Volume of mixing effect on fluid counter-diffusion

Gianni Orsi[a)] and Roberto Mauri[a),b)]
Department of Chemical Engineering, DICCISM, Università di Pisa, I-56126 Pisa, Italy

The counter-current diffusion-driven mixing process of two miscible fluids is studied in the absence of gravity, assuming that the mixture is non-regular, that is its volume is smaller than the sum of the initial volumes of the two components. Two competing effects are present in the mixing region: on one hand, the mass flow rate of each species increases, due to the larger density of the fluid; on the other hand, though, the volumetric flux is retarded by the inward convection due to volume disappearance, which opposes the outward velocity field due to diffusion. This intuition is confirmed by the analytical result of a 1D non-ideal mixing process, showing that, in the presence of the convection induced by a volume decrease: (a) the process is self-similar; (b) the mass flux of each species at the interface increases by approximately 0.8ϵ, where ϵ is the maximum relative volume decrease; and (c) the volume flux of each species decreases by approximately a 0.2ϵ amount. This result is further confirmed by a perturbation analysis for small ϵ. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4816500]

I. INTRODUCTION

The mixing process between two initially quiescent miscible fluids, say *A* and *B*, at uniform temperature and pressure, is particularly simple when the mixture is regular, that is, its volume (and enthalpy, as well) is constant and independent of its composition.[1] In this case, when we remove the partition separating the two fluids, mixing will be an equi-volumetric counter-diffusion process, occurring with no net volumetric flux, that is, the volumetric flux of *A* (i.e., the mean velocity of the *A* molecules) will be opposite to that of *B*, leading to the well-known error function, self-similar solution. When the fluids are ideal gases, the molar density of the mixture satisfies the equation of state of ideal gases and is independent of its composition, so that volume fractions are equal to molar fractions, and this process is an equi-molar counter-diffusion; for liquid mixtures, instead, when the mass density of the mixture is independent of its composition, volume fractions are equal to mass fractions and therefore the process is an equi-massive counter-diffusion.[2] In the following, we will assume that *A*, *B*, and the mixture are all liquids, as this is most relevant in our case; gaseous mixtures, however, can be treated in the same way, replacing massive with molar quantities.

In general, volumes are not additive, that is, the volume of a mixture is not equal to the sum of the volumes that are initially occupied by its components. For example, it is well known that upon mixing 1 liter of water with 1 liter of ethanol, the volume of the resulting mixture is 1.9 liter, corresponding to a 5% loss of volume.[3] In thermodynamics, the difference between the specific volume of the mixture and the sum of the volumes of the pure components at constant temperature and pressure is called *volume of mixing*, $\Delta\widehat{v}_{mix}$, a thermodynamic quantity whose value can be easily measured as a function of the mixture composition. Therefore, the mass density ρ, i.e., the inverse of the specific volume, can be expressed as

$$\frac{1}{\rho} = \frac{\phi}{\rho_A} + \frac{1-\phi}{\rho_B} + \Delta\widehat{v}_{mix},\tag{1}$$

[a)]Current address: Department of Civil and Industrial Engineering, Chemical Engineering Section, Università di Pisa, I-56126, Italy.
[b)]Author to whom correspondence should be addressed. Electronic mail: r.mauri@diccism.unipi.it.

where ρ_A and ρ_B are the densities of pure components A and B, respectively, while ϕ is the mass fraction of A. Accordingly, we see that, even for regular mixtures, where $\Delta \widehat{v}_{mix} = 0$, density is never a linear function of the molar, or mass, fraction, as most CFD codes assume.

Strangely, the effect of a volume change on the counter-diffusion process has not been studied carefully in the past, with the exception of the work by Perera and Sekerka,[4] who determined the advective non-solenoidal flow driven by diffusion-induced density changes in a two-dimensional rectangular box with zero gravity. To the best of our knowledge, the effects of this induced convection on mixing has not been studied, yet.

In the present work, we will determine both velocity and concentration fields resulting from the removal of the partition that initially, along the plane $x = 0$, separates two quiescent, miscible fluids. Now, a volume shrink, with $\Delta \widehat{v}_{mix} < 0$, will induce an inward (i.e., directed towards the interface) velocity field in the mixing region, opposing the outward velocity field due to diffusion, therefore decreasing the volumetric flux of the two fluids. On the other hand, in the mixing region the fluid is denser, so that the mass flux, i.e., the product between volumetric flux and density, will either increase or decrease, depending on which of the two effects will prevail. Obviously, a much rarer volume increase will instead produce the opposite effects. The objective of the present work is to study if and to what extent the above considerations are correct.

II. GOVERNING EQUATIONS

Consider the mixing process between two miscible fluids, A and B, following the removal of the partition that separates them initially. The equations of mass conservation for A and B are

$$\frac{\partial \widetilde{\rho}_A}{\partial t} + \nabla \cdot \mathbf{J}_A = 0; \qquad \frac{\partial \widetilde{\rho}_B}{\partial t} + \nabla \cdot \mathbf{J}_B = 0, \tag{2}$$

where $\widetilde{\rho}_A$ and $\widetilde{\rho}_B$ are the mass of A and B per unit volume within the mixture. Here, $\mathbf{J}_A$ and $\mathbf{J}_B$ are the mass fluxes (i.e., the mass of A and B crossing a section of unit area per unit time), and can be written as $\mathbf{J}_A = \widetilde{\rho}_A \mathbf{v}_A$ and $\mathbf{J}_B = \widetilde{\rho}_B \mathbf{v}_B$, where $\mathbf{v}_A$ and $\mathbf{v}_B$ are the mean velocities of the A and B species, respectively. Considering that $\mathbf{J} = \mathbf{J}_A + \mathbf{J}_B$ is the total mass flux, we obtain: $\mathbf{J} = \rho \mathbf{v}$, where $\rho = \widetilde{\rho}_A + \widetilde{\rho}_B$ is the density of the mixture (i.e., its total mass per unit volume), while $\mathbf{v}$ is the mass average, or barycentric, velocity. Defining $\phi = \widetilde{\rho}_A / \rho$ as the mass fraction of A (so that, obviously, $\widetilde{\rho}_B / \rho = 1 - \phi$), we obtain

$$\mathbf{v} = \phi \mathbf{v}_A + (1 - \phi) \mathbf{v}_B. \tag{3}$$

Now, summing Eq. (2), we obtain the continuity equation,[5]

$$\frac{D\rho}{Dt} = -\rho \left(\nabla \cdot \mathbf{v} \right), \tag{4}$$

where $D/Dt = \partial/\partial t + \mathbf{v} \cdot$ denotes the material time derivative. In addition, assuming the following Fickian constitutive relation,

$$\mathbf{J}_A = \phi \rho \mathbf{v} - \rho D \nabla \phi, \tag{5}$$

where D is the molecular diffusivity, Eq. (2) of conservation of the A-species becomes,

$$\rho \frac{D\phi}{Dt} = D\nabla \cdot (\rho \nabla \phi). \tag{6}$$

Equations (4) and (6) must be coupled with the equations of momentum and energy conservation, together with the equation of state (1); in the following, we will assume that the density is independent of pressure and the process is isothermal, so that $\rho = \rho(\phi)$.

Now, assume that initially A and B are separated by a partition located at $x = 0$ that, at time $t = 0$, is suddenly removed. Then, the above equations of motion must be solved with initial conditions,

$$\mathbf{v}(\mathbf{x}) = \mathbf{0}; \qquad \phi(x < 0) = 1; \qquad \phi(x > 0) = 0, \tag{7}$$

and boundary conditions,

$$\mathbf{v}(x \to \pm \infty) = \mathbf{0}; \qquad \phi(x \to -\infty) = 1; \qquad \phi(x \to +\infty) = 0, \tag{8}$$

where $\mathbf{x} = (x, y, z)$ is the position vector.

From Eqs. (4) and (6), considering that $d\rho/\rho = -\rho d\rho^{-1}$ and $d\rho = \rho' d\phi$, where $\rho' = d\rho/d\phi$, we obtain

$$\nabla \cdot \mathbf{v} = D\frac{d\rho^{-1}}{d\phi}\nabla \cdot (\rho\nabla\phi) = -\frac{D\rho'}{\rho^2}\left[\rho'|\nabla\phi|^2 + \rho\nabla^2\phi\right]. \tag{9}$$

For regular mixtures, volumes are additive, so that $\Delta\widehat{v}_{mix} = 0$ in Eq. (1); that means that the specific volume ρ^{-1} of the mixture is a linear function of the mass fraction ϕ, with $\lambda_\phi = d\rho^{-1}/d\phi$ denoting a constant concentration expansivity (obviously, here $\lambda_\phi = \rho_A^{-1} - \rho_B^{-1}$). Then, Eq. (9) can be rewritten as[6]

$$\nabla \cdot \mathbf{v}^\square = 0; \qquad \mathbf{v}^\square = \mathbf{v} - \lambda_\phi D\rho\nabla\phi = \mathbf{v} + D\,\nabla\ln\rho, \tag{10}$$

where, as shown by Brenner,[7] $\mathbf{v}^\square$ is the volume-average velocity, defined as[8]

$$\mathbf{v}^\square = \phi^\square\mathbf{v}_A + (1 - \phi^\square)\mathbf{v}_B. \tag{11}$$

Here, $\phi^\square = \phi\rho\overline{V}_A$ is the volume fraction of A, with $\overline{V}_A$ denoting its partial specific volume; in particular, for binary mixtures, we have[1]

$$\phi^\square = \phi\left[1 - (1 - \phi)\frac{d\ln\rho}{d\phi}\right]. \tag{12}$$

Note that the mass-average velocity, $\mathbf{v}$, is the ratio between the total mass flux (i.e., the quantity of mass crossing a unit surface cross section per the unit time) and the density of the mixture, while the volume-average velocity, $\mathbf{v}^\square$, is the total volumetric flux. If we consider a small volume (yet, containing a large number of molecules so that all averages can be properly defined), the former expresses the velocity of its center of gravity, while the latter is the velocity of its center of volume, i.e., the Lagrangian velocity along the fluid trajectory.[9]

Equation (10) shows that the volume-average velocity is divergence free when volumes are conserved, as one would expect. In particular, if $\mathbf{v}^\square = \mathbf{0}$ far from the interface, then $\mathbf{v}^\square = \mathbf{0}$ everywhere, confirming that, as we stated in the Introduction, the volumetric flux is zero during the counter-diffusion of regular mixtures. Therefore, in this case we obtain: $\mathbf{v} = -D\nabla\ln\rho$, indicating that the barycentric velocity of the mixture is directed towards less dense regions, where the mass fraction of the lighter fluid is larger. For example, if $\rho_A > \rho_B$, that means that the center of gravity will move towards the $x > 0$ region.

A similar treatment could also be carried over to describe the transport of heat in a single-phase single component fluid, whose density is a known function of the temperature T, $\rho = \rho(T)$. Then, Eq. (4) is still valid, while Eq. (6) is replaced by

$$\rho c_p\frac{DT}{Dt} = k\nabla^2 T, \tag{13}$$

where c_p is the specific heat and k is the thermal conductivity, both assumed to be constant. In most cases, we can assume that the specific volume ρ^{-1} is a linear function of T, with $\lambda_T = d\rho^{-1}/dT$ denoting a constant thermal expansivity. Accordingly, as during the transport of heat the total volume of the fluid is conserved, in this case it might be beneficial to describe the process using the volume average velocity,[10]

$$\mathbf{v}^\square = \mathbf{v} - (k\lambda_T/c_p)\nabla T = \mathbf{v} + \alpha\nabla\ln\rho, \tag{14}$$

with $\alpha = k/c_p\rho$ denoting thermal diffusivity.

In the following, as we want to investigate the effect of the volume of mixing alone, we will focus on the mixing process in a model mixture composed of two fluids having the same mass density, $\rho_A = \rho_B = \rho_0$, where the volume of mixing is such that the mixture mass density can be simply written as

$$\rho = \rho_0\left[1 + 4\epsilon\phi(1 - \phi)\right], \tag{15}$$

where ϵ expresses the difference between the density of a $50\% - 50\%$ mixture, referred to that of a pure liquid species. Since in most applications the volume of mixing is small, the last term on the RHS of Eq. (15) is the first-order correction to the equation of state of regular-mixtures.

In our problem, out of symmetry, both the volumetric and the mass fluxes are zero at the interface, which therefore will remain fixed at $x = 0$. Then, as $\left(\phi - \frac{1}{2}\right)$ is an odd function around the origin, we see that $\nabla^2\phi < 0$ and $\rho' < 0$ at $x < 0$, while $\nabla^2\phi > 0$ and $\rho' > 0$ at $x > 0$. Therefore, from Eq. (9), we see that $\nabla \cdot \mathbf{v} < 0$ everywhere, indicating that volume is consumed at both sides of the interface, as expected. When gravity effects are present, the same inequalities still hold across a moving interface.

In general, when $\epsilon \ll 1$, from Eq. (9), we see that at leading order we have

$$v = O\left(\epsilon D/L\right), \tag{16}$$

where L is the distance from the $x = 0$ interface, revealing that the convection induced by the volume disappearance is $O(\epsilon)$ times smaller than the typical diffusion speed. In Sec. IV, we will consider a perturbative analysis and show that indeed this scaling is correct.

III. 1D SELF-SIMILAR SOLUTION

The equations of motion (4) and (6) can be solved rather easily in 1D, assuming that gravity and all other forces are negligible (note, in particular, that in 1D the Korteweg force is identically zero[13]). In fact, Eqs. (4) and (6) can be solved, together with the equation of state (15), with the unknowns ρ, ϕ, and v. Then, the velocity and density fields can be substituted into the Navier-Stokes equation and determine the pressure. This last calculation will be omitted, as pressure is of no interest here.

Equations (4)–(6) become

$$\frac{\partial\phi}{\partial t} + v\frac{\partial\phi}{\partial x} = D\frac{1}{\rho}\frac{\partial}{\partial x}\left(\rho\frac{\partial\phi}{\partial x}\right) = D\frac{\partial^2\phi}{\partial x^2} + Dc\left(\frac{\partial\phi}{\partial x}\right)^2; \tag{17}$$

$$\frac{\partial v}{\partial x} = -D\frac{\rho'}{\rho^2}\frac{\partial}{\partial x}\left(\rho\frac{\partial\phi}{\partial x}\right) = -Dc\frac{\partial^2\phi}{\partial x^2} - Dc^2\left(\frac{\partial\phi}{\partial x}\right)^2, \tag{18}$$

where

$$c(\phi) = \frac{d\rho/d\phi}{\rho} = \frac{4\epsilon\left(1 - 2\phi\right)}{1 + 4\epsilon\phi\left(1 - \phi\right)}. \tag{19}$$

These equations can be solved within the half-space $x \geq 0$, imposing the following boundary and initial conditions:

$$v(x, t = 0) = v(x = 0, t) = 0; \quad \phi(x, t = 0) = \phi(x \to \infty, t) = 0; \quad \phi(x = 0, t) = \tfrac{1}{2}. \tag{20}$$

At the end, we want to determine the mass flux of A crossing the centerline (see Eq. (5)), where $v = 0$ and $\phi = 1/2$, so that $\rho = \rho_0(1 + \epsilon)$,
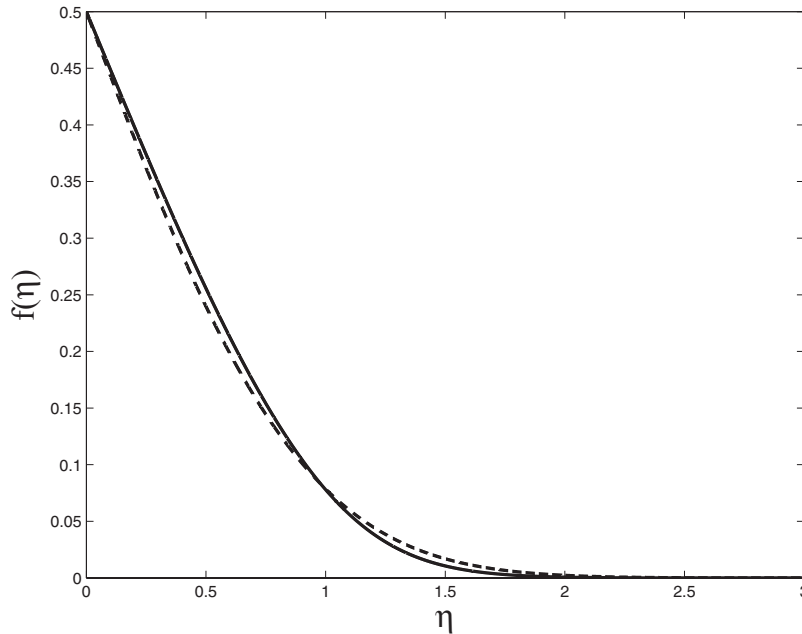
$$J_A(0) = \left[v\rho\phi - \rho D\frac{\partial\phi}{\partial x}\right]_{x=0} = -\rho_0 D\left(1 + \epsilon\right)\left[\frac{\partial\phi}{\partial x}\right]_{x=0}. \tag{21}$$

Clearly, the mass flux of B crossing the centerline is opposite, i.e., $J_B(0) = -J_A(0)$, so that the total mass flux at the interface is zero, as well as the mass average velocity.

The mass flux J_A can also be evaluated from an elementary mass balance, imposing that it must equal the temporal growth of the mass of the A component contained in the half-space $x \geq 0$, i.e.,

$$J_A(0) = \frac{d}{dt}\int_0^\infty \rho\phi dx. \tag{22}$$

This relation is not independent, as it coincides with the integral of Eq. (17).

FIG. 1. Plot of $f(\eta)$ for $\epsilon = 1$.

The problem (17)–(20) is self-similar. In fact, defining the following variables:

$$f(\eta) = \phi(x, t); \qquad g(\eta) = 2\sqrt{\frac{t}{D}}\, v(x, t), \quad \text{with} \quad \eta = \frac{x}{2\sqrt{Dt}}, \tag{23}$$

Eqs. (17) and (18) become

$$f''(\eta) + 2\eta f'(\eta) = g(\eta) f'(\eta) - c(f)\left[f'(\eta)\right]^2 \tag{24}$$

and

$$g'(\eta) = -c(f) f''(\eta) - c^2(f)\left[f'(\eta)\right]^2. \tag{25}$$

These equations must be solved for $\eta > 0$ with

$$f(0) = 1/2; \quad f(\infty) = 0; \quad g(0) = 0. \tag{26}$$

The two terms on the RHS of Eq. (24) represent the corrections to the purely diffusive solution (see Eq. (28)) due to volume of mixing effects: the first term is due to the inward velocity induced by the volume change and tends to decrease f, while the second term depends on the density increase in the interfacial region and tends to increase f.
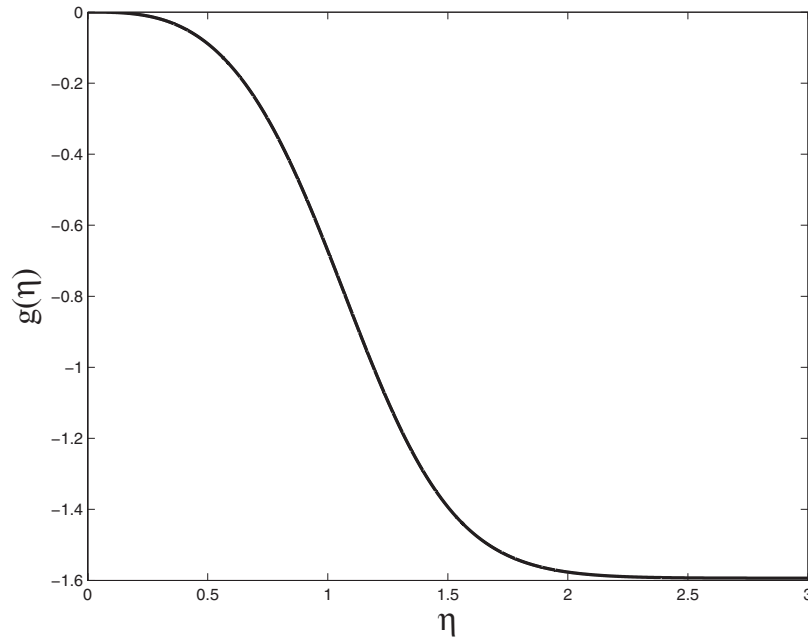
In Figs. 1 and 2, we show, respectively, the solutions $f(\eta)$ and $g(\eta)$ for $\epsilon = 1$. In particular, in Fig. 1, we see that the deviation of the concentration field from the purely diffusive solution (indicated with a broken line) is small, even for such an unphysically large volume of mixing.

At the end, we find the mass flow rate (21) crossing the centerline,

$$J_A(0) = -\rho_0 \sqrt{\frac{D}{4t}}\,(1 + \epsilon)\, f'(0). \tag{27}$$

In the absence of volume of mixing, i.e., when $\epsilon = 0$, then $c(\phi) = g(\eta) = 0$ and the solution reduces to the well known error function result, corresponding to an equi-massive countercurrent pure diffusion process,

$$f_0(\eta) = \frac{1}{2}\mathrm{erfc}(\eta); \qquad f_0'(0) = -\frac{1}{\sqrt{\pi}}; \qquad J_{A0}(0) = \rho_0\sqrt{\frac{D}{4\pi t}}. \tag{28}$$

FIG. 2. Plot of $g(\eta)$ for $\epsilon = 1$.

Now, defining the Sherwood number as the mass flow rate at the centerline referred to its $\epsilon = 0$ value, we obtain

$$Sh = \frac{J_A(0)}{J_{A0}(0)} = -\sqrt{\pi}(1+\epsilon)f'(0). \tag{29}$$

Integrating by parts Eq. (22), we can see that the Sherwood number can also be expressed in the following form:

$$Sh = \frac{2}{\sqrt{\pi}} \int_0^\infty [1 + 4\epsilon f(1-f)]f \, d\eta, \tag{30}$$

where we have considered that the unperturbed solution gives

$$\int_0^\infty f_0 \, d\eta = \frac{1}{2} \int_0^\infty \mathrm{erfc}(\eta) \, d\eta = \frac{1}{2\sqrt{\pi}}. \tag{31}$$

The Sherwood number is a function of ϵ only and does not depend on time, as a consequence of self-similarity. This is the most important result of this communication.

In Fig. 3, the Sherwood number, Sh, is plotted as a function of ϵ, showing that, with very good approximation,

$$Sh \approx 1 + 0.8\epsilon, \tag{32}$$

i.e., the mass flow rate grows almost linearly with the volume of mixing. Thus, the effect of the larger density at the interface, tending to increase the mass flow rate, prevails on the effect of the inward velocity induced by the volume change, which instead tends to decrease it. Overall, though, considering that ϵ is small, we may conclude that in most practical cases the effect of the volume of mixing is negligible.

Now, consider the volumetric flux of A, $J_A^\square = J_A/\tilde{\rho}_A = v_A$, where $\tilde{\rho}_A = \rho\phi$ is the mass of the A-species per unit volume and v_A is the mean velocity of the A-species. Considering that at the
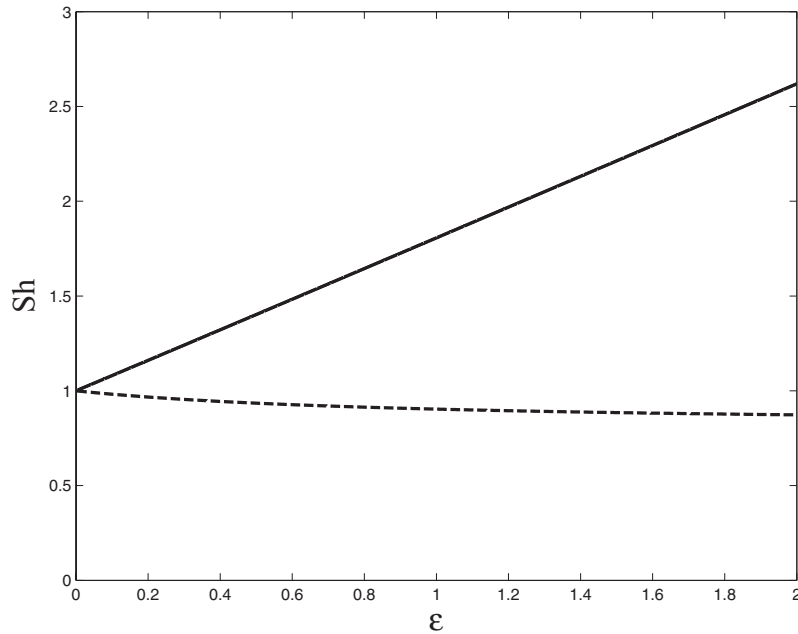
FIG. 3. Plot of the Sherwood number, Sh (continuous line), and the volumetric Sherwood number, $Sh^\square$ (broken line), as a function of ϵ.

interface $\widetilde{\rho}_A = \frac{1}{2}\rho_0 (1 + \epsilon)$, we can define the following volumetric Sherwood number,

$$Sh^\square = \frac{J_A^\square (0)}{J_{A0}^\square (0)} = \frac{Sh}{1 + \epsilon} = -\sqrt{\pi} f'(0), \tag{33}$$

where $J_{A0}^\square (0) = \sqrt{D/4\pi t}$ is the unperturbed (i.e., without volume shrink) volumetric flux of A at the interface. Clearly, the only volumetric effect of the density increase is the induced inward velocity field, so that the volumetric flux of A will be always smaller than its unperturbed value. This is confirmed in Fig. 3, where the broken line, representing $Sh^\square$ as a function of ϵ, is very well approximated by the following expression:

$$Sh^\square \approx 0.2 \left(4 + \frac{1}{1 + \epsilon} \right). \tag{34}$$

IV. 1D REGULAR PERTURBATION EXPANSION

The solution obtained in Sec. III can be validated considering the limit case $\epsilon \ll 1$, where an exact perturbative solution can be derived. This case corresponds to assuming that the volume of mixing is small compared to the total volume, a condition that applies to most practical cases: for example, for a water-ethanol mixture, $\epsilon \approx 0.05$. Accordingly, following the scaling (16), we can expand

$$f = f_0 + \epsilon f_1 + O\left(\epsilon^2\right); \qquad g = \epsilon g_1 + O\left(\epsilon^2\right), \tag{35}$$

where f_0 corresponds to the pure diffusive case (cf. Eq. (28)), so that Eq. (29) gives

$$Sh = 1 + \epsilon Sh_1 + O\left(\epsilon^2\right); \qquad Sh_1 = 1 - \sqrt{\pi} f_1'(0). \tag{36}$$

Note that at $O(1)$, the solvability condition (30) gives the known result:

$$Sh_0 = \frac{2}{\sqrt{\pi}} \int_0^\infty f_0 d\eta = \frac{1}{\sqrt{\pi}} \int_0^\infty \text{erfc}\,(\eta)\,d\eta = 1. \tag{37}$$

The leading-order, $O(\epsilon)$, correction to the pure diffusion case can be obtained substituting (35) into (24) and (25) and considering that $c(f) = 4\epsilon(1 - 2f_0) + O(\epsilon^2)$, obtaining

$$f_1''(\eta) + 2\eta f_1'(\eta) = g_1(\eta) f_0'(\eta) - 4[1 - 2f_0(\eta)][f_0'(\eta)]^2 \tag{38}$$

and

$$g_1'(\eta) = -4[1 - 2f_0(\eta)] f_0''(\eta) \tag{39}$$

with

$$f_1(0) = f_1(\infty) = 0; \quad g_1(0) = 0. \tag{40}$$

Integrating Eq. (39) by parts, we have

$$g_1(\eta) = -4[1 - 2f_0(\eta)] f_0'(\eta) - 8\int_0^\eta [f_0'(\xi)]^2 d\xi, \tag{41}$$

where we have considered that $g_1(0) = 0$ and $f_0(0) = 1/2$. Substituting this result into (38), we obtain

$$f_1'' + 2\eta f_1' = -8(1 - 2f_0)(f_0')^2 - 8f_0'\int_0^\eta (f_0')^2 d\xi' \tag{42}$$

with $f_1(0) = f_1(\infty) = 0$.

Solving this problem, we find $f_1'(0) = K$, where $K = 0.1132$, so that we can determine the leading-order correction of the mass flux crossing the centerline, i.e., the Sherwood number (36),

$$Sh_1 = 1 - \sqrt{\pi} K = W, \tag{43}$$

with $W = 0.7994$. Finally, we may conclude

$$Sh = 1 + 0.7994\,\epsilon + O\left(\epsilon^2\right) \tag{44}$$

in excellent agreement with Fig. 3.

The same result could be obtained applying the the solvability condition (30) at $O(\epsilon)$, obtaining

$$Sh_1 = \frac{2}{\sqrt{\pi}} \int_0^\infty [f_1 + 4f_0^2(1 - f_0)] d\eta. \tag{45}$$

We see that the correction to the mass flux crossing the centerline results to be the combination of two effects. The former, leading to the $+1$-term in the expression (43), is the increase in mass flux due to the density increase near the centerline, while the latter, with the $-\sqrt{\pi} K$-term, is due to the convection induced by the volume shrink and tends to decrease the mass flux. This latter term coincides with the first-order correction to the volumetric Sherwood number (33), i.e.,

$$Sh^\square = 1 + \epsilon Sh_1^\square + O\left(\epsilon^2\right); \qquad Sh_1^\square = -\sqrt{\pi} f_1'(0) = -0.2006. \tag{46}$$

V. CONCLUSIONS AND DISCUSSION

Mixing of non-regular mixtures is studied, considering the effect of the non-solenoidal velocity field induced by the volume reduction of two liquids as they are brought in contact with one another. In 1D, assuming that the two pure fluids have the same density, the mixing process consists of a counter-diffusion that is both equi-massive and equi-volumetric, and admits a self-similar solution. In the end, we find that the mass flux of each species at the interface increases by approximately 0.8ϵ, where ϵ is the maximum relative volume decrease, while the volumetric flux decreases by approximately a 0.2ϵ amount.

Now, we inquire to what extent this solution remains applicable when some of the simplifying assumptions are removed.

First, let us assume that $\rho_A \neq \rho_B$. In this case, as we have seen in Sec. II, in the absence of volume of mixing, i.e., when the mixture is regular, the interface will move towards the less dense

region. Considering that the volume of mixing will introduce a small correction, a multiple scale analysis can be developed, where the regular mixture behavior will constitute the leading-order solution. Consequently, most of the qualitative conclusions that we obtained in Sec. IV will be still valid. In particular, we can still conclude that the volume of mixing will give an $O(\epsilon)$ contribution to the mass and volumetric counter-diffusive fluxes.

More fundamental objections can be raised assuming that the constitutive relations are different than Eq. (5). For example, we should consider that, as shown by Cahn and Hilliard,[11] the diffusive material flux is proportional to the gradient of the generalized chemical potential difference, so that an additional non-local term must be added to the more conventional Fickian diffusion appearing in (5). Also, in the phase field model,[12] a Korteweg force should be added into the Navier-Stokes equation, that is also proportional to the gradient of the generalized chemical potential; therefore, a condition of chemical non-equilibrium (i.e., a non-uniformity of the chemical potential) would induce both a convection and an extra-diffusion, tending to restore thermodynamic chemical equilibrium. However, as both these terms, appearing in the equations of conservation of chemical species and of momentum, are proportional to $\nabla\phi \times \nabla\nabla^2\phi$, they are identically zero in 1D and so they do not play any role here.[12] In general, though, as shown by Lamorgese and Mauri,[13] these extra terms have a strong impact on the mixing process of regular mixtures in 2D and 3D, and so further studies are required to determine their influence when non-regular mixtures are used.

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