

Sidewall Effects in the Smoothing of an Initial Discontinuity of Concentration

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Abstract

The velocity field of a binary mixture of incompressible miscible liquids is non-solenoidal when the densities of the two liquids are different. If the mixture density is linear in the volume fraction, as in the case of simple (ideal) mixtures or very nearly for glycerin and water, then the velocity can be decomposed into a solenoidal and an expansion part. In the context of this theory, we derive a new solution which describes the smoothing of an initial plane discontinuity in concentration across a channel bounded by side walls. The requirement that the velocity vanishes on the side wall introduces a different initial discontinuity not present in the solenoidal theory. The problem may be reduced to a partial differential equation in two similarity variables one for the smoothing of a concentration discontinuity without sidewalls and the other for the smoothing the velocity discontinuity at the sidewall. The similarity equations are solved explicitly in a special case.

1. Introduction

In classical studies of mixing incompressible liquids (miscible displacements, boundary convection, Taylor dispersion, reaction and diffusion, transport of diffusing dyes, Marangoni convection, diffusion controlled solidification, etc.), it is universally assumed that the mixture is incompressible, hence $\nabla \cdot \mathbf{u} = 0$. This assumption is incorrect when the densities of the mixing fluids are constants but not the same. Incompressibility only implies that the density of the mixture will not vary with pressure;

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it may vary with temperature or concentration and in this case, $\nabla \bullet \mathbf{u} \neq 0$. Landau and Lifshitz [1987] have derived a continuum theory of binary mixtures of compressible miscible liquids which does not involve averaging over molecules of different species. Joseph [1990] extended this theory to the case of linear mixtures of incompressible liquids for where $\nabla \bullet \mathbf{u} \neq 0$; the theory was developed further by Galdi, Joseph, Preziosi, and Rionero [1991]. The theory takes an especially simple form when it is assumed that the density a linear function of the volume fraction as is true of glycerin and water mixtures. The velocity field \mathbf{u} of such a mixture of incompressible fluids is not in general solenoidal; instead, it 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. Hu and Joseph [1992] studied the instability of miscible displacement in a Hele-Shaw cell and found stability in cases where the classical theory gives rise to instability. A recent book by Joseph and Renardy [1992] is a convenient and comprehensive source for these and related results. The theory also embraces the possibility that stresses are induced by gradients of concentration and density in diffusing miscible liquids, as in the theory of Korteweg [1901]. Such stresses could be important in regions of high gradients giving rise to effects which can mimic surface tension. Even when the Korteweg stress is not considered, a simple, non-classical one-dimensional solution for diffusion in a pipe which gives rise to an exponential rather than linear variation of the water fraction along the axis can be derived. This solution is stable, but the decay rates depend strongly on non-classical terms (Joseph, Huang and Hu [1996] .)

Joseph and Renardy [1992] also derived their theory by ensemble averaging over molecules of different species. They identified \mathbf{u} as a mass averaged velocity and the solenoidal part \mathbf{w} as the volume averaged velocity. Recently, Camacho and Brenner [1995] rederived Joseph's theory, apparently without any knowledge of the prior work, for the case of more than two species in the special case in which the diffusion coefficient and viscosity of the mixture are constants independent of volume concentrations. They considered the problem of the smoothing of an initial discontinuity at a plane.

The nature of the boundary condition at a solid wall can be considered. For miscible liquids, like glycerin and water, the mixture looks and feels like any other liquid and it is natural to think that the no-slip condition $\mathbf{u} = 0$ which applies to solutions of Navier-Stokes equation, like (3) ought to apply. This is the point of view adopted by Landau and Lifshitz [1987], by Camacho and Brenner [1995], in our earlier work (see Joseph and Renardy [1992]) and here. However, in mixtures we do not know, at present, what is the

appropriate average of the species velocities to insert in the viscous stress terms in the momentum balance, or in the no-slip condition at a solid boundary. In simple (ideal) mixtures the volume averaged velocity is certainly solenoidal, but if some other averaged velocity satisfies the no-slip condition, then diffusional wall layers will be found in the neighborhood of solid boundaries. This phenomenon will be illustrated by adopting the common assumptions that it is the mass averaged velocity that appears in the viscous terms and does not slip at walls, then examining a problem of inter diffusion in a binary simple (ideal) mixture in the presence of a wall.

Gases are different than liquids, because the molecules between species of different types are not held together by short range forces at a distance; collisions are the dominating dynamical processes. It is perhaps more natural to consider averages over the two species of a binary mixture of gases, which unlike the constituents of miscible liquids, are not tied together in lock step by molecular fields of force. When viewed in this way, we may identify \mathbf{u} with the mass averaged velocity and the solenoidal part \mathbf{w} with the volume averaged velocity. We may then consider whether \mathbf{w} , \mathbf{u} or some combination of these ought to vanish at a solid wall.

Careful experiments on isobaric interdiffusion of binary gases in porous plugs by Graham [1833] and others lead to the conclusion that the total mass flux does not vanish even though the pressure is the same at either end of a capillary tube. Jackson [1977] has shown that Graham's law which implies the existence of a mass flux in isobaric conditions holds from free molecule to continuum flow. On pages 25 to 33 of his book, Jackson [1977] generalized a kinetic theory argument of Maxwell for a pure gas to a gas consisting of a mixture of two substances to show that a weighted mass averaged velocity, which is neither the mass or volume averaged velocity ought to vanish at a solid wall.

Mo and Rosenberger [1991] did molecular-dynamics simulations of flow with binary diffusion in a two-dimensional channel with atomically rough walls. They found that the no-slip condition for the mass averaged velocity arises when the mean free path in the gas mixture is of the same order of magnitude or smaller than the atomic-wall-roughness amplitude. However, if there are concentration gradients along the wall, the component velocities at the wall do not vanish. Thus, the no-slip condition is established via the mutual cancellation of the non-vanishing, opposing slip velocities of the components. Mo and Rosenberger note that their work does not settle the apparent contradiction between the results of isobaric interdiffusion experiments and the expected vanishing of

the mass averaged velocity at all locations; they speculate about possible reasons for the discrepancy.

The sidewall effects, which are the focus of this paper, would disappear if the volume averaged velocity were to vanish at solid wall. This possibility seems to have been rejected by all workers in their subject, but the nature of the boundary conditions at a solid wall still needs clarification.

In this paper, we consider the smoothing of an initial discontinuity at a plane in the presence of a sidewall. When no sidewall is present a transient velocity \mathbf{u} is generated, but the evolution of the concentration follows the same equation as in the classical case of matched densities in which $\mathbf{u} \equiv 0$. However, the solution with $\mathbf{u} \neq 0$ cannot hold when there are sidewalls on which $\mathbf{u} = 0$ is imposed. In this case, we shall show that there is an initial discontinuity also at the sidewall which is smoothed by diffusion. The physical problem which might be used to compare with analysis could be framed as molecular mixing of a glycerin-water mixture which evolves when fresh water is placed carefully on the top of glycerin in a container with bottom and top and sidewalls. In the classical case we get the famous error function similarity solution when we take the top and bottom to infinity, even with the sidewalls in place. We look at this problem again with the revised theory and we show that the boundary conditions at the sidewalls are incompatible with the one-dimensional similarity solution. Even in the two-dimensional case a PDE in x , y and t must be solved. We were astonished to find that this PDE could be rigorously reduced to a two-dimensional PDE in two similarity variables $(\xi, \eta) = (x, y) / \sqrt{D^* t}$ where D^* is the scaling factor for diffusion coefficient. This PDE can be posed as an inner solution supported at one of the walls and subject to the condition that it reduces to the one-dimensional outer solution far from the wall.

To simplify our study of the non-linear problem governed by (1), (2) and (3), we looked for solutions as a power series in the normalized density difference $\zeta = (\rho_G - \rho_W) / \rho_G$ (about 0.2 for glycerin and water) and truncated at first order. This is a sensible perturbation because the essential new features of the theory associate mainly with effects of the weight difference of the two species. The perturbation problem can be solved in principle by Fourier transform techniques and it can actually be solved in closed form for a certain special case. The special case is probably fairly representative and it satisfies precisely all the conditions required of the inner solution.

2. Governing Equations and Boundary Conditions

The governing equations (Joseph and Renardy [1992], Vol. 2, Chapter X) expressing the diffusion of species, balance of mass and momentum for simple incompressible binary mixtures can be formulated as

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

$$\nabla \cdot \left(\mathbf{u} - \frac{\zeta D}{1 - \zeta \phi} \nabla \phi \right) = 0 \quad (2)$$

and

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = \rho \mathbf{g} - \nabla p + \mu \left\{ \frac{1}{3} \nabla (\nabla \cdot \mathbf{u}) + \nabla^2 \mathbf{u} \right\} - \frac{2}{3} \nabla \mu (\nabla \cdot \mathbf{u}) + 2 \nabla \mu \cdot \mathbf{D}[\mathbf{u}] \quad (3)$$

where ϕ is the volume fraction, \mathbf{u} is the mass averaged velocity, ζ is the normalized density difference, D is the diffusion coefficient, ρ is the density and μ is the viscosity. Note that D , ρ and μ are functions of ϕ .

Define the expansion velocity \mathbf{u}_e and the vortical velocity \mathbf{w} as

$$\mathbf{u}_e \stackrel{def}{=} \nabla h = \frac{\zeta D}{1 - \zeta \phi} \nabla \phi \quad (4)$$

and

$$\mathbf{w} \stackrel{def}{=} \mathbf{u} - \mathbf{u}_e \quad (5)$$

where h is given by

$$h = h(\phi) = \int_0^\phi \frac{\zeta D}{1 - \zeta \phi} d\phi. \quad (6)$$

The expansion velocity \mathbf{u}_e has a zero curl and a non-zero divergence and $\nabla \wedge \mathbf{u} = \nabla \wedge \mathbf{w}$. Here ζ is a primary parameter. The expansion velocity \mathbf{u}_e is proportional to ζ and D , the diffusion coefficient, and is zero for two species with the same density. The viscosity, $\mu = \mu(\phi)$ is a rapidly varying function in general. We could think of ϕ as the water fraction of glycerin-water mixture, then empirically (Segur [1953]) $\mu(\phi)$ may be approximated by $\mu_G \exp[\alpha_1 \phi + \alpha_2 \phi^2 + \alpha_3 \phi^3]$ and, for example, at 60°C, the coefficients are $\alpha_1 = -10.8$,

$\alpha_2 = 9.47$, and $\alpha_3 = -3.83$. And according to the simple mixture assumption, the density is given by $\rho = \rho_G(1 - \zeta\phi)$. In the case of glycerin-water mixtures, the model gives less than 1% error with the maximum error near $\phi = 0.5$. Values of $D(\phi)$ for glycerin-water mixtures may be obtained from Table 1 in the paper on miscible displacement in capillary tubes by Petitjeans and Maxworthy [1996] (they measured $D(C_g)$, where C_g is the percentage of glycerin by weight, over the whole range $0 \leq C_g \leq 1$.) Their paper and the companion paper on numerical simulation of miscible displacement by Chen and Meiburg [1996] make some comparisons between the usual solenoidal theories in which the weight difference is neglected and the non-solenoidal theory under study here.

In terms of \mathbf{w} , h and ϕ , the governing equations (1), (2), (3) can be written as

$$\frac{\partial h}{\partial t} + (\mathbf{w} \cdot \nabla)h = D\nabla^2 h - \nabla h \cdot \nabla h, \quad (7a)$$

$$\frac{\partial \phi}{\partial t} + (\mathbf{w} \cdot \nabla)\phi = \nabla \cdot (D\nabla\phi), \quad (7b)$$

$$\nabla \cdot \mathbf{w} = 0 \quad (8)$$

and

$$\begin{aligned} & \rho \left(\frac{\partial \mathbf{w}}{\partial t} + (\mathbf{w} \cdot \nabla)\mathbf{w} + (\nabla \mathbf{w}) \cdot \nabla h - \nabla h \cdot (\nabla \mathbf{w}) \right) + \rho \nabla \cdot \left\{ D\nabla^2 h - \frac{1}{2}(\nabla h \cdot \nabla h) \right\} \\ & = \rho \mathbf{g} - \nabla p + \mu \nabla^2 \mathbf{w} + \frac{4}{3} \mu \nabla(\nabla^2 h) - \frac{2}{3} \nabla \mu \nabla^2 h + 2 \nabla \mu \cdot \mathbf{D}[\mathbf{w}] + 2 \nabla \mu \cdot \mathbf{D}[\nabla h]. \end{aligned} \quad (9)$$

The diffusive flux of any species across an impermeable, bounding surface vanishes. If \mathbf{n} is the outward at such a surface (from the fluid to solid), we have

$$\mathbf{n} \cdot \nabla \phi = 0 \quad (10)$$

at an impermeable boundary.

3. Problem setup

The problem under consideration is shown in Figure 1. Species 1 with density ρ_W is placed over species 2 with density ρ_G , $\rho_G > \rho_W$, in the semi-infinite $y > 0$ to the right of a rigid wall at $y = 0$, $-\infty < x < \infty$. We can think that species 1 is fresh water and species 2 is glycerin.

The fluids are at rest and of uniform composition initially,

$$\mathbf{u}(x,y,0) = 0 \text{ and } \phi(x,y,0) = \begin{cases} 0 & \text{for } x > 0 \\ 1 & \text{for } x < 0 \end{cases} \quad (11)$$

and, at the rigid wall $y = 0$, we have

$$\mathbf{u}(x,0,t) = 0 \text{ and } \left. \frac{\partial \phi}{\partial y} \right|_{y=0} = 0. \quad (12)$$

We also require that

$$\lim_{\substack{x \rightarrow \pm\infty \\ y > 0, t > 0}} \mathbf{u}(x,y,t) = 0, \quad \lim_{\substack{x \rightarrow +\infty \\ y > 0, t > 0}} \phi(x,y,t) = 0, \quad \lim_{\substack{x \rightarrow -\infty \\ y > 0, t > 0}} \phi(x,y,t) = 1 \quad (13)$$

and

$$\lim_{\substack{y \rightarrow \infty \\ t > 0}} \mathbf{u}(x,y,t) = \mathbf{U}(x,t), \quad \lim_{\substack{y \rightarrow \infty \\ t > 0}} \phi(x,y,t) = \Phi(x,t) \quad (14)$$

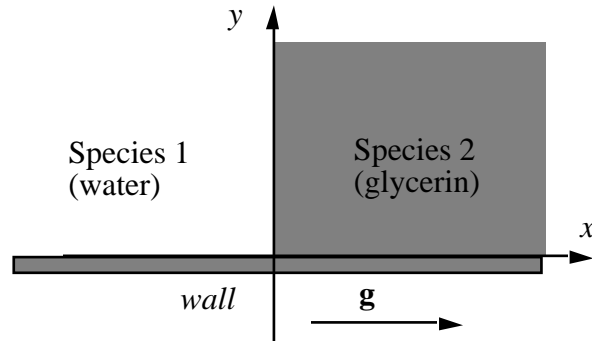


Figure 1. Two miscible liquids occupy the upper half plane. Initially, heavy fluid is on the right and light fluid is on the left with gravity $\mathbf{g} = g\mathbf{e}_x$ in the direction of increasing x .

where \mathbf{U} and Φ are the solutions for the one-dimensional problem which are given in Joseph and Renardy [1992]. Explicitly, we have

$$\mathbf{U} = \mathbf{U}_e = \frac{\zeta D}{1 - \zeta \Phi} \nabla \Phi = \frac{\zeta D}{1 - \zeta \Phi} \frac{\partial \Phi}{\partial x} \mathbf{e}_x \quad (15)$$

or, equivalently,

$$\mathbf{W} = 0 \quad (16)$$

and Φ satisfies the equation:

$$\frac{\partial \Phi}{\partial t} = \frac{\partial}{\partial x} \left(D(\Phi) \frac{\partial \Phi}{\partial x} \right). \quad (17)$$

4. Similarity Transformation

In two dimensions, let

$$\mathbf{g} = g \mathbf{e}_x, \quad \mathbf{w} = w_x \mathbf{e}_x + w_y \mathbf{e}_y,$$

$$\mathbf{D}[\mathbf{w}] = \frac{\partial w_x}{\partial x} \mathbf{e}_x \otimes \mathbf{e}_x + \frac{1}{2} \left(\frac{\partial w_y}{\partial x} + \frac{\partial w_x}{\partial y} \right) (\mathbf{e}_x \otimes \mathbf{e}_y + \mathbf{e}_y \otimes \mathbf{e}_x) + \frac{\partial w_y}{\partial y} \mathbf{e}_y \otimes \mathbf{e}_y$$

and

$$\mathbf{D}[\nabla h] = \frac{\partial^2 h}{\partial x^2} \mathbf{e}_x \otimes \mathbf{e}_x + \frac{\partial^2 h}{\partial x \partial y} (\mathbf{e}_x \otimes \mathbf{e}_y + \mathbf{e}_y \otimes \mathbf{e}_x) + \frac{\partial^2 h}{\partial y^2} \mathbf{e}_y \otimes \mathbf{e}_y,$$

then, the equation of motion (9) gives rise to two scalar equations:

$$\begin{aligned} & \rho \left(\frac{\partial w_x}{\partial t} + (w_x \frac{\partial w_x}{\partial x} + w_y \frac{\partial w_x}{\partial y}) + \frac{\partial h}{\partial y} \frac{\partial w_x}{\partial y} - \frac{\partial h}{\partial y} \frac{\partial w_y}{\partial x} \right) + \rho \frac{\partial}{\partial x} \left\{ D \nabla^2 h - \frac{1}{2} (\nabla h \cdot \nabla h) \right\} \\ & = \rho g - \frac{\partial p}{\partial x} + \mu \nabla^2 w_x + \frac{4}{3} \mu \frac{\partial}{\partial x} (\nabla^2 h) - \frac{2}{3} \frac{\partial \mu}{\partial x} \nabla^2 h \\ & + 2 \frac{\partial \mu}{\partial x} \frac{\partial w_x}{\partial x} + \frac{\partial \mu}{\partial y} \left(\frac{\partial w_y}{\partial x} + \frac{\partial w_x}{\partial y} \right) + 2 \frac{\partial \mu}{\partial x} \frac{\partial^2 h}{\partial x^2} + 2 \frac{\partial \mu}{\partial y} \frac{\partial^2 h}{\partial x \partial y} \end{aligned} \quad (18)$$

and

$$\begin{aligned}
& \rho \left(\frac{\partial w_y}{\partial t} + (w_x \frac{\partial w_y}{\partial x} + w_y \frac{\partial w_y}{\partial y}) + \frac{\partial h}{\partial x} \frac{\partial w_y}{\partial x} - \frac{\partial h}{\partial x} \frac{\partial w_x}{\partial y} \right) + \rho \frac{\partial}{\partial y} \left\{ D \nabla^2 h - \frac{1}{2} (\nabla h \bullet \nabla h) \right\} \\
& = -\frac{\partial p}{\partial y} + \mu \nabla^2 w_y + \frac{4}{3} \mu \frac{\partial}{\partial y} (\nabla^2 h) - \frac{2}{3} \frac{\partial \mu}{\partial y} \nabla^2 h \\
& + \frac{\partial \mu}{\partial x} \left(\frac{\partial w_y}{\partial x} + \frac{\partial w_x}{\partial y} \right) + 2 \frac{\partial \mu}{\partial y} \frac{\partial w_y}{\partial y} + 2 \frac{\partial \mu}{\partial x} \frac{\partial^2 h}{\partial x \partial y} + 2 \frac{\partial \mu}{\partial y} \frac{\partial^2 h}{\partial y^2}. \tag{19}
\end{aligned}$$

The components w_x and w_y of \mathbf{w} may be expressed in terms of a stream function ψ :

$$w_x = -\frac{\partial \psi}{\partial y} \quad \text{and} \quad w_y = \frac{\partial \psi}{\partial x}. \tag{20}$$

Now we introduce Boltzmann similarity variables:

$$\xi \stackrel{def}{=} \frac{x}{\sqrt{D^* t}} \quad \text{and} \quad \eta \stackrel{def}{=} \frac{y}{\sqrt{D^* t}} \tag{21}$$

where D^* is the scaling factor of the diffusion coefficient D and carry out the transformation on the basic equations, putting down details of routine but tedious calculations in the Appendix. We find that the diffusion equation (7) and the equation of motion (18) and (19) transform into the following equations:

$$-\frac{D^*}{2} \left(\xi \frac{\partial h}{\partial \xi} + \eta \frac{\partial h}{\partial \eta} \right) - \frac{\partial \psi}{\partial \eta} \frac{\partial h}{\partial \xi} + \frac{\partial \psi}{\partial \xi} \frac{\partial h}{\partial \eta} + \hat{\nabla} h \bullet \hat{\nabla} h = D \hat{\nabla}^2 h, \tag{22a}$$

$$-\frac{D^*}{2} \left(\xi \frac{\partial \phi}{\partial \xi} + \eta \frac{\partial \phi}{\partial \eta} \right) - \frac{\partial \psi}{\partial \eta} \frac{\partial \phi}{\partial \xi} + \frac{\partial \psi}{\partial \xi} \frac{\partial \phi}{\partial \eta} = \hat{\nabla} \bullet (D \hat{\nabla} \phi), \tag{22b}$$

$$\begin{aligned}
& \rho \left\{ \frac{D^*}{2} \left(\frac{\partial \psi}{\partial \eta} + \xi \frac{\partial^2 \psi}{\partial \eta \partial \xi} + \eta \frac{\partial^2 \psi}{\partial \eta^2} \right) + \frac{\partial \psi}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi \partial \eta} - \frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial h}{\partial \eta} \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial h}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi^2} \right\} \\
& + \rho \frac{\partial}{\partial \xi} \left\{ D \hat{\nabla}^2 h - \frac{1}{2} (\hat{\nabla} h \bullet \hat{\nabla} h) \right\} = (D^* t)^{3/2} \rho g - D^* t \frac{\partial p}{\partial \xi} - \mu \hat{\nabla}^2 \frac{\partial \psi}{\partial \eta} + \frac{4}{3} \mu \frac{\partial}{\partial \xi} (\hat{\nabla}^2 h) \\
& - \frac{2}{3} \frac{\partial \mu}{\partial \xi} \hat{\nabla}^2 h - 2 \frac{\partial \mu}{\partial \xi} \frac{\partial \psi}{\partial \xi \partial \eta} + \frac{\partial^2 \mu}{\partial \eta} \left(\frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial^2 \psi}{\partial \eta^2} \right) + 2 \frac{\partial \mu}{\partial \xi} \frac{\partial^2 h}{\partial \xi^2} + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 h}{\partial \xi \partial \eta} \tag{23}
\end{aligned}$$

and

$$\begin{aligned}
& \rho \left(\frac{-D^*}{2} \left(\frac{\partial \psi}{\partial \xi} + \xi \frac{\partial^2 \psi}{\partial \xi^2} + \eta \frac{\partial^2 \psi}{\partial \eta \partial \xi} \right) - \frac{\partial \psi}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi^2} + \frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \xi \partial \eta} + \frac{\partial h}{\partial \xi} \frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial h}{\partial \xi} \frac{\partial^2 \psi}{\partial \eta^2} \right) \\
& + \rho \frac{\partial}{\partial \eta} \left\{ D \hat{\nabla}^2 h - \frac{1}{2} (\hat{\nabla} h \cdot \hat{\nabla} h) \right\} = -D^* t \frac{\partial p}{\partial \eta} + \mu \hat{\nabla}^2 \frac{\partial \psi}{\partial \xi} + \frac{4}{3} \mu \frac{\partial}{\partial \eta} (\hat{\nabla}^2 h) \\
& - \frac{2}{3} \frac{\partial \mu}{\partial \eta} \hat{\nabla}^2 h + \frac{\partial \mu}{\partial \xi} \left(\frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial^2 \psi}{\partial \eta^2} \right) + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi \partial \eta} + 2 \frac{\partial \mu}{\partial \xi} \frac{\partial^2 h}{\partial \xi \partial \eta} + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 h}{\partial \eta^2} \quad (24)
\end{aligned}$$

where

$$\hat{\nabla} \stackrel{def}{=} \mathbf{e}_x \frac{\partial}{\partial \xi} + \mathbf{e}_y \frac{\partial}{\partial \eta} \quad \text{and} \quad \hat{\nabla}^2 \stackrel{def}{=} \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}. \quad (25)$$

Equation (22) is in similarity form but (23) and (24) are not because the variable t appears on the coefficients of pressure gradient and gravity terms. The pressure gradient terms may be eliminated by cross differentiation of (23) and (24) which gives

$$\begin{aligned}
& \frac{\partial}{\partial \eta} \left\langle \rho \left\{ \frac{D^*}{2} \left(\frac{\partial \psi}{\partial \eta} + \xi \frac{\partial^2 \psi}{\partial \eta \partial \xi} + \eta \frac{\partial^2 \psi}{\partial \eta^2} \right) + \frac{\partial \psi}{\partial \eta} \frac{\partial \psi}{\partial \xi \partial \eta} - \frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial h}{\partial \eta} \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial h}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi^2} \right\} \right\rangle \\
& - \frac{\partial}{\partial \xi} \left\langle \rho \left(\frac{-D^*}{2} \left(\frac{\partial \psi}{\partial \xi} + \xi \frac{\partial^2 \psi}{\partial \xi^2} + \eta \frac{\partial^2 \psi}{\partial \eta \partial \xi} \right) - \frac{\partial \psi}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi^2} + \frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \xi \partial \eta} + \frac{\partial h}{\partial \xi} \frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial h}{\partial \xi} \frac{\partial^2 \psi}{\partial \eta^2} \right) \right\rangle \\
& + \frac{\partial \rho}{\partial \eta} \frac{\partial}{\partial \xi} \left\{ D \hat{\nabla}^2 h - \frac{1}{2} (\hat{\nabla} h \cdot \hat{\nabla} h) \right\} - \frac{\partial \rho}{\partial \xi} \frac{\partial}{\partial \eta} \left\{ D \hat{\nabla}^2 h - \frac{1}{2} (\hat{\nabla} h \cdot \hat{\nabla} h) \right\} \\
& = -\frac{2}{3} \frac{\partial \mu}{\partial \xi} \frac{\partial (\hat{\nabla}^2 h)}{\partial \eta} + 2 \frac{\partial^2 \mu}{\partial \eta \partial \xi} \frac{\partial^2 h}{\partial \xi^2} + \frac{\partial}{\partial \eta} \left\langle -2 \frac{\partial \mu}{\partial \xi} \frac{\partial \psi}{\partial \xi \partial \eta} + \frac{\partial \mu}{\partial \eta} \left(\frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial^2 \psi}{\partial \eta^2} \right) + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 h}{\partial \xi \partial \eta} \right\rangle \\
& + \frac{2}{3} \frac{\partial \mu}{\partial \eta} \frac{\partial (\hat{\nabla}^2 h)}{\partial \xi} - 2 \frac{\partial^2 \mu}{\partial \xi^2} \frac{\partial^2 h}{\partial \xi \partial \eta} - \frac{\partial}{\partial \xi} \left\langle \frac{\partial \mu}{\partial \xi} \left(\frac{\partial^2 \psi}{\partial \xi^2} - \frac{\partial^2 \psi}{\partial \eta^2} \right) + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 \psi}{\partial \xi \partial \eta} + 2 \frac{\partial \mu}{\partial \eta} \frac{\partial^2 h}{\partial \eta^2} \right\rangle \\
& - \frac{\partial}{\partial \eta} \left\langle \mu \hat{\nabla}^2 \frac{\partial \psi}{\partial \eta} \right\rangle - \frac{\partial}{\partial \xi} \left\langle \mu \hat{\nabla}^2 \frac{\partial \psi}{\partial \xi} \right\rangle + \frac{4}{3} \frac{\partial \mu}{\partial \eta} \frac{\partial (\hat{\nabla}^2 h)}{\partial \xi} - \frac{4}{3} \frac{\partial \mu}{\partial \xi} \frac{\partial (\hat{\nabla}^2 h)}{\partial \eta} + \frac{\partial \rho}{\partial \eta} g (D^* t)^{3/2}. \quad (26)
\end{aligned}$$

This equation is in similar form whenever the last term of (26) vanishes as in the situations of negligible gravity or at first order in ζ where $\rho(\xi, \eta; \zeta) \rightarrow \rho_0(\xi)$. More generally, the spoiler term may be neglected precisely at the early times for which non-classical effects are most important.

To actually solve problems by similarity methods the governing equations as well as the initial and the boundary conditions have to be successfully transformed. Under the similarity transform (21), the initial condition and boundary conditions given in (11), (12), (13) and (14) can be transformed into the following similar forms:

$$A.) \left\{ \begin{array}{l} \lim_{\substack{\xi \rightarrow +\infty \\ \eta \rightarrow \infty}} \phi(\xi, \eta) = 0 \text{ and } \lim_{\substack{\xi \rightarrow -\infty \\ \eta \rightarrow \infty}} \phi(\xi, \eta) = 1, \\ \lim_{\eta \rightarrow 0} \frac{\partial \phi}{\partial \eta} = 0, \\ \lim_{\substack{\xi \rightarrow +\infty \\ \eta > 0}} \phi(\xi, \eta) = 0 \text{ and } \lim_{\substack{\xi \rightarrow -\infty \\ \eta > 0}} \phi(\xi, \eta) = 1, \\ \lim_{\eta \rightarrow \infty} \phi(\xi, \eta) = \Phi(\xi), \end{array} \right. \quad (27)$$

$$B.) \left\{ \begin{array}{l} \lim_{\substack{\xi \rightarrow \pm\infty \\ \eta \rightarrow \infty}} \frac{\partial \psi(\xi, \eta)}{\partial \xi} = \lim_{\substack{\xi \rightarrow \pm\infty \\ \eta \rightarrow \infty}} \frac{\partial \psi(\xi, \eta)}{\partial \eta} = 0, \\ \lim_{\eta \rightarrow 0} \frac{\partial \psi(\xi, \eta)}{\partial \xi} = \lim_{\eta \rightarrow 0} \frac{\zeta D}{1 - \zeta \phi} \frac{\partial \phi}{\partial \eta} \text{ and } \lim_{\eta \rightarrow 0} \frac{\partial \psi(\xi, \eta)}{\partial \eta} = \lim_{\eta \rightarrow 0} \frac{-\zeta D}{1 - \zeta \phi} \frac{\partial \phi}{\partial \xi}, \\ \lim_{\substack{\xi \rightarrow \pm\infty \\ \eta > 0}} \frac{\partial \psi(\xi, \eta)}{\partial \xi} = \lim_{\substack{\xi \rightarrow \pm\infty \\ \eta > 0}} \frac{\partial \psi(\xi, \eta)}{\partial \eta} = 0, \\ \lim_{\eta \rightarrow \infty} \frac{\partial \psi(\xi, \eta)}{\partial \xi} = \lim_{\eta \rightarrow \infty} \frac{\partial \psi(\xi, \eta)}{\partial \eta} = 0, \end{array} \right. \quad (28)$$

$$C.) \lim_{\xi \rightarrow \infty} \psi(\xi, \eta), \lim_{\xi \rightarrow -\infty} \psi(\xi, \eta), \lim_{\eta \rightarrow \infty} \psi(\xi, \eta) \text{ and } \lim_{\eta \rightarrow 0} \psi(\xi, \eta) \text{ are constants,} \quad (29)$$

where $\Phi(\xi)$ satisfies the similarity equation from (17):

$$\frac{-D^*}{2} \left(\xi \frac{\partial \Phi}{\partial \xi} \right) = \frac{\partial}{\partial \xi} \left(D(\Phi) \frac{\partial \Phi}{\partial \xi} \right). \quad (30)$$

Note that both Φ and D only depend on ξ . Therefore, whenever (26) admits a similarity form, the problem prescribed in section 3 will be governed by (22) and (26) with conditions (27), (28), and (29).

The foregoing reduction shows that we are here dealing with the smoothing of **two** discontinuities; of the concentration at $x = 0$ when $t = 0_+$, and the tangential component of \mathbf{u} at the sidewall $y = 0$ at $t = 0_+$. The smoothing of the concentration discontinuity generates a velocity $\mathbf{e}_x \cdot \mathbf{u}$ in the diffusion layer which is incompatible with no-slip on the wall at $y = 0$. The mechanism for carrying out the reduction of the velocity is also

diffusive and propagates from the point $(x, y, t) = (0, 0, 0)$ into the interior with a speed proportional to $\sqrt{D/t}$.

5. Perturbation equations

For better understanding, we shall carry out our perturbation on the un-transformed system (7), (8), and (9) with initial and boundary conditions given in (11), (12), (13), and (14). Let the Taylor expansion of a function f on ζ around $\zeta = 0$ be denoted by $f(\zeta) = f_0 + f_1\zeta + O[\zeta^2]$ and expand \mathbf{u} , \mathbf{w} , p , h , ρ , μ , D , and ϕ . Immediately, (4) and (5) imply

$$\mathbf{w}_0 = \mathbf{u}_0 \text{ and } \mathbf{w}_1 = \mathbf{u}_1 - D_0 \nabla \phi_0 \quad (31)$$

and (4) and (6) imply

$$h_0 = 0 \text{ and } \nabla h_1 = D_0 \nabla \phi_0. \quad (32)$$

Since $\mu = \mu(\phi)$ and $D = D(\phi)$, we have

$$\mu_0 = \mu(\phi_0) \text{ and } D_0 = D(\phi_0). \quad (33)$$

Moreover, since $\rho = \rho_G(1 - \zeta\phi)$, we find that

$$\rho_0 = \rho_G \text{ and } \rho_1 = -\rho_0 \phi_0. \quad (34)$$

After expanding the equations and using (32), we identify the equations which hold at zero and first order. Thus, at zero order, we have

$$\frac{\partial \phi_0}{\partial t} + \mathbf{w}_0 \cdot \nabla \phi_0 = \nabla \cdot (D_0 \nabla \phi_0), \quad (35)$$

$$\nabla \cdot \mathbf{w}_0 = 0 \quad (36)$$

and

$$\rho_0 \left\{ \frac{\partial \mathbf{w}_0}{\partial t} + (\mathbf{w}_0 \cdot \nabla) \mathbf{w}_0 \right\} = \rho_0 \mathbf{g} - \nabla p_0 + \mu_0 \nabla^2 \mathbf{w}_0 + \nabla \mu_0 \cdot 2\mathbf{D}[\mathbf{w}_0] \quad (37)$$

with the initial and boundary conditions

$$\mathbf{w}_0(x,y,0) = 0 \text{ and } \phi_0(x,y,0) = \begin{cases} 0 & \text{for } x > 0 \\ 1 & \text{for } x < 0 \end{cases}$$

$$\mathbf{w}_0(x,0,t) = 0 \text{ and } \left. \frac{\partial \phi_0}{\partial y} \right|_{y=0} = 0,$$

$$\lim_{\substack{x \rightarrow \pm\infty \\ y > 0, t > 0}} \mathbf{w}_0(x,y,t) = 0, \quad \lim_{\substack{x \rightarrow +\infty \\ y > 0, t > 0}} \phi_0(x,y,t) = 0, \quad \lim_{\substack{x \rightarrow -\infty \\ y > 0, t > 0}} \phi_0(x,y,t) = 1$$

and

$$\lim_{\substack{y \rightarrow \infty \\ t > 0}} \mathbf{w}_0(x,y,t) = 0, \quad \lim_{\substack{y \rightarrow \infty \\ t > 0}} \phi_0(x,y,t) = \Phi(x,t)$$

where Φ is the 1-D solution. The solutions of this system are

$$\phi_0 = \Phi(x,t), \quad \mathbf{w}_0 = 0 \text{ and } p_0 = \rho_0 \mathbf{g} \cdot \mathbf{x}. \quad (38)$$

Therefore, (31), (33) and (34) give

$$\mathbf{u}_0 = 0 \text{ and } \mathbf{u}_1 = \mathbf{w}_1 + D_0 \nabla \Phi = \mathbf{w}_1 + D_0 \frac{\partial \Phi}{\partial x} \mathbf{e}_x \quad (39)$$

and

$$\mu_0 = \mu_0(x,t) = \mu(\Phi), \quad D_0 = D_0(x,t) = D(\Phi) \text{ and } \rho_1 = \rho_1(x,t) = -\rho_G \Phi \quad (40)$$

which do not depend on y . From (32), we have

$$\nabla h_1 = (\nabla h_1)(x,t) = D_0 \nabla \Phi = D_0 \frac{\partial \Phi}{\partial x} \mathbf{e}_x \quad (41)$$

which also does not depend on y .

Applying (38), (40) and (41), we find that the governing equations at the first order are

$$\frac{\partial h_1}{\partial t} = D_0 \nabla^2 h_1, \quad (42a)$$

$$\frac{\partial \phi_1}{\partial t} + \mathbf{w}_1 \cdot \nabla \phi_0 = D_0 \nabla^2 \phi_1 + D_1 \nabla^2 \phi_0, \quad (42b)$$

$$\nabla \cdot \mathbf{w}_1 = 0 \quad (43)$$

and

$$\rho_0 \frac{\partial \mathbf{w}_1}{\partial t} = -\nabla p_1 + \mu_0 \nabla^2 \mathbf{w}_1 + 2\nabla \mu_0 \bullet \mathbf{D}[\mathbf{w}_1] + \mathbf{f} \quad (44)$$

where

$$\begin{aligned} \mathbf{f} &= \mathbf{f}(x,t) = f_x(x,t)\mathbf{e}_x + f_y(x,t)\mathbf{e}_y \\ &\stackrel{def}{=} \rho_1 \mathbf{g} + \frac{4}{3} \mu_0 \nabla(\nabla^2 h_1) - \frac{2}{3} \nabla \mu_0 \nabla^2 h_1 + 2\nabla \mu_0 \bullet \mathbf{D}[\nabla h_1] - \rho_0 \nabla(D_0 \nabla^2 h_1) \end{aligned} \quad (45)$$

And the initial and boundary conditions are

$$\mathbf{w}_1(x, y, 0) = \phi_1(x, y, 0) = 0, \quad (46)$$

$$\mathbf{w}_1(x, 0, t) = -D_0 \nabla \Phi|_{y=0} = -D_0 \nabla \Phi, \quad \left. \frac{\partial \phi_1}{\partial y} \right|_{y=0} = 0, \quad (47)$$

$$\lim_{\substack{x \rightarrow \pm\infty \\ y > 0, t > 0}} \mathbf{w}_1(x, y, t) = \lim_{\substack{x \rightarrow \pm\infty \\ y > 0, t > 0}} \phi_1(x, y, t) = 0 \quad (48)$$

and

$$\lim_{\substack{y \rightarrow \infty \\ t > 0}} \mathbf{w}_1(x, y, t) = \lim_{\substack{y \rightarrow \infty \\ t > 0}} \phi_1(x, y, t) = 0. \quad (49)$$

Note that because $\nabla h_1 = D_0 \nabla \phi_0$ and $\mathbf{w}_0 = 0$, equations (42a) and (35) are identical. Since the gravity term in (45) does not depend on y , the condition required for the similarity transformation under (26) are satisfied. Using (40), (41), $\mathbf{g} = g\mathbf{e}_x$ and the property that Φ , μ_0 and D_0 are independent of y , we find that (45) reduces to

$$\begin{aligned} \mathbf{f} &= f_x \mathbf{e}_x + f_y \mathbf{e}_y \\ &= \left\{ -\rho_G \Phi g + \left(\frac{4}{3} \mu_0 - \rho_G D_0 \right) \frac{\partial^2}{\partial x^2} \left(D_0 \frac{\partial \Phi}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_0 \frac{\partial \Phi}{\partial x} \right) \left(\frac{4}{3} \frac{\partial \mu_0}{\partial x} - \rho_G \frac{\partial D_0}{\partial x} \right) \right\} \mathbf{e}_x, \end{aligned} \quad (50)$$

that is, $\mathbf{f} = \mathbf{f}(x,t)$ and $f_y = \mathbf{f} \bullet \mathbf{e}_y = 0$.

Introducing a dimensionless stream function $\hat{\psi}$ for \mathbf{w}_1 such that

$$\mathbf{w}_1 = \frac{-D^*}{2\sqrt{\pi}} \left(-\frac{\partial \hat{\psi}}{\partial y} \mathbf{e}_x + \frac{\partial \hat{\psi}}{\partial x} \mathbf{e}_y \right) = \frac{-1}{2} \sqrt{\frac{D^*}{\pi t}} \left(-\frac{\partial \hat{\psi}}{\partial \eta} \mathbf{e}_x + \frac{\partial \hat{\psi}}{\partial \xi} \mathbf{e}_y \right) \quad (51)$$

and applying cross differentiation on (44), we find that the \mathbf{f} term and the pressure term are eliminated and obtain

$$\begin{aligned} \rho_0 \frac{\partial}{\partial t} \left(\frac{\partial^2 \hat{\psi}}{\partial x^2} + \frac{\partial^2 \hat{\psi}}{\partial y^2} \right) &= \mu_0 \left(\frac{\partial^4 \hat{\psi}}{\partial x^4} + 2 \frac{\partial^4 \hat{\psi}}{\partial x^2 \partial y^2} + \frac{\partial^4 \hat{\psi}}{\partial y^4} \right) \\ &+ 2 \frac{\partial \mu_0}{\partial x} \left(\frac{\partial^3 \hat{\psi}}{\partial x^3} + \frac{\partial^3 \hat{\psi}}{\partial x \partial y^2} \right) + \left(\frac{\partial^2 \mu_0}{\partial x^2} \right) \left(\frac{\partial^2 \hat{\psi}}{\partial x^2} - \frac{\partial^2 \hat{\psi}}{\partial y^2} \right). \end{aligned} \quad (52)$$

The similarity form of this equation is

$$\begin{aligned} \mu_0 \left(\frac{\partial^4 \hat{\psi}}{\partial \xi^4} + 2 \frac{\partial^4 \hat{\psi}}{\partial \xi^2 \partial \eta^2} + \frac{\partial^4 \hat{\psi}}{\partial \eta^4} \right) &+ 2 \frac{\partial \mu_0}{\partial \xi} \left(\frac{\partial^3 \hat{\psi}}{\partial \xi^3} + \frac{\partial^3 \hat{\psi}}{\partial \xi \partial \eta^2} \right) + \frac{\partial^2 \mu_0}{\partial \xi^2} \left(\frac{\partial^2 \hat{\psi}}{\partial \xi^2} - \frac{\partial^2 \hat{\psi}}{\partial \eta^2} \right) \\ + \rho_0 D \left\{ \frac{\partial^2 \hat{\psi}}{\partial \xi^2} + \frac{1}{2} \left(\xi \frac{\partial^3 \hat{\psi}}{\partial \xi^3} + \eta \frac{\partial^3 \hat{\psi}}{\partial \eta \partial \xi^2} + \xi \frac{\partial^3 \hat{\psi}}{\partial \xi \partial \eta^2} + \eta \frac{\partial^3 \hat{\psi}}{\partial \eta^3} \right) + \frac{\partial^2 \hat{\psi}}{\partial \eta^2} \right\} &= 0 \end{aligned} \quad (53)$$

and the conditions are similar to those in (28) and (29) except that conditions on the wall $\eta = 0$ now read

$$\lim_{\eta \rightarrow 0} \frac{\partial \hat{\psi}}{\partial \xi} = 0 \quad \text{and} \quad \lim_{\eta \rightarrow 0} \frac{\partial \hat{\psi}}{\partial \eta} = E(\xi) \quad (54)$$

where

$$E(\xi) \stackrel{def}{=} - \frac{2\sqrt{\pi}}{D^*} \left(D_0 \frac{\partial \Phi}{\partial \xi} \right). \quad (55)$$

Defining a similarity-type of dimensionless velocity $\hat{\mathbf{u}}_1$ for \mathbf{u}_1 by

$$\hat{\mathbf{u}}_1 = 2 \sqrt{\frac{\pi t}{D^*}} \mathbf{u}_1 \quad (56)$$

and using (39) and (51), we find that

$$\hat{\mathbf{u}}_1 = \left(\frac{\partial \hat{\psi}}{\partial \eta} + \frac{2\sqrt{\pi}}{D^*} D_0 \frac{\partial \Phi}{\partial \xi} \right) \mathbf{e}_x - \frac{\partial \hat{\psi}}{\partial \xi} \mathbf{e}_y. \quad (57)$$

This can be calculated after (53) is solved.

After the stream function is found, the pressure can be obtained from (44) which may be written as follows:

$$\left\{ \begin{array}{l} \frac{\partial p_1}{\partial x} = \rho_0 \frac{\sqrt{D^*}}{4\sqrt{\pi}} \frac{1}{t\sqrt{t}} \left(\frac{\partial \hat{\psi}}{\partial \eta} + \xi \frac{\partial^2 \hat{\psi}}{\partial \eta \partial \xi} + \eta \frac{\partial^2 \hat{\psi}}{\partial \eta^2} \right) \\ \quad + \frac{1}{2\sqrt{\pi}\sqrt{D^*}} \frac{1}{t\sqrt{t}} \left\{ \mu_0 \hat{V}^2 \frac{\partial \hat{\psi}}{\partial \eta} + 2 \frac{\partial \mu_0}{\partial \xi} \frac{\partial^2 \hat{\psi}}{\partial \xi \partial \eta} - \frac{\partial \mu_0}{\partial \eta} \left(\frac{\partial^2 \hat{\psi}}{\partial \xi^2} - \frac{\partial^2 \hat{\psi}}{\partial \eta^2} \right) \right\} + f_x \\ \frac{\partial p_1}{\partial y} = -\rho_0 \frac{\sqrt{D^*}}{4\sqrt{\pi}} t^{-3/2} \left(\frac{\partial \hat{\psi}}{\partial \xi} + \xi \frac{\partial^2 \hat{\psi}}{\partial \xi^2} + \eta \frac{\partial^2 \hat{\psi}}{\partial \eta \partial \xi} \right) \\ \quad - \frac{1}{2\sqrt{\pi}\sqrt{D^*}} t^{-3/2} \left\{ \mu_0 \hat{V}^2 \frac{\partial \hat{\psi}}{\partial \xi} + \frac{\partial \mu_0}{\partial \xi} \left(\frac{\partial^2 \hat{\psi}}{\partial \xi^2} - \frac{\partial^2 \hat{\psi}}{\partial \eta^2} \right) + 2 \frac{\partial \mu_0}{\partial \eta} \frac{\partial^2 \hat{\psi}}{\partial \xi \partial \eta} \right\} + f_y \end{array} \right. \quad (58)$$

where f_x and f_y are given by (50). Similarly, ϕ_1 can be calculated from (42b) once the stream function is known.

The equations just given express well the changes in the fluid mechanics of diffusion in a binary mixture when a small difference of density of the mixing fluids is not neglected. The equations are all linear and could be solved by numerical methods. In the absence of any particular application the motivation for such a solution is basically to understand the new features. We may enhance our understanding more efficiently by solving the problem by quadrature in a special case in which the equations simplify greatly.

6. Exact Solution

In order to simplify equation (53) further, we may consider the case in which the viscosity μ_0 is constant independent of ϕ as was done by Camacho and Brenner [1995]. For glycerin-water mixtures, the viscosity is rapidly varying, so that the assumption of constant viscosity would introduce errors. For glycerin-water mixtures,

$$\frac{\rho_0 D_{\max}}{\mu_0} \ll 1 \quad (59)$$

where D_{\max} is the maximum of $D(\phi)$. When (59) holds and μ_0 is constant, (53) reduces to a biharmonic equation:

$$\frac{\partial^4 \hat{\psi}}{\partial \xi^4} + 2 \frac{\partial^4 \hat{\psi}}{\partial \xi^2 \partial \eta^2} + \frac{\partial^4 \hat{\psi}}{\partial \eta^4} = 0. \quad (60)$$

Using Fourier transform on ξ and applying the convolution theorem, we find that the solution of (60) can be expressed by a Poisson type of integral:

$$\hat{\psi}(\xi, \eta) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\eta^2 E(s)}{(\xi - s)^2 + \eta^2} ds. \quad (61)$$

Moreover, when the diffusion coefficient is a constant, that is, $D = D_0 = D^* = D_{\max}$, we find that

$$\Phi(\xi) = \frac{1}{2} - \frac{1}{2} \operatorname{erf}\left[\frac{\xi}{2}\right] \quad (62)$$

and

$$E(\xi) = \exp\left[-\frac{1}{4}\xi^2\right]. \quad (63)$$

In this case, the streamlines given by (61) with (63) are shown in Figure 2, where

$$\lim_{\xi \rightarrow \pm\infty} \hat{\psi}(\xi, \eta) = \lim_{\eta \rightarrow 0} \hat{\psi}(\xi, \eta) = 0 \quad \text{and} \quad \lim_{\eta \rightarrow \infty} \hat{\psi}(\xi, \eta) = \frac{2}{\sqrt{\pi}}.$$

In Figure 3 we plotted the perturbation velocity field of $\hat{\mathbf{u}}_1$. And Figure 4 shows the velocity magnitude of $\hat{\mathbf{u}}_1$.

To compute ϕ_1 , we find that, from (42b), ϕ_1 is governing by the following similarity equation when μ_0 and D are constants.

$$\hat{\nabla}^2 \phi_1 + \frac{1}{2} \left(\xi \frac{\partial \phi_1}{\partial \xi} + \eta \frac{\partial \phi_1}{\partial \eta} \right) = \frac{-1}{4\pi} \exp\left[-\frac{1}{4}\xi^2\right] \cdot \frac{\partial \hat{\psi}}{\partial \eta} \quad (64)$$

with the conditions similar to those in (27) except that the non-zero terms there are replaced by zeros. This system requires a numerical solution which we will not pursue here at this moment.

To compute pressure p_1 , we find that when μ_0 and D are constants, and under the assumption of (59), equation (58) gives rise to

$$p_1(x, y, t) = \frac{2\mu_0 D}{\pi^{3/2}} \int_{-\infty}^{\infty} \frac{y(x - \sqrt{D}ts)}{[(x - \sqrt{D}ts)^2 + y^2]} E(s) ds$$

$$+ \frac{\mu_0}{3\sqrt{\pi}\sqrt{D}} \frac{1}{t^{3/2}} \left(x \exp\left[\frac{-1}{4} \frac{x^2}{Dt}\right] \right) - \rho_G g \int \Phi(x,t) dx. \quad (65)$$

Note that p_1 does not have a solution in similarity form for reasons apparent in the discussion following (25).

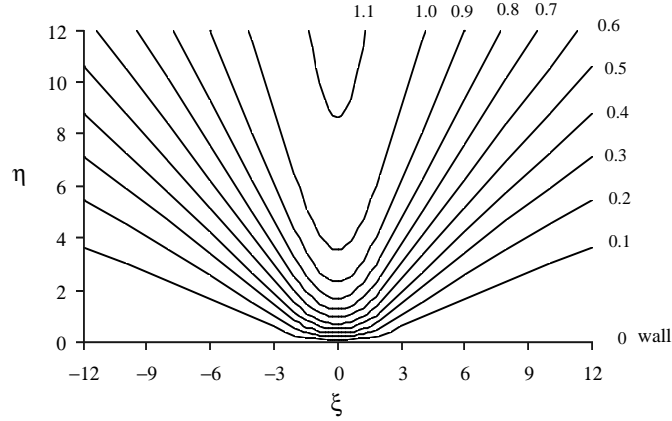


Figure 2. Dimensionless Streamline for \mathbf{w}_1 obtained from the stream function (56) with (60).

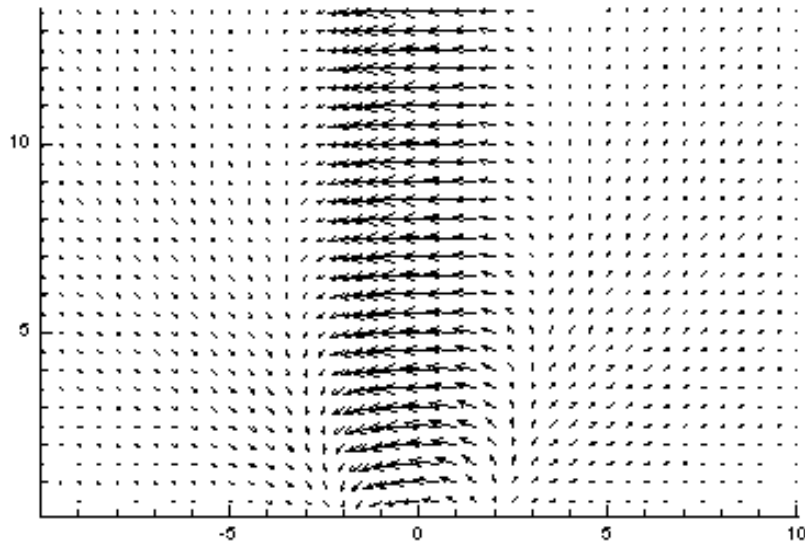


Figure 3. The perturbation velocity $\hat{\mathbf{u}}_1$ where $\xi \in [-10, 10]$ $\eta \in [0, 14]$

$\eta=20$

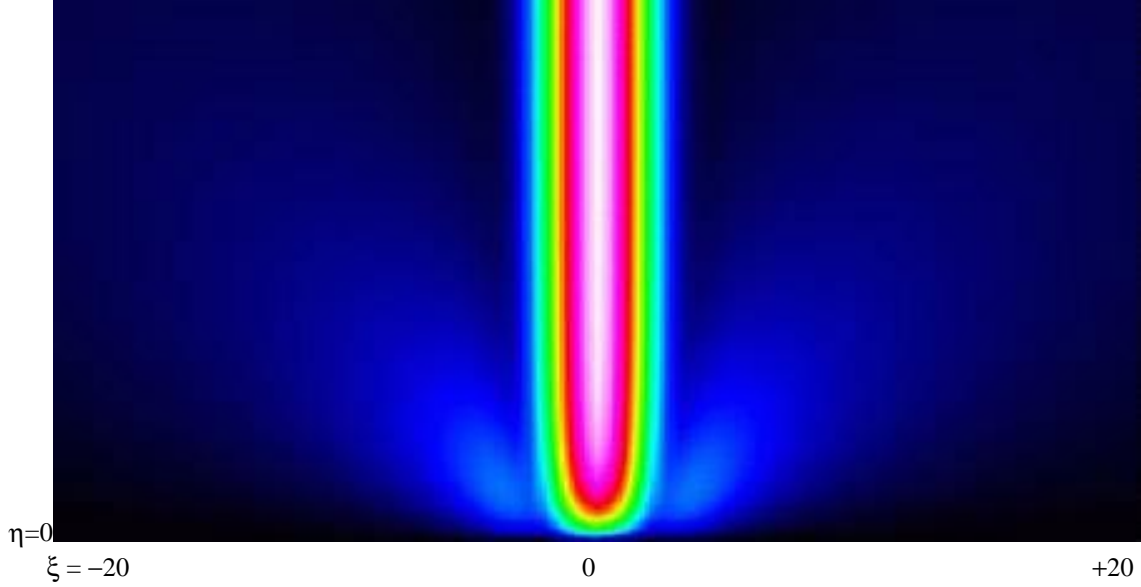


Figure 4. Contour plot of the velocity magnitude of the perturbation velocity $\hat{\mathbf{u}}_1$ within $\xi \in [-20, 20]$ $\eta \in [0, 20]$. The black region has the magnitude 0; the blue region, about 0.1; the green region, about 0.5 and the white region has the maximal magnitude 1.0.

7. Discussion

We considered the problem of smoothing of an initial discontinuity of concentration of a simple binary mixture, like glycerin-water, in the presence of a sidewall. The assumption that the velocity is solenoidal, which is usually made in fluid mechanics studies of diffusion, is incorrect when the difference in the density of the diffusing fluids is taken into account; if there are concentration gradients or the concentration is evolving, then the velocity is not solenoidal. In the density matched solenoidal case, no velocity is generated, and the presence of a sidewall will not effect the evolution of concentration. When the fluid mechanics of diffusing liquids is corrected to account for different densities, then a velocity must develop and then decay. If no sidewall is present, the evolution equation for the concentration reduces to the one for matched densities in which there is no velocity; the concentration equations are the same. When the sidewall is present, and $\mathbf{u} = 0$ there, the corrected theory cannot remain one dimensional because the velocity generated in the diffusing layer is not compatible with the no-slip condition. The resolution of this second discontinuity is also carried out by diffusion; a great surprise is that the whole system of very nonlinear PDE's can be reduced by two similarity variables, one for x to smooth the concentration discontinuity and one for y to smooth the velocity discontinuity at the sidewall. We derived a perturbation theory for a

small density difference which is a typical case and is particularly focused on the underlying physics and solved it by quadrature in a special but perhaps representative case. The pressure also is given here as a quadrature, but unlike the stream function and concentration the pressure cannot be put into similarity form.

The double similarity solution given here is the first of its kind. The velocity discontinuity which is at the bottom of this kind of mathematics arises when the (mass averaged) velocity \mathbf{u} vanishes there, or some combination of \mathbf{u} and \mathbf{w} vanishes there. But if the solenoidal part (volume averaged) velocity \mathbf{w} vanishes at the sidewall, then the velocity discontinuity will disappear.

The discussion issue raised here by the analysis of diffusion at sidewalls focuses on a correct mathematical description of boundary conditions for diffusing mixtures of liquids and gases; this issue has not yet been satisfactorily resolved.

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Appendix. Change of variable for the similarity transformation

$$\left(\frac{\partial \xi}{\partial t}, \frac{\partial \eta}{\partial t} \right) = \frac{-1}{2t} \left(\frac{x}{\sqrt{D^*t}}, \frac{y}{\sqrt{D^*t}} \right) = \left(\frac{-\xi}{2t}, \frac{-\eta}{2t} \right),$$

$$\nabla = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} = \frac{1}{\sqrt{D^*t}} \hat{\nabla}, \quad \hat{\nabla} \stackrel{def}{=} \mathbf{e}_x \frac{\partial}{\partial \xi} + \mathbf{e}_y \frac{\partial}{\partial \eta},$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{D^*t} \hat{\nabla}^2, \quad \hat{\nabla}^2 \stackrel{def}{=} \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}$$

$$\frac{\partial h}{\partial t} = \frac{-1}{2t} \left(\xi \frac{\partial h}{\partial \xi} + \eta \frac{\partial h}{\partial \eta} \right),$$

$$\frac{\partial w_x}{\partial t} = -\frac{\partial}{\partial t} \left(\frac{\partial \Psi}{\partial y} \right) = -\frac{\partial}{\partial t} \left(\frac{1}{\sqrt{D^*_t}} \frac{\partial \Psi}{\partial \eta} \right) = \frac{1}{2t\sqrt{D^*_t}} \left(\frac{\partial \Psi}{\partial \eta} + \xi \frac{\partial^2 \Psi}{\partial \eta \partial \xi} + \eta \frac{\partial^2 \Psi}{\partial \eta^2} \right)$$

and

$$\frac{\partial w_y}{\partial t} = \frac{\partial}{\partial t} \left(\frac{\partial \Psi}{\partial x} \right) = \frac{\partial}{\partial t} \left(\frac{1}{\sqrt{D^*_t}} \frac{\partial \Psi}{\partial \xi} \right) = \frac{-1}{2t\sqrt{D^*_t}} \left(\frac{\partial \Psi}{\partial \xi} + \xi \frac{\partial^2 \Psi}{\partial \xi^2} + \eta \frac{\partial^2 \Psi}{\partial \eta \partial \xi} \right).$$

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