneous liquids separated by an interface across which interface conditions are applied. This kind of approximation has been applied in the literature to determine motion of each fluid and the shape of the interface between them assuming that the stress traction vector and velocity are continuous across the interface. This is the same formulation as in the case of immiscible liquids, except that interfacial tension is put to zero; it misses out on surface tension like forces associated with the stresses induced by the expansion velocity and Korteweg stresses, which have been discussed here and, of course, it neglects diffusion.
4. In driven problems, like miscible displacement or forced flow such as might be induced by mass accretion in solidification problems, the solenoidal part of the velocity is forced by body forces or by the motion of the boundary. Suppose that \( A \) is some representative of the solenoidal field \( \mathbf{u}_s \) and \( L \) is a typical length. In this case \( \mathbf{u}_s \cdot \nabla \phi \) is an important term in the diffusion equation. An effective dimensionless diffusion parameter \( S = \frac{D}{AL} \) replaces \( D \) in the dimensionless formulation. If \( S \) is small and a variation of \( \phi \) is forced by external prescription, the variation of \( \phi \) can be confined to a mixing layer in which the expansion velocity is important. Presumably for such problems the one dimensional studies given in this paper are relevant. If \( S \) is not small, the expansion velocity can be important over rather large regions of flow, as we have shown in the one dimensional steady problem analyzed in section 8 and in Hele Shaw problems studied in section 9.

5. 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

\[
u_e(r,t) = \frac{\zeta D}{1-\zeta \phi} \frac{\partial \phi}{\partial r}(r,t)
\]

6. The problem of diffusion driven by convection can be solved in elementary terms in one dimensional steady problems in which the solenoidal velocity \( A \) is constant. We may use this explicit solution to evaluate the expansion velocity in the plane case. In the driven case the dimensionless diffusion coefficient \( S = \frac{D}{AL} \) is relevant. The expansion velocity is confined to a mixing layer when \( S \) is small, but \( S \) need not be small even if \( D \) is small.
7. 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.

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References


