How valid is Taylor dispersion formula in slugs?

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Abstract

In a landmark paper, Taylor predicted that shear flow increases the effective diffusivity of species [Taylor, *Proc. Roy. Soc. A*, 219:186-203,1953]. This paper focused on Poiseuille flow in a circular pipe and predicted the existence of an effective species diffusion much greater than molecular diffusion. The ratio between the effective and molecular diffusion was shown to scale with the square of the Peclet number (product of the pipe diameter with the mean flow velocity divided by the molecular diffusivity). Taylor's study assumed two infinite columns of miscible fluids initially juxtaposed in a pipe and transported by the flow. A question of high practical interest is how valid this prediction is when a finite-sized slug is considered instead of an infinite fluid column. This paper sheds light on the finite-size effects on the mixing of two miscible fluids in a slug and quantifies how accurate Taylor's prediction

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is for finite length liquid columns. Results show that Taylor's dispersion formula is most accurate for lower Peclet numbers and longer slugs. Results also show that mixing is quite insensitive to the Reynolds number.

Subject class: 76R05

Keywords: Dispersion; Slug; Mixing

Contents

1 Introduction

The concept of further miniaturizing a lab-on-a-chip system can potentially be realized by combining multiple functions using a lab-in-a-tube system [22]. As reviewed by Smith et al., fluidic manipulation techniques presently explored could play a pivotal role in future applications of lab-in-a-tube devices because the reaction time of reagents under testing is paramount [23, 7]. The study of slug mixing has garnered considerable interest from researchers. In passive micromixers, mixing can be enhanced using certain channel designs that either increase the contact area or the contact time of liquid, or both [24, 11, 5, 27, 17, 20, 13]. Compared to parallel flow streams, Burns et al. showed an enhanced mass transfer using slug flows in capillaries due to the internal circulation within the slugs [6]. Kashid et al. showed the optimization of liquid slug interfacial area by tuning the dimensions of a capillary microreactor, which may be used as a technique for enhanced mixing [15]. The dynamics of a slug falling in a dry and pre-wetted vertical capillary tube was studied by Bico and Quéré [3] and Chebbi [8]. Self-propulsion of slugs in a capillary tube was reported for both immiscible [2, 4] and miscible fluids [21]. In their numerical study, Tanthapanichakoon et al. [25] proposed a modified Peclet number for enhanced liquid slug mixing. These studies provide further insights into how effective mixing can be achieved in microfluidics. For laminar flows, mixing occurs due to molecular diffusion as it would for quiescent fluid, but flow-enhanced mixing also occurs as described by Taylor [26]. The latter phenomenon is known as Taylor dispersion, in which shear flow acts along with diffusion to increase the effective diffusivity. A variation in the direction of flow causes sharp gradients perpendicular to flow, which is then smoothed out by diffusion. Taylor's analysis lead to the well-known formula for effective diffusivity $\mathsf{D}_{\mathsf{eff}}$ in a channel given by $\mathsf{D}_{\mathsf{eff}} = \mathsf{D}\left(1+\frac{1}{48}\mathsf{Pe}^2\right)$, where D is the molecular diffusivity and Pe the Peclet number, a measure of the strength of convective transport relative to diffusive transport. Though studies involving Taylor dispersion have been undertaken both experimentally and numerically for infinite liquid columns [16, 14, 10, 1, 9], we aim in this paper to assess the validity of Taylor's effective diffusion concept for a finite length slug.

2 Numerical model

The slug is assumed to be a body of revolution with length L and diameter W, with curved menisci at both ends, which meet the wall with a contact angle θ_e, see Figure 1. The slug is a binary mixture of two miscible, non-reacting

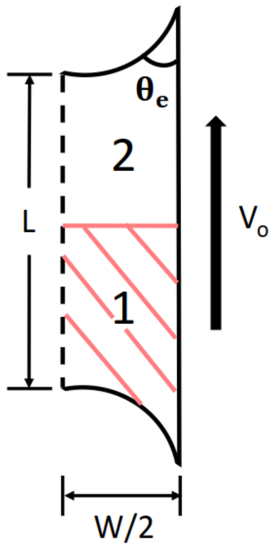

Figure 1: Illustration of the 2D axisymmetric model showing the slug of length L, diameter W, and equilibrium contact angle θ_e moving with velocity V_0. The slug is composed of two miscible liquids in equal proportion.

fluids and it travels in the tube with velocity V_0. The liquid is assumed to have constant density ρ and viscosity μ. The questions of interest are how long will it take for the two initially separated phases to mix in the slug and how does this mixing time depend on the slug size and the contact angle? As it is, the problem is a free boundary problem since it involves a free surface but we will assume that surface tension is sufficiently strong to make the free surface non-deformable.

To study the mixing, a 2D axisymmetric slug was modelled in the *Single Phase Flow* module of COMSOL Multiphysics. The two miscible fluids are initially separated but allowed to mix at $t = 0$. One of the two phases is solved for using the *Transport of Diluted Species* in COMSOL. The system is solved in a reference frame which moves at the same constant velocity as the slug. In this reference frame, the slug is therefore static and the wall moves with an equal and opposite velocity. This model solves for the velocity and pressure fields based on the Navier-Stokes equation. The latter was made dimensionless by substituting the appropriate parameters into COMSOL.

The Navier-Stokes equations for an incompressible fluid in dimensionless form read

$$\frac{\partial \vec{v}}{\partial t} + \left(\vec{v} \cdot \nabla\right) \vec{v} = -\nabla p + \frac{1}{\mathrm{Re}} \nabla \cdot \left(\nabla \vec{v}\right) , \qquad (1)$$

$$\nabla \cdot \vec{v} = 0 , \qquad (2)$$

where the coordinates were scaled with the capillary radius R, the flow velocity with the slug travelling velocity V_0, the pressure with ρV_0^2, time with $\frac{R}{V_0}$, and $\mathrm{Re} = \frac{\rho V_0 R}{\mu}$ is the Reynolds number. In COMSOL, which operates in a dimensional space, the density was set to unity and the viscosity to $\frac{1}{\mathrm{Re}}$.

The menisci were assumed to be a non-deformable interface and a slip boundary condition was imposed there. A no-slip boundary condition was applied at the wall with a constant upward, axial velocity V_0, corresponding to a downward travelling slug. The pressure was set to zero at the meniscus to constrain the solver. Consistent stabilization through streamline diffusion and crosswind diffusion were included to reduce the numerical diffusion as the solution approaches the exact solution. Streamline diffusion and crosswind diffusion adds diffusion in the directions along and orthogonal to the flow velocity, respectively. Linear P1 elements were chosen for both the velocity and pressure components since they were less prone to introducing oscillations.

The *Transport of Diluted Species* module of COMSOL Multiphysics was used to compute the concentration field according to the following dimensionless transport equation

$$\frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c = \frac{1}{\mathrm{Pe}} \nabla^2 c , \qquad (3)$$

where the concentration is scaled with c_0, the initial concentration of one of the species and $\mathsf{Pe} = \frac{V_0 R}{D}$ is the Peclet number with D the species' molecular diffusivity.

The initial condition for the concentration was defined as a step function that ranges from 0 to 1 at the centre of the slug with a smooth transition zone that is 4% of the slug length. This transition helps with convergence, which could be difficult for steep concentration gradients. No flux boundary condition was imposed on the capillary wall, the axis of symmetry, and the free surface. It now becomes apparent that the mixing problem only depends on Re and Pe, the slug aspect ratio $\frac{L}{R}$, and the contact angle.

We define the effectiveness of volumetric mixing by the mixing index M.I. expressed as follows:

$$\text{M.I.} = \frac{1}{2}\int_{\Omega} (c - c_{eq})^2 \, d\omega \,, \tag{4}$$

where Ω is the computational domain and c_{eq}, the equilibrium species concentration. Since we have defined the concentration as a step function located half-way through the slug, the concentration at equilibrium will be 0.5.

3 Methodology

By our definition, the effective diffusivity D_{eff} is such that the solution of the one-dimensional diffusion equation (eq. (5)) with this effective diffusivity in a reference frame that moves with the slug produces a mixing index variation, which best matches the one obtained by solving the full axisymmetric convection-diffusion problem (eqs. (1), (2), and (3)). The diffusion problem is defined as follows

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_{eff}\frac{\partial c}{\partial x}\right) \,, \tag{5}$$

where x is the dimensionless axial coordinate relative to the lower end of the slug and D_{eff} is a dimensionless diffusion coefficient scaled with the characteristic dimensions mentioned above. The following initial and boundary conditions are assumed:

$$
\begin{aligned}
c(x, t=0) &= 1 - H\left(x = l_1\right) \,, && (6)\\
\frac{\partial c}{\partial x}\Big|_{x=0} &= \frac{\partial c}{\partial x}\Big|_{x=l} = 0 \,, && (7)
\end{aligned}
$$

where H is the Heaviside function. The boundary conditions specify zero concentration flux at either end of the slug. The analytical solution that satisfies eqs. (5), (6), and (7) reads [21]

$$
c(x,t) = \frac{l_1}{l} + \sum_{k=1}^{N} \frac{2}{k\pi} \sin\left(\frac{k\pi l_1}{l}\right) \cos\left(\frac{k\pi x}{l}\right) \exp\left(-D_{eff}\left(\frac{k\pi}{l}\right)^2 t\right) \,, \quad (8)
$$

where $l_1 = l/2$. The corresponding mixing index is therefore defined as

$$
\text{M.I.} = \frac{1}{2}\int_0^l \left[\sum_{k=1}^{N} \frac{2}{k\pi} \sin\left(\frac{k\pi l_1}{l}\right) \cos\left(\frac{k\pi x}{l}\right) \exp\left(-D_{eff}\left(\frac{k\pi}{l}\right)^2 t\right)\right]^2 A_c dx \,, \quad (9)
$$

where A_c is the capillary cross-section area. This equation was then implemented and evaluated in MATLAB, with the number of terms in the Fourier series N set to 100. Note that eq. (9) can be simplified to the following form:

$$
\text{M.I.} = \sum_{k=1}^{N} \frac{lA_c}{k^2\pi^2} \sin^2\left(\frac{k\pi l_1}{l}\right) \exp\left(-2D_{eff}\left(\frac{k\pi}{l}\right)^2 t\right) \,, \quad (10)
$$

According to Taylor [26], the mixing of two solutes in a tube can be represented by an effective diffusion coefficient, D_{eff}, which combines both molecular diffusion and dispersion due to convection. Accordingly:

$$
D_{eff} = D\left(1 + \frac{1}{48} Pe^2\right) \,. \quad (11)
$$

The dimensionless effective diffusion counterpart is expressed as follows:

$$\mathsf{D}_{\mathsf{eff,Taylor}} = \frac{1}{\mathsf{Pe}}\left(1 + \frac{1}{48}\mathsf{Pe}^2\right) . \tag{12}$$

The subscript *Taylor* is used to emphasize the inclusion of Taylor dispersion, in addition to molecular diffusion. This equation is key in our study, as it will be used later to compare with the effective diffusion coefficient obtained numerically.

The effective diffusion was calculated as follows:

- For a given Re and Pe, the true Mixing Index variation was computed by running COMSOL. Simulations were run until a “fully mixed state”, defined arbitrarily as the time when the Mixing Index falls below 2×10^{-3}, is reached. For a given Pe, we calculate the corresponding value of $\mathsf{D}_{\mathsf{eff,Taylor}}$.
- This Mixing Index very rapidly follows an exponential decay $\mathsf{M.I} \sim \mathsf{A}\exp^{-\lambda_c t}$ defined by the decay rate λ_C.
- The $\mathsf{D}_{\mathsf{eff}}$ value in eq. (9) was then adjusted such that the decay rate λ_M for the pure diffusion mixing matches the decay rate λ_C to within 1% λ_C.

In essence, this gives us a good approximation of the optimum effective diffusion coefficient arising from our numerical model, which we shall denote as $\mathsf{D}_{\mathsf{eff,num}}$. To compare how close our numerical model matches $\mathsf{D}_{\mathsf{eff,Taylor}}$, we calculated the error defined as

$$\epsilon = \left|\frac{\mathsf{D}_{\mathsf{eff,Taylor}} - \mathsf{D}_{\mathsf{eff,num}}}{\mathsf{D}_{\mathsf{eff,Taylor}}}\right| \times 100\% . \tag{13}$$

A representation of our methodology process is shown in Figure 2.

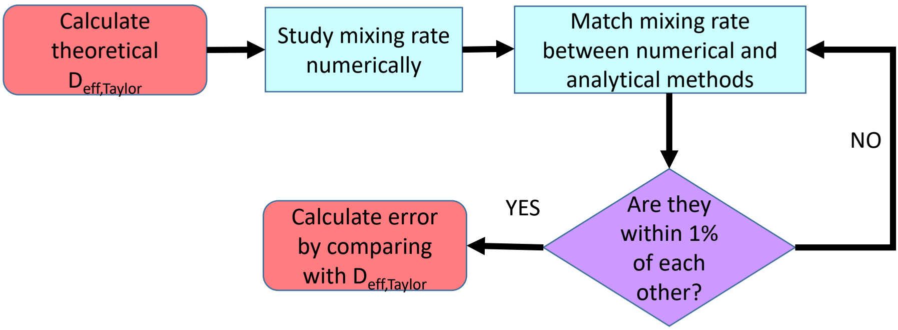

Figure 2: Methodology flow chart to calculate error between $\mathsf{D}_{\mathtt{eff,num}}$ and $\mathsf{D}_{\mathtt{eff,Taylor}}$.

4 Results and discussion

Our numerical model was mesh-independent, as we found that different mesh sizes tested did not impact the mixing index results. The Pe numbers tested were 0.001, 0.01, 0.1, 10, 100 and 1000. The same set of values were used for the Re number to test with each Pe number. Therefore, we obtained 36 data points for analysis in a two-dimensional parameter space. Our results showed an exponential decay of the mixing index, in which for a given Re number, mixing is completed sooner when Pe number is smaller. This agrees with the formula, where a smaller Pe number corresponds to a larger diffusion coefficient, hence the shorter time to complete mixing. However, mixing rate is unaffected by the Re number, as our results showed no difference in mixing time for a given Pe number. These results are shown in Figure 3. The fact that the effective mixing is only weakly dependent on the Reynolds number should not come as such a surprise since this is what Taylor dispersion formula predicts. Moreover, the fact that the Reynolds number only has a weak effect has also been reported in [19, 18]. Based on our initial conditions, the numerical results showed that concentration was higher at the top-half of

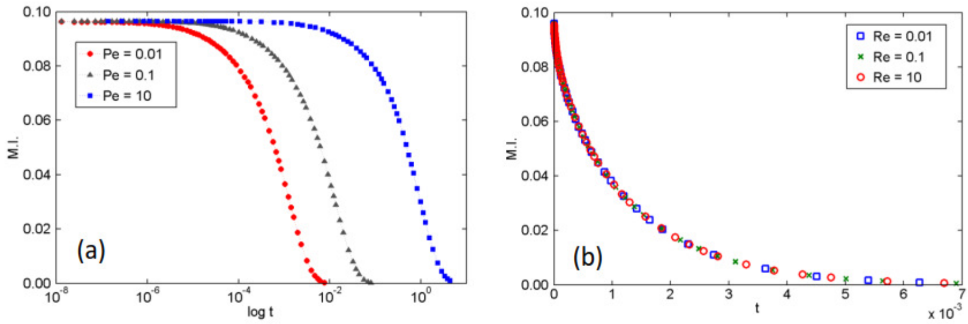

Figure 3: Mixing index distribution for (a) various Pe numbers ($\mathsf{Re} = 0.01$), and (b) various Re numbers ($\mathsf{Pe} = 0.01$), for a slug with $\mathsf{L}/\mathsf{R} = 4$ and $\theta_e = 60^\circ$.

the tube. However, over time, the concentration becomes homogenous with a concentration of 0.5 at equilibrium (see Figure 4), which agrees with our definition of complete mixing. Further, as shown by the arrows in Figure 4, a recirculation occurred within the slug, where the flow is directed downstream in the middle of the tube, followed by a change in direction at the meniscus, which leads to an upstream flow along the wall. The recirculation of liquid flow enhances mixing by reducing the striation length, i.e. the distance over which mixing occurs by diffusion [12]. By evaluating the natural logarithm of the mixing index from $t = 0$ until it reaches $\sim 2 \times 10^{-3}$, the instant when complete mixing is hereby defined, our fitted linear regression showed an average R^2 value of 0.9866. We studied the effect of slug length, and found that our numerical model yields a better approximation of $D_{\mathrm{eff,Taylor}}$ for a longer slug, as shown by the wider area corresponding to lower error percentages (see Figure 5). Contact angle did not impact the percentage difference, as shown by our results for a slug of $\frac{L}{R} = 26$ (see Figure 6). This suggests that our model is not sensitive to the change in contact angle, and that the length of the slug itself plays a more important role for $D_{\mathrm{eff,Taylor}}$ approximation, all else equal.

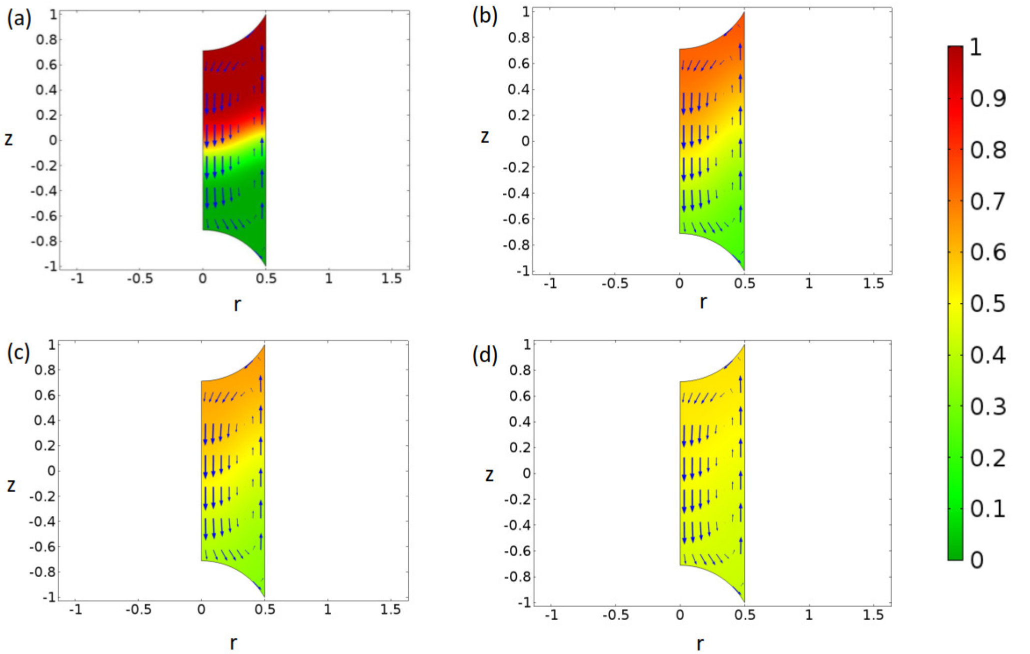

Figure 4: Velocity field and concentration gradient of a slug ($\frac{L}{R} = 4$, $\theta_e = 60^o$) in a capillary tube, with $\mathsf{Re} = 0.01$ and $\mathsf{Pe} = 10$, at (a) $t = 0.1$, (b) $t = 2$, (c) $t = 3$, and (d) $t = 5$.

5 Conclusions

We have developed a dimensionless numerical model that allows for the study of liquid slug mixing, with the introduction of a concentration gradient. Only the Re number, the Pe number, and the slug geometrical parameters are required to perform the study. From our definition of complete mixing, we showed that a lower Pe number resulted in a shorter mixing time. The Re number, however, did not affect the mixing time strongly. We then assessed the validity of Taylor dispersion formula for finite length slugs. The methodology consisted in finding the effective diffusion coefficient ($D_{eff,num}$)

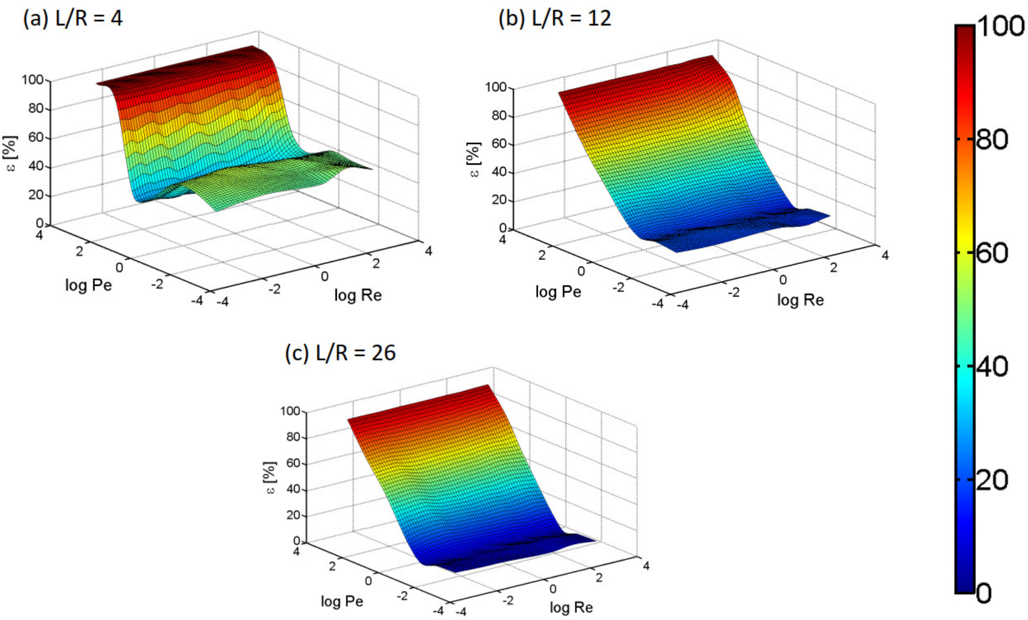

Figure 5: Surface plots showing the percentage difference between $\mathsf{D}_{\mathsf{eff,Taylor}}$ and $\mathsf{D}_{\mathsf{eff,num}}$ for (a) $\frac{L}{R} = 4$, (b) $\frac{L}{R} = 12$, and (c) $\frac{L}{R} = 26$, at a fixed contact angle of 60°.

of an equivalent one-dimensional, purely diffusive model which best replicate the mixing index curve of the full model based on the Navier-Stokes and species transport equations. This effective diffusion coefficient was then compared to values predicted by Taylor dispersion formula ($\mathsf{D}_{\mathsf{eff,Taylor}}$). The results showed that agreement with Taylor dispersion formula is best when (a) the slug is longer, and (b) the Pe number is low (diffusion-dominated regime), even if the corresponding Re number is high. The fact that agreement is better for longer slugs is intuitively sound since Taylor dispersion formula should apply in the limit of an infinite slug. The effect of the contact angle appeared minimal for the slug considered here. The ability to better understand the validity range of Taylor dispersion formula is expected to be useful to

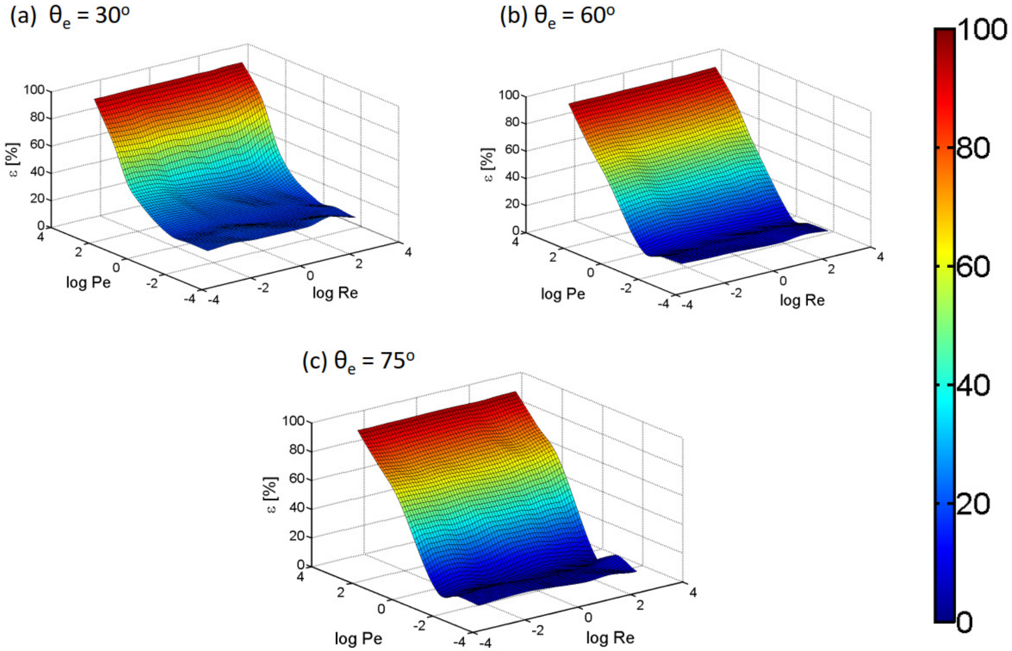

Figure 6: Surface plots showing the percentage difference between $D_{\mathtt{eff,Taylor}}$ and $D_{\mathtt{eff,num}}$ for contact angles (a) 30°, (b) 60°, and (c) 75°, for a slug of $\frac{L}{R} = 26$.

quicky and reliably estimate the mixing time of species in finite length slugs or droplets. This is of high practical importance in the context of digital microfluidics, for example, where one often aims to mix chemical reactants in slugs confined in micro-channels.

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