AES/PE/11-19  Numerical study on dispersion of dilute glycerol-water mixtures in channel flow

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Abstract

In this work we developed a numerical model for channel flow on a pore or micro scale. A straight channel was simulated with a flow regime of Re=0.03 and Re=0.3 (comparable to typical fluid flow in petroleum reservoirs) to visualize the characteristics of flow and dispersion up to the Fickian limit. The objective of this study was to quantify the effect of the dilute assumption on the channel averaged longitudinal dispersion of glycerol in water flow and to qualitatively assess the specific contribution of the diffusion, viscosity and density of the solute. In all cases a mixture with a concentration of 200 mol/m$^3$ solute was injected into the channel. The ideal tracer flow model was verified by comparing it to theory. A literature study on the properties of glycerol-water mixtures was done to incorporate the correct property behaviour for variable glycerol concentration. In addition, the creeping flow assumption was tested. Detailed analysis of the changes in flow velocity components and concentration distribution was performed. The dilute, non-dilute and creeping flow models have also been tested and analysed for a tenfold increased velocity. For the base model (with Re=0.03), diffusion showed to be the main contributor to a different dispersive behaviour, followed by viscosity and density respectively. Viscosity and density variability caused changes in the velocity profiles of the flow. Longitudinal dispersion appeared to be 0.35% higher when all variability was included, compared to an ideal tracer flow simulation. Higher flow velocity (Re=0.3) appears to increase the dispersion differences, mainly caused by viscosity variability.
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1. Introduction

Petroleum production generally deals with combinations of several fluid phases and multiple components. With maturing oil and gas fields nowadays even more fluids like carbon dioxide, polymers and solvents are being injected in an attempt to improve the oil recovery in the later production stages. The success of these recovery methods depends on the extent to which the flow of the several components can be affected. However, the behaviour of flow of multiple components, whether it is multi-phase or single-phase, is not yet fully understood. With an increasing amount of components and phases, the behaviour of flow becomes increasingly more complex, and a detailed understanding of its behaviour becomes more essential for accurate predictions.

This research will treat single-phase flow of two miscible liquid components to improve the understanding in this area. Even small perturbation of the fluid composition may significantly alter the fluid flow behaviour and may make the modelling a lot more complex. This is especially the case when characteristic properties of the fluids, like density and viscosity, are rapidly varying with composition.

1.1 Background

The total process of spreading of one chemical species into the other is what is called dispersion. Convection or diffusion, as well as an interaction of these two phenomena, can contribute to create the total dispersion.

In early research, Taylor (1953 and 1954) developed an analytical theory on longitudinal dispersion by convection and diffusion for long times in a very narrow tube. This resulted in a method to experimentally determine molecular solute diffusion.

For dispersion in porous media theoretical relations were developed by Saffman (1960), Pfannkuch (1963) and Bear and Bachmat (1965, 1968) in the 1960’s and very well summarized in (Bear 1972), together with experimental data from a wide range of authors. They were the first to relate the dispersion to the dimensionless Peclet number, which is a measure for the ratio of convection over diffusion.

Based on an extensive set of experiments, Delgado and Guedes de Carvalho (D&G) developed empirical relations for transverse (Delgado and Guedes de Carvalho 2001) and longitudinal (Guedes de Carvalho and Delgado 2003, 2005) dispersion in packed beds (Delgado 2005, 2006). D&G quantified dispersion as function of Peclet number as well as the Schmidt number (being the ratio of momentum diffusion over mass diffusion) establishing a link on the viscosity dependency of dispersion.

All these descriptions have in common that they deal with solutes that are diluted and for which it is accordingly assumed that the properties of the carrier fluid are still valid for the behaviour of the mixture. This assumption will be valid in a lot of cases, depending on the type of fluids and the concentration of the tracer. It is not easy however, to quantify exactly up to what combination of properties this assumption still holds.

When looking at fluid flow through petroleum reservoirs, the involved components are present in proportions that can definitely not be assumed diluted. Different fluid properties are then very important to the combined flow process. Research on this has been done, mostly on a reservoir scale. (Koval 1963) developed a method to predict recovery of oil through miscible displacement by a solvent, where the viscosity ratio of the liquids causes fingering of the solvent into the oil. (Todd and Longstaff 1972) built and applied a numerical simulator for a similar miscible displacement in which they incorporated density differences as well. A nice overview of the methods for miscible flooding of petroleum reservoirs was given by (Stalkup Jr. 1983). First contact miscibility (FCM) has by then become the name for the process in which liquids mix directly on first contact and for which the mixtures will always remain single phase. These types of research on miscible flow are very empirical and a fundamental description of finer scale processes is absent.
The goal of this thesis is to characterize the error that is made, by assuming a solute that is diluted, in pore scale longitudinal tracer dispersion. Ultimately, this could help to create a more fundamental description of miscible displacement in a reservoir.

1.2 Ideal tracer dispersion in a channel

Ideal dispersion for a dilute tracer in fully developed laminar flow through a channel can be analytically described. For the convective contribution to the description we first need to determine the velocity profile. The velocity profile \( v{\text{[m/s]}} \) of flow in the \( x \)-direction is a function of the (by convention negative) pressure gradient in the flow direction \( \frac{-dp}{dx} \) [Pa/m], the viscosity \( \mu[\text{Pa-s}] \) and the channel width \( H[\text{m}] \):

\[
v(y) = \frac{1}{2\mu}\left(\frac{-dp}{dx}\right)(Hy - y^2) \quad \text{for} \quad y \in [0, H]
\]

Averaging over the width of the channel to obtain the mean velocity \( v_0[\text{m/s}] \) gives

\[
v_0 = \frac{1}{12\mu}\left(\frac{-dp}{dx}\right)H^2
\]

Substituting (1.2) in (1.1) gives an expression of the velocity profile in terms of mean velocity:

\[
v(y) = 6v_0\left(\frac{y}{H} - \left(\frac{y}{H}\right)^2\right)
\]

This parabolic velocity profile for fully developed laminar flow (or so-called Poiseuille flow) and its average velocity are shown in Figure 1-1.

![Figure 1-1 Poiseuille flow velocity profile and its average velocity.](image)

Taylor (1953, 1954) quantified dispersion for flow through a tube in the Fickian limit. He found that the channel dispersion is proportional to the diameter of the tube squared and inversely proportional to the magnitude of the molecular diffusion coefficient. Aris (1956) added the analysis of the longitudinal moments of the distribution of the solute. His description describes the evolution of the second spatial moment over the entire time domain. Camacho (1993) extended the theory for longitudinal dispersion in laminar channel flow by deriving an evolution equation for the dispersive flux.

It was found (Camacho 1993, Berentsen 2003) that the longitudinal spatial variance of the tracer front, \( \sigma_{c,x}^2 [\text{m}^2] \), is accurately represented by

\[
\sigma_{c,x}^2 = 2D_{\text{mol}}t + 2\sigma_v^2\tau_{\text{eff}}\left(t + \tau_{\text{eff}}\left(e^{-\frac{t}{\tau_{\text{eff}}}} - 1\right)\right)
\]

(1.4)
Here $D_{\text{mol}}[\text{m}^2/\text{s}]$ is the molecular diffusion coefficient; $\sigma_y^2[\text{m}^2/\text{s}^2]$ is the variance of the velocity that in terms of mean velocity $v_0$ is given by

$$\sigma_y^2 = \frac{1}{2} \left( \frac{\partial \sigma_{y,x}^2}{\partial t} = D_{\text{mol}} + \sigma_y^2 \tau_{\text{eff}} \left( 1 - e^{-\frac{t}{\tau_{\text{eff}}}} \right) \right)$$

(1.5)

And $\tau_{\text{eff}}[\text{s}]$ is the time that a particle is still correlated with its travel path, the so-called effective relaxation time. This effective relaxation time is inversely proportional to the diffusion coefficient and proportional to the effective transverse mixing length $L_{\text{T,eff}}[\text{m}]$:

$$\tau_{\text{eff}} = \frac{L_{\text{T,eff}}^2}{D_{\text{mol}}}$$

(1.6)

The effective transverse mixing length $L_{\text{T,eff}}$ is proportional to the height of the channel ($H$) and is related to the correlation of the longitudinal velocity field in the transverse direction:

$$L_{\text{T,eff}} = \frac{1}{2\pi} \frac{H}{n_{\text{eff}}}$$

(1.7)

This transverse correlation is quantified by the so-called effective modal number $n_{\text{eff}}[-]$. For a smaller transverse correlation, $\tau_{\text{eff}}$ is smaller and $n_{\text{eff}}$ is larger. Both $\tau_{\text{eff}}$ and $n_{\text{eff}}$ can be calculated from the Fourier representation of the system. The derivation of $\tau_{\text{eff}}$ and $n_{\text{eff}}$ can be found in detail in Appendix C. For our case of Poiseuille flow the effective modal number takes the value $n_{\text{eff}}=1.0314$.

Hereafter the local effective dispersion $D_{\text{eff,local}}[\text{m}^2/\text{s}]$ is defined as the time derivative of the spatial variance:

$$D_{\text{eff,local}} = \frac{1}{2} \frac{\partial \sigma_{x,x}^2}{\partial t} = D_{\text{mol}} + \sigma_y^2 \tau_{\text{eff}} \left( 1 - e^{-\frac{t}{\tau_{\text{eff}}}} \right)$$

(1.8)

While the global effective dispersion $D_{\text{eff,global}}[\text{m}^2/\text{s}]$ reads

$$D_{\text{eff,global}} = \frac{1}{2} \frac{\sigma_{x,x}^2}{t}$$

(1.9)

For asymptotic times both local and global effective dispersion coefficient converge to the following constant:

$$D_{\text{eff,\infty}} = D_{\text{mol}} + \sigma_y^2 \tau_{\text{eff}} = D_{\text{mol}} + \sigma_y^2 \frac{L_{\text{T,eff}}^2}{D_{\text{mol}}}$$

(1.10)

which is in line with the early observation of Taylor (1953, 1954).

### 1.3 Present study

This research aims at improvement of the understanding of single-phase miscible displacement. We focus on a small part of this behaviour, namely the binary dispersion of two miscible liquids. The objectives of this study are to:

- quantify the error that is made in assuming a dilute solute in channel averaged longitudinal dispersion of glycerol in two dimensional channel flow of water on a pore/micro scale,
- qualitatively analyse the specific contribution of the density, viscosity and diffusion of the tracer fluid to channel averaged longitudinal dispersion on a pore/micro scale.

We looked at a 2D channel, initially filled with water (solvent) that was replaced by water with a small fraction of glycerol (solute) under a fully developed laminar Poiseuille flow regime. Investigation of the solute’s dispersive behaviour was done by analysis of numerical simulations. The simulations were performed by the software package COMSOL Multiphysics, which is a finite element method (FEM) based solver for problems with coupled physical phenomena. Simulation results were subsequently analysed using the computer programme MATLAB. The model was based on the conventionally recognised Navier-Stokes descriptions of (pore scale) fluid flow and molecular mass transport as described by (Bird, Stewart, and Lightfoot 2007). Mixture properties were taken
into account through empirical relations that were available from literature, (Cheng 2008) and (D'Errico et al. 2004).

1.4 Outline of the report

Section 2 deals with the description of the theory of miscible flow. After formulating the basic balance laws for Newtonian fluids we describe the equations that deal with molecular mass transport. Next we state the constitutive relations that describe the properties and behaviour of the glycerol-water mixture as function of composition. For these we combined several sources from literature. Section 3 presents the numerical model that was constructed with use of the software package COMSOL Multiphysics. In addition it describes the cases that we simulated. Chapter 4 presents and discusses the simulation results. We end with conclusions and recommendations at the end of the report.
2. **Theory of miscible flow**

To compose the system of equations that represent miscible flow we need to describe fluid flow and mass transport. To couple the two phenomena, constitutive relations are required that describe the behaviour of density, viscosity and diffusion as function of mixture composition.

2.1 **Fluid flow**

Fluid flow can be fully described by a set of partial differential equations that describe the transport of mass, momentum and energy. This set of equations is usually referred to as the Navier-Stokes equations. The first equation is called the continuity equation and describes the conservation of mass. The conservation of momentum and energy are separately described by the momentum equation and energy equation. Because the simulation setup in this research is assumed to be isothermal, the energy equation becomes redundant. The other two equations will be stated below and shortly explained. For an elaborate derivation of the equations, please see (Panton 2005) or (Bird, Stewart, and Lightfoot 2007).

2.1.1 **Continuity equation**

As the underlying physical principle is the conservation of mass, this mass balance describes the rate of change of mass in time resulting from a net mass influx:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0
\]  

(2.1)

where \(\rho\) [kg/m\(^3\)] is the density, \(t\) [s] is time and \(\mathbf{u}\) [m/s] is the velocity.

2.1.2 **Momentum equation**

The momentum balance states that the rate of change of momentum in a domain in time and the net momentum flux out of that domain balance the forces acting on that domain.

\[
\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla T + \mathbf{F}
\]  

(2.2)

The left hand side shows the accumulation and acceleration terms for momentum. The right hand side contains the force terms. \(\mathbf{F}\) is the volume force vector which could be used for example to incorporate gravity in the simulation. The stress tensor \(\mathbf{T}\) [Pa] consist of a compressional stress (\(\rho I\)) and a deviatoric shear stress part \(\tau\) [Pa].

\[
\mathbf{T} = \rho I + \tau
\]  

(2.3)

**Newtonian fluids**

Fluids for which the stress versus strain rate relationship is linear are called Newtonian fluids (Batchelor 2000). In Newtonian fluids the shear stress or friction force per unit area acting in the \(x\)-direction \(\tau_{yx}\) [Pa] is linear proportional to the shear deformation, being the derivative of the \(x\)-velocity in the \(y\)-direction:

\[
\tau_{yx} = -\mu \frac{du_x}{dy}
\]  

(2.4)

The constant of proportionality, \(\mu\), is called the dynamic viscosity (in Pa·s). Alternatively, the shear stress actually expresses the molecular momentum flux (Akker and Mudde 2005).

In this thesis we assume that the fluids behave Newtonian.

For Newtonian fluids the shear stress tensor is the multidimensional analogue of (2.4) and reads

\[
\tau = -\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^\top) + \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) I
\]  

(2.5)
The continuity equation and the momentum equation provide the system to solve for the pressure and velocity field.

**Creeping flow**

Single phase flow is often characterized by the dimensionless Reynolds number \( \text{Re}[-] \), which is a measure for the relation between inertial and viscous forces in a fluid flow situation:

\[
\text{Re} = \frac{\rho u d}{\mu}
\]  
(2.6)

Here \( d[\text{m}] \) is a representative size for the flow, which for channel flow is the width of the channel. Fluid flow through reservoir rock is generally very slow and the Reynolds number very small. This means that inertial forces become less important compared to viscous forces. A conventionally recognized assumption is that when \( \text{Re}<<1 \), inertial forces can be neglected and flow is called creeping flow. For creeping flow the second term in equation (2.2), a non-linear inertial acceleration term, is neglected. This makes the momentum equation linear and therefore numerically easier to solve.

Flow at very low Reynolds numbers is often erroneously called Stokes flow. However, the Stokes flow equations assume that the flow is also independent of density, so that the temporal term in (2.2) may be neglected as well (Bird, Stewart, and Lightfoot 2007), (Panton 2005). In this research we will always work with density dependent formulations. Therefore we would like to emphasize that we specifically refer to creeping flow and not Stokes flow.

**2.2 Mass transport**

**2.2.1 Mass transport equation**

Mass transport can be described by the component version of the conservation of mass or continuity equation as described in paragraph 2.1.1, which for component \( i \) reads

\[
\frac{\partial \rho_i}{\partial t} + \nabla (\rho_i u_i) = 0
\]  
(2.7)

Here \( \rho_i[\text{kg/m}^3] \) is the mass of component \( i \) per unit volume of the mixture (differently said, mass concentration of component \( i \)) and \( u_i[\text{m/s}] \) is the average component velocity.

Direct computation of the (average) component velocity \( u_i \) requires a proper description of the (average) momentum interaction of the various components within the fluid. Since, this interaction is generally unknown a common approach is to express the component velocity in terms of the mass averaged fluid phase velocity.

To do this, we first describe the relation between the mass transport equations of the components and the phase. The sum taken over all mass balances for all components (2.7) must equal the phase mass balance (2.1). The density of the mixture is obtained by the sum of all the component’s masses per unit volume:

\[
\rho = \sum_{i=1}^{N_c} \rho_i
\]  
(2.8)

Where \( N_c[-] \) is the total number of components in the mixture. In the same way the phase momentum is the sum of the momentum for all components:

\[
\rho \mathbf{u} = \sum_{i=1}^{N_c} \rho_i \mathbf{u}_i
\]  
(2.9)

Note, that by convention (Bird, Stewart, and Lightfoot 2007) the mass average phase velocity is defined by the sum of the product of mass fraction and velocity of all the components:

\[
\mathbf{u} = \sum_{i=1}^{N_c} \omega_i \mathbf{u}_i
\]  
(2.10)
Now, using these relations, we incorporate the phase velocity into the component mass balance by expressing the component velocity in terms of the mass average velocity and the difference between these two, also referred to as diffusion velocity (Bird, Stewart, and Lightfoot 2007):

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = -\nabla \cdot (\rho_i [\mathbf{u} - \mathbf{u}])$$  \hspace{1cm} (2.11)

The term on the right side between parenthesis is now representing the component molecular mass flux with respect to mass average velocity $j_i[kg/(m^3\cdot s)]$.

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = -\nabla j_i$$  \hspace{1cm} (2.12)

2.2.2 Molecular mass flux

According to Fick’s first law of diffusion, the mass flux due to the difference between the component velocity and the mass average velocity is proportional to the mass fraction gradient by a factor $D_{ij}[m^2/s]$ that is known as Fick’s binary diffusion coefficient (Bird, Stewart, and Lightfoot 2007):

$$j_i = \rho_i \mathbf{u} - \mathbf{u} = -\rho D_{ij} \nabla \omega_i$$  \hspace{1cm} (2.13)

Substituting (2.13) in equation (2.12) and using the algebraic relation $\rho_i = \omega_i \rho$ we obtain the desired form of the mass transport equation in term of the mass average phase velocity:

$$\frac{\partial \rho \omega_i}{\partial t} + \nabla \cdot (\rho \omega_i \mathbf{u}) = \nabla \cdot \left( \rho D_{ij} \nabla \omega_i \right)$$  \hspace{1cm} (2.14)

This is the equation that we use to solve for the mass fraction distribution of the smallest component of the binary mixture.

Another more general description for multicomponent diffusion in gases or liquids can be thermodynamically derived as a special case of the Maxwell-Stefan equations (Bird, Stewart, and Lightfoot 2007). For binary diffusion in liquids these two different descriptions are related but require different diffusivities, of which Fick’s diffusivity is the easiest applicable form. Further explanation can be found in the appendix, paragraph B.3.

2.3 Mixture properties

One of the focuses of this thesis is to find the contribution of variation in mixture properties to microscale dispersion. Mixture properties like density, viscosity and diffusion are very difficult to calculate analytically. Interaction of fluid particles and differences in shape of the molecules are sources for non-linear development of the properties. But for certain mixtures extensive experimental results have been collected and empirical relations have been deduced accordingly.

Water and glycerol will be used for the simulations. These two fluids are widely used for studies on flow phenomena because they facilitate to do this for a large range of Reynolds numbers (Cheng 2008). The property relations that were used to perform the simulation will be explained below and checked with available mixture data from literature.

2.3.1 Viscosity

(Cheng 2008) discussed the behaviour of density and viscosity of glycerol-water mixtures. He developed an empirical formula for the mixture viscosity, based on data from several other authors:

$$\mu_{mix} = \left( \mu^{(w)} \right)^{\alpha} \left( \mu^{(g)} \right)^{1-\alpha}$$  \hspace{1cm} (2.15)

This relation is applicable to situations with a temperature from 0 °C to 100 °C and glycerol mass fractions from 0 to 1. In (2.15) $\mu^{(w)}$ and $\mu^{(g)}$ are the viscosities of pure water and glycerol and $\alpha$ is a mass fraction dependent weighting factor. At atmospheric pressure, the viscosities of the pure components are depending solely on temperature $T$ (in °C) and calculated as follows (in cP):

$$\mu^{(w)} = 1.790 \cdot \exp \left( \frac{-1230 - T}{36100 + 360 \cdot T} \right)$$  \hspace{1cm} (2.16)
The weighting factor $\alpha[-]$ depends on the glycerol mass fraction $\omega_g[-]$, 
\[
\alpha = 1 - \omega_g + \frac{a \omega_g (1 - \omega_g)}{a \omega_g + b (1 - \omega_g)}
\]  
(2.18)
in which the two coefficients $a[-]$ and $b[-]$ are related to the temperature and calculated by 
\[
a = 0.705 - 0.0017 \cdot T
\]
\[
b = (4.9 + 0.036 \cdot T) a^{2.5}
\]  
(2.19)
Simulations were done at a constant temperature of 25°C. As a consequence the component viscosities and the coefficients $a$ and $b$ are constant. Figure 2-1 shows a graph of the glycerol-water mixture viscosity $\mu_{mix}$ versus glycerol mass fraction $\omega_g$ as described above. For completeness the relation of viscosity versus mole fraction has been plotted as well because in literature both relations are used. In order to check and confirm the equation by (Cheng 2008), it has been compared with two sets of viscosity data at the same temperature from an article (Ernst, Watkins, and Ruwe 1936) and a chemical company that sells the mixtures (Dow Chemical Company 2011). Note the logarithmic vertical axis.

2.3.2 Density
The density of the glycerol-water mixture can be expressed as a function that depends linearly on the glycerol mass fraction $\omega_g$ (Cheng 2008):
\[
\rho_{mix} = \rho^0 \omega_g + \rho^w (1 - \omega_g)
\]  
(2.20)
In which $\rho^0[\text{kg/m}^3]$ and $\rho^w[\text{kg/m}^3]$ are the pure densities of glycerol and water respectively. This expression is found to be in line with the experimental results of several other authors, (Adamenko et al. 2006), (Behrends et al. 2006), (Uosaki, Kitaura, and Moriyoshi 2006), (Dow Chemical Company 2011). Although ideally the density of the mixture should be linearly dependent on the volume contributions of the components (Behrends et al. 2006), excess behaviour by mixing glycerol and water creates a decrease in total volume, as well described by (Adamenko et al. 2006) and (Behrends et al. 2006).
Also the pure component densities are now needed. For the conditions in this research, $T=298.15$ K and atmospheric pressure, the water and glycerol densities were calculated as constants according to empirical equations by (Cheng 2008): $\rho_{(w)}=997 \text{ kg/m}^3$ and $\rho_{(g)}=1261 \text{ kg/m}^3$. These densities match with the findings of other authors (Lemmon, McLinden, and Friend 2011), (Adamenko et al. 2006).

Figure 2-2 shows graphs of Cheng’s relation, as well as the comparative experimental data, versus mass and mole fraction. The ‘ideal’ mixture density, calculated from component densities by (Cheng 2008), has been added to see the effect of the volume change.

\[
D_{wg} = \frac{1.024 - 0.91x_g}{1 + 7.5x_g} \times 10^{-9}
\]  

(2.21)
The mole fraction is related to the mass fraction by

\[ x_g = \frac{\omega_g M_g}{M} \]

in which \( M \) is the molar mass of the mixture and \( M_g \) is that of glycerol. The molar masses of the components are \( M_w = 0.018 \) kg/m³ for water and \( M_g = 0.092 \) kg/m³ for glycerol. For the mixture the molar mass varies linearly with molar composition and harmonically with mass:

\[
M = x_g M_g + x_w M_w = \left( \frac{\omega_g}{M_g} + \frac{\omega_w}{M_w} \right)^{-1}
\]  

(2.22)

Figure 2-3 shows the plots of the diffusivity versus mass and mole fraction of glycerol. The two endpoints of the graph, at the limits \( x_g \to 0 \) and \( x_g \to 1 \), are the diffusivities at infinite dilution. We will give these tracer diffusion constants the following symbols and values:

\[ D_{gw} = D_{wg} \left( x_g \to 0 \right) = 1.024 \cdot 10^{-9} \text{ m}^2\text{s}^{-1} \] for infinitely diluted glycerol in water,

\[ D_{wg} = D_{wg} \left( x_g \to 1 \right) = 1.341 \cdot 10^{-11} \text{ m}^2\text{s}^{-1} \] for infinitely diluted water in glycerol.

Comparative experimental data from a few authors have been found about diffusion, (D’Errico et al. 2004), (Ternström et al. 1996) and (Rutten 1992). The equation by (D’Errico et al. 2004) that will be used for the simulations is in the article indicated with uncertainty ranges:

\[
D_{wg} = \left( \frac{1.024 \pm 0.010}{1 + (7.5 \pm 0.3)x_g} \right) \left( 0.91 \pm 0.05 \right) x_g \cdot 0.004 \cdot 10^{-9}
\]  

(2.23)

Found data and this equation including its lower and higher boundaries have been plotted in Figure 2-3.
3. Numerical model

3.1 COMSOL Multiphysics

To simulate the channel flow system under consideration the software package COMSOL Multiphysics version 4.1 was used. This is a program that applies the finite element method (FEM) to solve multiphysics systems with coupled phenomena. COMSOL is a modular program in which each physical phenomena is described by a different module. For our problem, COMSOL requires two modules. The first module is the Laminar Flow module that describes the flow behaviour of the phase. It solves for Navier-Stokes fluid flow equations as explained in paragraph 2.1. The second, so-called Transport of Concentrated Species module, describes the movement of each component (using the mass transport equation of paragraph 2.2).

3.1.1 Finite Element Method (FEM)

Physical processes, like the ones in this research, are often described by partial differential equations (PDE’s). It is often impracticable or even impossible to solve the equations in an analytical way. Several numerical techniques have been developed to provide an approximate solution to the system of PDE’s. The finite element method is one of these numerical techniques and has been developed from the 1940’s onwards and is nowadays widely used by engineers (Süli 2011).

The principle of FEM modelling is to discretize the physical continuum into a finite number of elements, such that the behaviour over the continuum can be approximated by polynomials within the individual elements. Finite element analysis is the most flexible numerical method when geometries become more complex, as opposed to the simpler and less compatible finite difference (FDM) and finite volume (FVM) methods. To make the PDE’s usable for FEM they need to be rewritten into a so called weak form. This usually reduces the validity of the solution to the particular set of boundary conditions, but makes it possible to decrease the highest order of differentiation (Vermolen 2005).

In this research discretization of the geometry and choosing the boundary conditions and PDE’s was done ourselves. Any further part of the FEM was left to be solved by COMSOL.

3.1.2 Adaptations to the Transport of Concentrated Species module

The mass transport equation (2.14) is the equation that we use in COMSOL to solve for the mass fraction of the smallest component, in our research this is glycerol. A small adjustment had to be made to the built in mass transport equation in COMSOL, because we believe this built in equation is incorrect for the part of molecular mass flux. An elaborate analysis of the theory for diffusion and the error in COMSOL can be found in Appendix B: Diffusion.

3.1.3 COMSOL issues

COMSOL showed to be a useful tool to do the simulations for this research. However, some errors as well as underdeveloped features showed up. At first the error in the mass transport equation that was found. As shown in Appendix B, it seems as if this is simply the result of inaccurate derivations. Another trace of inaccuracy comes up when we tried to plot a graph of the concentration gradient. The unit that arises is [1/m] while we would expect [mol/m$^3$]. Closer inspection of the underlying equation reveals that it is the mass fraction gradient that is plotted instead.

The equation view for the modules displayed some coding inconsistency. One example is about different mass fluxes. The diffusive and convective flux are both defined. Then a total flux is defined, which should be diffusive plus convective flux. But instead of using both the earlier defined fluxes, the diffusive flux is incorporated using the composing formula again. Equally, in the weak expression the diffusive flux is composed again. As a consequence, adapting one equation does not mean that the change is taken into consideration throughout the entire program.
Another example is that there are definitions for the three components (x, y, z direction) of diffusive flux and for three components of a diffusive flux vector. It is unclear why they are separately defined, and besides that, they are exactly the same for corresponding directions. So again, adjusting one of these does not change the other while it should be equal.

Altogether the programme is a very useful and relatively user friendly tool, although extreme care must be taken to adapt modelling parameters and definitions. A thorough check of all the involved equations is definitely necessary.

3.1.4 COMSOL limitation on injected solute concentration

Unfortunately, we had to limit the injected solute concentration to 200 mol/m$^3$. This appeared to be the highest concentration for which our model would still converge in COMSOL. For the realistic case with glycerol this yields very low mole and mass fractions ($x_g=0.0036$, $\omega_g=0.018$). Generally solute mole fraction up to 0.1 can be considered dilute (COMSOL AB. 2010)). However, because of the large differences in properties of water and glycerol this might not be valid in our case. It would have been useful to see how the influences of solute properties that we found in this research develop for larger solute concentrations.

3.2 Geometry

The geometry that was used in all the simulations was a two dimensional channel with a width of 0.5 mm (x-direction) and a length of 8 mm (y-direction). This 2D geometry would mean in 3D that the geometry is infinite in the third z-direction, thus flow between two parallel plates.

3.2.1 Mesh

Discretization of a 2D geometry in COMSOL can be done using triangular or quadrilateral elements. The quality of the elements is measured by COMSOL depending on the symmetry of the elements, on a scale from 0 to 1. For a rectangular geometry it is therefore optimal to use a square mesh which results in only elements with maximum quality. Choosing a triangular mesh results in a lower average and minimum quality of the elements. A mesh was used with square sides of 0.125e-4 m, which means that the geometry is divided into a total of 25600 grid cells that provide 105124 degrees of freedom that have to be solved for. The effect of grid coarsening and refinement will be shown by two simulations that are presented in the next section.

3.3 Simulation cases

To investigate the contribution of various fluid properties (diffusion, viscosity and density) to the fluid flow behaviour and in particular the dispersion, we simulated various cases. In all cases water with 200 mol/m$^3$ solute is injected at time $t=0$ in the channel that is initially filled with water. Properties of the solute-water mixture are set equal to a glycerol-water mixture, as described in section 2.3, or equal to a water-water mixture. Table 3-1 summarizes the settings of the different cases that we will discuss in detail below.

As inlet flow boundary condition we set a constant Poiseuille velocity profile as described in paragraph 1.2. The inlet velocity profile is calculated as if it is created by fully developed laminar water flow through a channel of 0.5 mm wide with an average velocity of 5.8344e-5 m/s (corresponding to $dp/dx=0.02/0.008$[Pa/m]). The outlet boundary is conditioned with a pressure at 0 Pascal. This is only a reference pressure because pressure dependency of the fluid is not taken into account.

These conditions for the water-water situation represent a Reynolds number of Re=0.03. This suggests, as explained in section 2.1.2, that the flow can be seen as creeping flow and the momentum equation can be accordingly simplified. We will check if this assumption holds for a simulation with glycerol-water mixture injection.

A few adaptations on the cases will be done to examine the effect of grid coarsening and refinement, as well as to show the result for a higher Reynolds number. This will be further explained below.
### Table 3-1 Details of different simulation cases.

<table>
<thead>
<tr>
<th>#</th>
<th>Constant properties</th>
<th>Variable properties</th>
<th>Short explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Ideal tracer flow for water</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Fully concentrated species flow</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Tracer flow with added diffusivity variability</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Tracer flow with added viscosity variability</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Tracer flow with added density variability</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \mu_{\text{mix}} = \mu^{(w)} )</td>
<td>( \rho_{\text{mix}} = \rho^{(w)} )</td>
<td>Fully concentrated species creeping flow</td>
</tr>
<tr>
<td></td>
<td>( D_{\text{wg}} = D_{\text{gw}} )</td>
<td>( M = M_{w} )</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.3.1 Case #1: Ideal tracer flow

The injected fluid has exactly the same properties as the initial liquid in the domain, except for a different label. This simulates ideal tracer flow, in which the tracer does not affect the properties of the bulk fluid. Dispersion for this case should reflect the theory as described in paragraph 1.2.

#### 3.3.2 Case #2: Concentrated species flow

A glycerol-water mixture (200 mol/m\(^3\) glycerol, \( x_{g} = 0.0036 \), \( \omega_{g} = 0.018 \)) is injected in pure water. Properties of the mixture are calculated according to the empirical relations from literature as explained in paragraph 2.2. This simulation is suspected to come closest to a realistic situation and allows a quantitative analysis of the dilute assumption for the dispersion of glycerol in water flow.

#### 3.3.3 Case #3: Tracer flow with added diffusivity variability

Viscosity and density of the injected fluid (and the mixture) are the same as for the fluid initially in place, but the diffusivity varies as in a glycerol-water mixture. Qualitative analysis of the effect of variable diffusion is the purpose of this case.

#### 3.3.4 Case #4: Tracer flow with added viscosity variability

The density and diffusion coefficient are kept constant and the viscosity behaves as in a glycerol-water mixture. The result should allow a qualitative analysis of the contribution of changing viscosity with mixture composition to the flow and dispersion behaviour.
3.3.5 Case #5: Tracer flow with added density variability
The density of the injected fluid differs from the density of the fluid initially in place. The density behaves according to a glycerol-water mixture as given in equation (2.20), resulting in an injected mixture density of 1001.7 kg/m$^3$. Viscosity and diffusion remain constant at the values for tracer flow. This case should improve the understanding of the contribution of mixture dependent density.

3.3.6 Case #6: Concentrated species with creeping flow assumption
Simulation is equal to case #2 except for the used momentum equation. Because of the creeping flow assumption the second term in equation (2.2) is neglected. The outcome of this simulation can be used to show the influence and validity of this assumption.

3.3.7 Increased flow velocity
A higher flow velocity will change the ratio of inertial to viscous forces, as represented by the Reynolds number (paragraph 2.1.2). Simulation cases #1, #2 and #6 will be carried out with a ten times increased velocity, representing Re=0.3. This will allow to analyse if the inertial forces have become more prominent and again a validity check of the creeping flow assumption.

3.3.8 Grid coarsening and refinement
We discuss two simulations to demonstrate the effect that grid coarsening and refinement have on the results. The ideal tracer flow simulation (case #1) is modified for this purpose. First we change the sides of the square grid cells to 0.0625e-4 m. This increases the total amount of grid cells to 102400 and the total degrees of freedom to 415044. Secondly the grid cell side is increased to 0.5e-4 m. Now the amount of grid cells is decreased to 1500 and the total degrees of freedom to 7084.

3.4 Quantification of simulated dispersion
In MATLAB the 2D simulated COMSOL data is averaged across the channel to obtain longitudinal data. For the analysis of longitudinal dispersion we will take the first derivative of the channel averaged tracer concentration to retrieve the distribution of the front. Then the mean of the distribution is calculated and subsequently the longitudinal variance of the tracer front:

$$\sigma_{c,x}^2 = \frac{\sum_{i=1}^{n} \partial_x c(X_i)(X_i - \mu_{c,x})^2}{\sum_{i=1}^{n} \partial_x c(X_i)}$$

(3.1)

Here $c$[mol/m$^3$] is the concentration of which the derivative in the $x$ direction is taken to calculate the distribution of the concentration front. To retrieve an accurate approximation for the effective local dispersion as in equation (1.8) would require a very large amount of simulation data. Therefore we use the global effective dispersion (1.9) for comparison.
4. **Data analysis**

COMSOL solves the simulation cases as composed in the last section. Subsequently, simulation data is exported to and analysed in MATLAB.

4.1 **Simulation results**

At first we want to validate the performance of the model by comparing the result of case #1 to the theoretical results for ideal tracer dispersion in a channel. Figure 4-1 (left) compares the simulated data to the theory, by means of the spatial standard deviation ($\sigma_{c,x}$), computed with equation (3.1) and (1.4) respectively. Figure 4-1 (right) compare the global effective dispersion obtained with (1.9) for case #1 with the theory. In addition, Figure 4-1 (right) shows the theoretical local effective dispersion (1.10) and the asymptotic Fickian limit (for $t \gg \tau$). These were added to investigate if the dispersion reaches the asymptotical limit for long times.

![Figure 4-1 Comparison of longitudinal tracer dispersion in theory and simulation results. Left: the standard deviation as function of time; right: the effective dispersion as function of time.](image)

For analyses of the influence of the several properties in the different cases we will compare the various cases by means of the resulting concentration and velocity fields at the last simulated output time $t=69$ s. Molar concentration and velocity data of cases #2, #3, #4 and #5 has been subtracted from the corresponding data of case #1 to obtain the resulting differences that changes in the input properties cause. In addition, differences in concentrations are normalised by the injected molar concentration. Figure 4-2 shows the resulting differences in concentration fields. Figure 4-3 and Figure 4-4 show the differences in longitudinal (or $x$) velocity and the transverse (or $y$) velocity, respectively. Take care regarding the different scales of the colour ranges. They are adapted to the different magnitudes of the data ranges to clearly visualize all effects.

Figure 4-5 shows the differences in concentration and velocity fields caused by the creeping flow assumption. The fully concentrated cases #2 and #6 are compared here. Figure 4-6 shows the comparison of the fully concentrated species model (case #2) to the dilute reference case (case #1), but now at a higher average velocity ($Re=0.3$). The three pictures demonstrate the differences in concentration and velocity fields at the time $t=7$ s. The creeping flow assumption is evaluated for this higher average velocity as well. Figure 4-7 shows this comparison of the fully concentrated cases #2 and #6.

Figure 4-8 shows the development of the effective global dispersion for case #1, including the results for simulations with a finer and a coarser grid.
Figure 4-9 shows the development of the average velocities for the different cases at position $x=0.002m$ with respect to time. The bottom picture is a magnification that better shows the implications of a concentration dependent viscosity (case #4).

Figure 4-10 shows how the different properties influence the effective longitudinal dispersion, as compared to the ideal tracer case. Both the absolute and relative deviations from case #1 are shown.

Figure 4-2 Differences in concentration fields at $t=69s$ of cases #2, #3, #4 and #5 with respect to case #1.
Figure 4-3 Differences in x-direction velocity fields at $t=69s$ of cases #2, #3, #4 and #5 with respect to case #1.
Figure 4-4 Differences in y-direction velocity fields at t=69s of cases #2, #3, #4 and #5 with respect to case #1.
Figure 4-5 Differences created by assuming creeping flow for concentrated species simulation at Re=0.03, case #6 with respect to case #2 at t=69s. Upper: relative concentration difference; middle: x-velocity difference; bottom: y-velocity difference.
Figure 4-6 Differences for higher velocity simulation at Re=0.3, case #2 with respect to case #1 at t=7s. Upper: relative concentration difference; middle: x-velocity difference; bottom: y-velocity difference. The interfering wiggles are likely to be numerical artefacts.
Figure 4.7 Differences created by assuming creeping flow for concentrated species simulation at Re=0.3, case #6 with respect to case #2 at t=7s. Upper: relative concentration difference; middle: x-velocity difference; bottom: y-velocity difference. The high-amplitude wiggles are likely to be numerical artefacts.
Figure 4-8 Influence of grid size on dispersion. Plotted with lines are the theoretical effective global and local dispersions and the limit for $t \gg \tau$. The markers are the simulation results for the base case #1 and two simulations using a coarser and a finer grid.

Figure 4-9 Average velocity development at position $x=0.002m$ as a function of time. The bottom picture shows a magnification of the upper picture.
Figure 4-10 Deviations of effective longitudinal global dispersion for cases #2, #3, #4, #5 and #6 from dispersion of case #1. Left: absolute difference as function of time; right: relative difference as function of time. The bottom pictures show a magnification of the top pictures.
Figure 4-11 Comparison of longitudinal tracer dispersion in theory and simulation results at Re=0.3. Left: the standard deviation as function of time; right: the effective dispersion as function of time.

4.2 Discussion of the results

4.2.1 Ideal tracer flow

In Figure 4-1 we see that the simulated global dispersion for ideal tracer flow follows the theoretical development over time very well. A major difference is that at the limit $t \to 0$ s, theoretically the effective dispersion should be equal to the molecular diffusion, but our simulated effective dispersion is still below that level at $t=1$ s. For $t=1$ s the simulated value is only 66.3% (4.53e-10 m$^2$/s lower) of the theoretical value, as for $t=69$ s it already reaches 98.8% (5.57e-11 m$^2$/s lower) of the theoretical dispersion. This difference is possibly caused by the fact that for small $t$ the grid cells are large compared to the total displacement. By convection, the front has moved on average over only about five grid cells in the flow direction at $t=1$ s. It is therefore difficult for the model to simulate the concentration front accurately over the relatively small amount of grid cells.

For this research we are especially interested in the differences between the different simulations at the endpoint, rather than the absolute dispersion value for a separate case. Therefore we think that this validation shows that this model can be used to investigate our objectives.

4.2.2 Influence of variable diffusion (Case #3)

The fluid flow equations are not affected by variability of the diffusivity. When looking at the comparisons of the velocity fields (Figure 4-3 and Figure 4-4) for the diffusivity influence we see a noise-like pattern of very small magnitude ($10^{-19}$). These patterns are caused by round-off errors. These errors are in the order of the machine precision and are therefore of negligible magnitude. This means that, as expected, the velocity field is not affected by the diffusion variability.

However, Figure 4-2 clearly shows that the concentration distribution has been affected by the variable diffusion. This is obviously an effect of the mass balance (2.14) that is dependent on it.

Due to ‘parabolic’ shape of the concentration front, caused by the parabolic velocity profile, a mass fraction gradient in the $y$-orientation arises on both sides of the channel midline. The diffusion in case #3 is everywhere lower than in case #1 except in the pure water ahead of the advancing tracer.
Because of this, less solute is transported to the sides of the channel which causes a concentration 'low' on the sides and 'high' in the middle.

Convection is the dominating process in the longitudinal tracer dispersion. Transverse diffusion reduces the longitudinal convective spreading. Since the diffusion in this case is decreased by the mixture, the total longitudinal dispersion is larger than in the ideal tracer case (Figure 4-10). This is in agreement with Taylor’s result on Taylor dispersion.

4.2.3 Influence of variable viscosity (Case #4)

Variability in viscosity directly affects the momentum equation. This must be reflected in the velocity fields. In the homogeneous areas far ahead of and far behind the concentration front, the Poiseuille velocity profile is maintained because the viscosity is constant in these areas. However, the pressure gradient behind the mixing area is slightly larger to correct for the change in viscosity in the momentum equation. In the transition zone the velocity profile goes through a deformation.

As we see in Figure 4-3, around the concentration front, the velocity in the x-direction decreases in the middle of the channel and increases on the sides. This ‘flattening’ (see Figure 4-12) of the x-velocity creates a ‘mass shortage’ ahead of the concentration front and a ‘mass surplus’ behind it, when compared to case #1. Consequently, the y-velocity behaviour in Figure 4-4 is to balance these changes, first towards the middle and behind the front towards the sides.

The concentration picture of Figure 4-2 adds to this story that the balancing behaviour of the y-velocity creates a lower tracer concentration ahead of the front with a maximum in the middle and a higher concentration behind it with maxima on the sides.

Effective longitudinal dispersion is slightly decreased under the influence of a variable viscosity that is equal or higher than in the ideal tracer flow case (Figure 4-10). This is a direct consequence of the flattening of the velocity profile and the associated reduction of the variance within the velocity field.

![Figure 4-12 Deformation of velocity profile due to viscosity increase by the injected liquid (500x magnified). Velocity in horizontal direction with respect to the vertical channel width.](image)

4.2.4 Influence of variable density (Case #5)

Mixing glycerol and water causes a decrease in total volume. As explained in section 2.3.2, this is incorporated in the density equation that we use. This decrease is maximum at around a mole fraction of glycerol of 0.2. Our injected mixture has a glycerol mole fraction of 0.0036. Upon mixing with pure water the glycerol mole fraction decreases, hence the total volume increases. The larger volume, or smaller density, that is created in the mixing area must be compensated through the fluid flow equations. As a result the velocity increases perpendicular to the concentration front. This is the phenomenon that is seen in Figure 4-3 and Figure 4-4.

Due to this velocity increase in the mixing area, all the fluid ahead of this area has to move faster. This effect can be visualized if we adjust the scale of the colorbar of the change in longitudinal velocity. In Figure 4-13 we see that the changes in the mixing area develop into an increased parabolic velocity ahead of the dispersive region.
Figure 4-13 Difference in x-direction velocity field of case #5 with case #1.

Figure 4-10 shows that the magnitude of the concentration difference that is created by the density variability has hardly any influence on the effective dispersion. Regarding the velocity changes, we would expect the concentration difference plot at least to have maxima on the sides of the channel. However, the picture in Figure 4-2 shows a general lower concentration than for the ideal tracer flow case. This means that the front simply has travelled less far. The cause for this can be found in Figure 4-9 which shows a severe dip in average velocity from the moment injection of the tracer starts at \( t = 0 \) s that takes up to \( t = 10 \) s to restore to its ‘normal’ value. The physical meaning of this velocity dip is unclear to us and is most likely caused by the sudden change in density.

4.2.5 Concentrated species (Case #2)

Looking at the magnitudes of the concentration difference profiles of diffusion, viscosity and density already gives an idea of the combined influence of the properties. The picture of the difference in concentration between case #2 and #1 can be expected to resemble the diffusion influence picture mostly, slightly corrected by the viscosity influence and hardly influenced by the density variability. At the top in Figure 4-2 we actually see this scenario for a large part. However, because all properties interact with each other in the governing system of equations, it is not just a simple sum of the separate contributions. Figure 4-14 shows the result when we simply sum the three separate effects of diffusivity, viscosity and density influence from Figure 4-2. The most obvious difference is that the minima on the sides and the maximum in the middle in Figure 4-14 are of equal magnitude, while Figure 4-2 (case #2) shows that the minima are of much smaller magnitude than the maximum. The shape of the profile is considerably different as well. Most important message from this comparison is that the different properties, especially diffusion and viscosity because of the magnitude of their contribution, induce interacting effects to the dispersion of the solute.

The magnitude of the colorbar range in Figure 4-14 is approximately one fifth of the range of the picture in Figure 4-2. This is mainly caused by the molar masses that were used and the different mass fraction this means for the injection concentration. Because the molar mass of glycerol is more than five times that of water (0.092/0.018=5.11), the injected mass fraction is multiplied by that factor for case #2. All the differences in concentration are multiplied by that factor because of that.
The difference in effective longitudinal dispersion with the ideal tracer case #1, shows a high offset at the start (Figure 4-10), followed by a rapid decrease and a slow increase that is in line with the other cases. This offset is caused by the influence of the molar mass of the solute. For a constant injection concentration, the injected mass fraction increases with an increased molar mass. Through the mass transport equation, this change will cause the high offset in Figure 4-10. However, because we expect a higher injection mass fraction only to scale the results, the process is unclear to us. The slow increase at larger times seems to be created mainly by concentration dependency of the diffusion. At the endpoint of our simulation, the concentrated species case shows a 0.35% or 1.6e-11 m²/s increase in channel averaged longitudinal dispersion when compared to the tracer case.

4.2.6 Creeping flow (Case #6)

Theoretically the Reynolds number of 0.03 for the flow regime under investigation dictates that creeping flow can be assumed.

Figure 4-5 shows that this assumption has some effect on the resulting concentration profile, but the magnitude is significantly smaller than the magnitudes of influence of any of the other comparisons we did in Figure 4-2. The corrections in the velocity fields seem to be opposite to the effects caused by viscosity. That suggests that creeping flow reduces the velocity profile flattening due to viscosity variability. These velocity corrections are of very small magnitude as well. Conclusively the creeping flow assumption is a valid assumption for this flow regime.

4.2.7 Increased flow velocity

Model verification

In Figure 4-11 we can clearly see how a tenfold higher flow velocity creates a dispersion that is approximately one hundred times larger. This is in agreement with the theory of section 1.2 that dictates that both the spatial variance of the solute front and the corresponding effective dispersion are quadratically dependent on the velocity. In this flow regime, the effective dispersion is of much larger magnitude than the molecular diffusion (10⁻⁷ versus 10⁻⁹), which means that convection is of much larger influence than diffusion. While for the flow regime at Re=0.03 we saw that convection and diffusion were still of comparable magnitude (Figure 4-1). The simulated dispersion follows the behaviour of the theory quite accurately.

Numerical anomalies (Case #2 and Case #6)

The upper and bottom picture of Figure 4-6 show oscillatory features that are most likely of numerical origin. A possible reason for these oscillations might be that at a grid block level physical diffusion has insufficient time to remove instabilities generated by a higher order but intrinsically unstable approximation of the convective part of the flux. An indicator for this is the so-called grid Peclet number, defined as the ratio of diffusive grid block mixing time over the convective grid block travel time, is very large:

\[ Pe_{grid} = \frac{t_{diff}/D_{mol}}{\Delta x/v_0} = \frac{\Delta x \cdot v_0}{D_{mol}} = \pm 73 \]  

(4.1)

In case the convective fluxes are approximated by a central scheme, grid Peclet numbers larger than 2 are known to produce oscillations as present in Figures 4.6 and 4.7. A more thorough analysis of this behaviour is outside the scope of this thesis.

Figure 4-7 shows even much larger oscillations compared to the effects that we investigate. Because of the higher flow velocity, the behaviour of the numerical model is clearly not good enough to simulate this flow regime accurately. Nevertheless we will still attempt to qualitatively interpret the differences that are visible.

Concentrated species flow (Case #2) compared to ideal tracer flow (Case #1)

The difference in concentration between the concentrated species model (case #2) and case #1 is not dictated by diffusion anymore, like it was for Re=0.03. The pictures in Figure 4-6 clearly show this. If
we compare Figure 4-6 to pictures of the Re=0.03 simulations at a more comparable relaxation state \((t/\tau)\) at \(t=9\) s, we see a similar difference. Where the upper picture in Figure 4-15 shows an increased concentration along the front, we now see (upper picture of Figure 4-6) a minimum in the middle and maxima on the sides. Because the influence of diffusion does not change for a larger velocity it is clear that these differences must have been created by viscosity or density variability.

Comparison of Figure 4-6 (middle) with Figure 4-3 shows that viscosity variability is mainly responsible for differences in longitudinal velocity with respect to case #1. For Re=0.03 (Figure 4-4) we observed that density variability has a slightly larger influence on the transverse velocity than viscosity variability. However, for Re=0.3, Figure 4-6 (bottom) shows a change in the order of influence between viscosity and density. We may now recognize the same peaks in different proportions. The two peaks on the right side, creating velocity to the middle of the channel, are most likely caused by viscosity changes. The left peaks, creating velocity to the sides, can be created by both density and viscosity variability.

Figure 4-6 shows that the relative differences in concentration are approximately ten times larger for Re=0.3 than for Re=0.03 (Figure 4-15). This shows that the deviation from the ideal tracer case is clearly more significant at a higher flow velocity. We expect that the increased ratio of diffusive mixing time over convective travel time causes the dispersive differences created by convective terms to become more significant while the diffusive effects remain constant.

Figure 4-15 Differences for the simulation at Re=0.03, case #2 with respect to case #1 at \(t=9\)s. Upper: relative concentration difference; middle: x-velocity difference; bottom: y-velocity difference.

For the Re=0.03 case, the maximum deformation of the front is reached after approximately 25-30 seconds (\(\pm 5 \cdot \tau_{eff}\)), when the dispersive behaviour reaches the Fickian limit (Figure 4-1). We expect this to be the same for the Re=0.3 regime. To confirm this, simulations for longer times are needed, which requires a model of a significantly longer channel. However, after that moment, the front deformation does not disappear. The differences in dispersion due to variability of the fluid properties, compared to ideal tracer flow, were mainly caused by the concentration front deformation. Therefore we think that the forming of these differences will continue in the Fickian
limit. It will be interesting for further research to see how these effects develop for significantly longer travel times at different flow velocities and injection concentrations.

**Creeping flow assumption**

If we neglect the (numerical) oscillations of Figure 4-7, we see that the differences in concentration and velocity are comparable to what we saw in the flow regime at lower Reynolds. Considering the magnitude of the changes, these differences are still very small. Therefore we think that the creeping flow is still a valid assumption for this flow regime.

**4.2.8 Grid coarsening and refinement**

Figure 4-8 shows that the grid refinement we tested is of hardly any influence to the dispersion. This suggests that the accuracy of our model cannot be increased much further by refining the grid. The results of the coarser grid simulation show that the effective global dispersion starts higher than in our base case and ends lower. Although it starts closer to the theoretical dispersion, the value at the endpoint has a larger deviation.
5. Conclusions and recommendations

In this research we investigated channel averaged longitudinal dispersion of a binary glycerol-water mixture on a micro scale. We formulated a numerical model with the software package COMSOL Multiphysics version 4.1 and postprocessed the data in MATLAB. The objectives were to investigate the contribution of the separate solute properties to the dispersion and to examine the behaviour in the dilute limit. We observed and conclude:

- The solute caused a decrease in diffusivity. Together with the deformed concentration front caused by the parabolic velocity profile this created a higher longitudinal dispersion when compared to an ideal tracer simulation. This is in agreement with theory by Taylor. Ahead of the front and in the middle of the channel a higher solute concentration was created. On the sides of the channel, behind the concentration front, the variable diffusivity created a lower solute concentration. The velocity field remains unaltered.

- A variable viscosity that increases as function of the solute concentration results in flattening of the velocity profile in the mixing zone. Flattening of the velocity profile reduces the variance within the velocity field and as a consequence the longitudinal convective dispersion.

- A solute concentration dependent density appears to have a smaller influence on the solute dispersion than diffusion and viscosity. An interesting characteristic of glycerol and water is that mixing decreases volume. After mixing of the injected mixture with pure water the volume increases. This results in an increase in the average velocity in and downstream of the mixing zone. A large dip of the average velocity at the start of solute injection caused the concentration front to not travel as far as the dilute tracer case. Longitudinal dispersion was hardly influenced.

- Analysis of the results for the concentrated species flow showed clearly the combined effects of the different properties. The change in longitudinal velocity profile is mainly caused by viscosity variability, for transverse velocity both viscosity and density are of comparable influence. For the flow regime of Re=0.03, solute concentration differences were largely determined by diffusivity variability, with significant influence by viscosity. Density was of very small influence to the concentration profile. Channel averaged longitudinal dispersion increased by only 0.35% or 1.6e-11 m^2/s when compared to an ideal tracer simulation.

- Investigation of changes in velocity and concentration when applying the creeping flow assumption for low Reynolds numbers showed that the magnitude of this adjustment is much smaller than the influence of the solute properties. Therefore it is an assumption that is valid for this flow regime and can be used in further research.

- Simulations at a ten times larger Reynolds number (Re=0.3) were done for the same geometry. The results showed that convective dispersion became heavily dominant above diffusive effects. Diffusion variability did not have much influence at this flow regime, whereas viscosity variability became very important. The variable density was still not of large influence. Relative concentration difference between a fully concentrated species case and a dilute case was of the order 0.1. This suggests that the dilute assumption is more restrictive for this flow regime. Creeping flow simulations showed that the acceleration term was still of very low influence. A drawback of these simulations is that heavy unwanted numerical oscillatory effects interfered with the results.

- Ideal tracer flow simulations were evaluated for grid refinement and coarsening. The model showed hardly any accuracy improvement for grid refinement. Coarsening of the grid created a larger dispersion in the beginning and a smaller dispersion for longer times.

This project gives rise to a lot of opportunities for further research. Increasing the injected solute concentration would allow to see how the influence of the solute properties develops for non-dilute mixtures.

Our simulations at higher Reynolds numbers were unfortunately not very accurate. An improved model can investigate the magnitude of the dilute assumption for a range of flow velocities. We
expect the dilute assumption to become much more restrictive between Re=0.03 and Re=0.3. In addition, simulations for longer times are needed, which requires a model of a significantly longer channel. Such a model is expected to show how the preserved front deformation in the Fickian limit continues to create dispersion differences due to variability of the properties, compared to an ideal tracer case.

While in this model the injected mixture decreases diffusion and increases viscosity and density, creating a model that simulates the opposite effects would make a more complete picture of the understanding of the influence of these properties.
Bibliography


Bear, Jacob. 1972. _Dynamics of fluids in porous media_. Elsevier.


## Appendix A: List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>coefficient for viscosity calculations</td>
<td>-</td>
</tr>
<tr>
<td>$b$</td>
<td>coefficient for viscosity calculations</td>
<td>-</td>
</tr>
<tr>
<td>$c$</td>
<td>total molar concentration</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$c_i$</td>
<td>molar concentration of species $i$</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$d$</td>
<td>representative size for fluid flow</td>
<td>m</td>
</tr>
<tr>
<td>$D_{\text{eff,global}}$</td>
<td>global effective dispersion</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{\text{eff,local}}$</td>
<td>local effective dispersion</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{\text{eff},\infty}$</td>
<td>effective dispersion for asymptotic times</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Fick binary diffusivity</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{ij}^*$</td>
<td>Maxwell-Stefan binary diffusivity</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{ij}^{0}$</td>
<td>$D_{ij}$ for infinitely diluted component $i$ in component $j$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{\text{mol}}$</td>
<td>molecular diffusion coefficient</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$F$</td>
<td>volume force vector</td>
<td>n/m$^3$</td>
</tr>
<tr>
<td>$H$</td>
<td>channel width</td>
<td>m</td>
</tr>
<tr>
<td>$I$</td>
<td>identity matrix</td>
<td>-</td>
</tr>
<tr>
<td>$j_i$</td>
<td>mass flux of component $i$ with respect to mass averaged velocity</td>
<td>mol/(m$^3$s)</td>
</tr>
<tr>
<td>$L_{\text{eff}}$</td>
<td>effective transverse mixing length</td>
<td>m</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass of mixture</td>
<td>kg/mol</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molar mass of species $i$</td>
<td>kg/mol</td>
</tr>
<tr>
<td>$n$</td>
<td>modal number</td>
<td>-</td>
</tr>
<tr>
<td>$n_{\text{eff}}$</td>
<td>effective modal number</td>
<td>-</td>
</tr>
<tr>
<td>$N_c$</td>
<td>total number of components in the mixture</td>
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</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>J/(mol·K)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
<td>-</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$T$</td>
<td>stress tensor</td>
<td>Pa</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>°C or K</td>
</tr>
<tr>
<td>$u_x$</td>
<td>velocity in x direction</td>
<td>m/s</td>
</tr>
<tr>
<td>$u$</td>
<td>velocity vector</td>
<td>m/s</td>
</tr>
<tr>
<td>$u_i$</td>
<td>component velocity vector</td>
<td>m/s</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$v_0$</td>
<td>mean velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$v_n$</td>
<td>$n^{th}$ Fourier mode of the velocity field</td>
<td>m/s</td>
</tr>
<tr>
<td>$x_i$</td>
<td>mole fraction of species $i$</td>
<td>-</td>
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<tr>
<td>$X_i$</td>
<td>position of species $i$</td>
<td>m</td>
</tr>
<tr>
<td>$x,y$</td>
<td>Cartesian coordinates</td>
<td>m</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>weighting factor in viscosity calculations</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>activity coefficient of species $i$</td>
<td>-</td>
</tr>
<tr>
<td>$\mu$</td>
<td>viscosity</td>
<td>Pa.s</td>
</tr>
<tr>
<td>$\mu^{(i)}$</td>
<td>viscosity of pure species $i$</td>
<td>Pa.s</td>
</tr>
<tr>
<td>$\mu_{\text{mix}}$</td>
<td>viscosity of mixture</td>
<td>Pa.s</td>
</tr>
<tr>
<td>$\mu_{c,x}$</td>
<td>mean of distribution of $c$ over $x$</td>
<td>m</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>mass of species $i$ per unit volume of mixture (mass concentration)</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho^{(i)}$</td>
<td>pure density of species $i$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>$\rho_{\text{mix}}$</td>
<td>density of mixture</td>
<td>kg/m³</td>
</tr>
<tr>
<td>$\sigma_{c,x}$</td>
<td>standard deviation of distribution of $c$ over $x$</td>
<td>m</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>standard deviation of velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$\tau$</td>
<td>deviatoric shear stress</td>
<td>Pa</td>
</tr>
<tr>
<td>$\tau_{\text{eff}}$</td>
<td>effective relaxation time</td>
<td>s</td>
</tr>
<tr>
<td>$\tau_n$</td>
<td>$n^{th}$ modal relaxation time</td>
<td>s</td>
</tr>
<tr>
<td>$\tau_{y,x}$</td>
<td>shear stress parallel to $x$ orientation</td>
<td>Pa</td>
</tr>
<tr>
<td>$\omega_i$</td>
<td>mass fraction of species $i$</td>
<td>-</td>
</tr>
</tbody>
</table>
Appendix B: Diffusion

Diffusion is the relative motion of a chemical species through a mixture. This movement can be caused by several driving mechanisms or forces. A gradient in concentration, temperature or pressure can act as driving forces as well as unequal external forces on the molecules like gravity (Bird, Stewart, and Lightfoot 2007). When charged species are involved an electric potential gradient is another driving force.

In this thesis, temperature will be regarded as constant so this will not be a driving force for diffusion. Although it must be noted that when temperature is not constant it will have a significant effect (Rutten 1992). Diffusion will increase with temperature.

Pressure gradients do not have a large influence on diffusion. With an increasing pressure the diffusivity decreases slightly because of a rising intermolecular friction. Significant effects will be seen only at gradients in the order of megapascals (Rutten 1992), therefore this will be not taken into account in this thesis.

External forces will not be regarded as well and there are no charged species involved in this research either.

Now a concentration gradient is the only driving force left to be described. Transport of chemical species due to a concentration gradient can be described using Fick’s first law of diffusion in several ways which will be shown below, as well as the confusing character of the different descriptions. We believe COMSOL uses an erroneous transport balance as will be explained closely. For completeness, diffusion derived from a thermodynamic point of view will be covered, including the relation to Fick’s law.

B.1 Fick’s diffusion

Transport of chemical species can be described in a mass balance, as explained in paragraph 2.2.1, but a molar concentration balance is equally possible, among other. These two transport balances are respectively:

\[
\frac{\partial \rho_i}{\partial t} + \nabla (\rho_i u_i) = 0 \tag{B.1}
\]

\[
\frac{\partial c_i}{\partial t} + \nabla (c_i u_i) = 0 \tag{B.2}
\]

In order to get rid of the component’s velocity like was done in paragraph 2.2.1, the transport balance need to be rewritten in terms of an average phase velocity and the difference of this velocity with the component velocity. We will do this here for the mass average velocity \( \bar{u} \) and for the molar average velocity \( \bar{u}^* \), which result in four different transport balances:

\[
\frac{\partial \rho}{\partial t} + \nabla (\rho \bar{u}) = -\nabla (\rho [u - \bar{u}]) \tag{B.3}
\]

\[
\frac{\partial \rho^*}{\partial t} + \nabla (\rho^* \bar{u}^*) = -\nabla (\rho^* [u - \bar{u}^*]) \tag{B.4}
\]

\[
\frac{\partial c}{\partial t} + \nabla (c \bar{u}) = -\nabla (c [u - \bar{u}]) \tag{B.5}
\]

\[
\frac{\partial c^*}{\partial t} + \nabla (c^* \bar{u}^*) = -\nabla (c^* [u - \bar{u}^*]) \tag{B.6}
\]

According to Fick’s first law of diffusion all the terms on the right sides of the four transport balances can be rewritten with respect to Fick’s diffusion coefficient (Bird, Stewart, and Lightfoot 2007) in Table B-1.
The most remarkable fact that arises from these derivations is that it seems like $\mathbf{j}_i = \mathbf{j}_{i,\text{dil}}^\star$ and $\mathbf{j}_i = \mathbf{j}_{i,\text{dil}}^\star$, although the difference in the average velocities is then forgotten. Consequently a mix up of fluxes and their related average velocities is easily made. It will be true however when the dilute limit holds, because then mole and mass fractions are assumed to be equal as well as the mass and molar average velocities. Hence rewriting will equate all fluxes in the dilute limit.

B.2 Remarks to COMSOL Multiphysics 4.1

Finite element simulator programme COMSOL Multiphysics version 4.1 has two modules built in that use a version of Fick’s first law of diffusion in a convection-diffusion equation. The first one is the Transport of Diluted Species Module. This module uses the following expression:

$$
\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = \nabla \cdot (D_i \nabla c_i)
$$

In this equation $c_i$ is the concentration of the diluted species. Because of the dilute assumption this equation holds for both mass and molar average velocity.

The second module COMSOL has is the Transport of Concentrated Species Module. Models that do not allow a dilute approximation can be simulated using the equation

$$
\frac{\partial (\rho \omega)}{\partial t} + \nabla \cdot (\rho \omega \mathbf{u}) = \nabla \cdot \left( \rho D_i \nabla \omega + \frac{\omega}{M_i} D_i \nabla M \right)
$$

where $\omega_i$ is the mass fraction of the species that is solved for. The explanation of this equation in the COMSOL Multiphysics User’s Guide (COMSOL AB. 2010) states that it represents mass flux with respect to mass average velocity. However, looking at the derivations in Table B-1 shows that the correct way to express this should be

$$
\frac{\partial (\rho \omega)}{\partial t} + \nabla \cdot (\rho \omega \mathbf{u}) = \nabla \cdot \left( \rho D_i \nabla \omega \right)
$$

as how we used it in our research.

Having a closer look at COMSOL’s expression (B.8) raises the suspicion that COMSOL derived molar flux with respect to molar average velocity and rewrote the equation by dividing all terms by $M_i$ and applying $\rho = cM$ which yields exactly equation (B.8).

For the Transport of Concentrated Species Module by itself it does not influence the outcome as long as the right velocity field is used. However, when this module is coupled to a flow module to provide...
the velocity field to the convection-diffusion equation, trouble could arise. The conventional set of
Navier-Stokes equations that COMSOL uses in the Laminar Flow Module clearly solves for the mass
average velocity field:
\[
\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{u}) = 0 \quad \text{(B.10)}
\]
\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \nabla \mathbf{u} = \nabla \sigma + \mathbf{F}
\]
Conclusively, the Transport of Diluted Species Module can be directly coupled to the Laminar Flow
Module through their velocity field, whereas the Transport of Concentrated Species cannot without
recalculating the mass average velocity into the molar average velocity or deleting the rightmost
term from equation (B.8).

B.3 Diffusion from a thermodynamic point of view

From a thermodynamic point of view the concentration gradient driving force for diffusion is
represented by a gradient in chemical potential \( \mu_i \text{[J/mol]} \) (Rutten 1992),
\[
\mu_i = \mu_i^0 + RT \ln (a_i) \quad \text{(B.11)}
\]
that depends on the chemical potential constant for standard conditions \( \mu_i^0 \text{[J/mol]} \), the gas constant
R[J/(mol·K)], temperature \( T \) and the activity \( a_i[-] \). Taking the gradient of the chemical potential and
applying that the activity is a function of an activity coefficient \( \gamma_i[-] \) and the mole fraction \( x_i[-] \) by
\( a_i = \gamma_i x_i \) rewrites to
\[
\nabla_{\tau,\rho} \mu_i = RT \frac{1 + \left( \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right)_{\tau,\rho}}{x_i} \nabla x_i \quad \text{(B.12)}
\]
The movement of the molecules due to the chemical potential gradient is proportional to and
counteracted by frictional force caused by the other species (Rutten 1992). To equate these two
forces, the Maxwell-Stefan (MS) diffusivity \( D_{ij} \text{[m}^2/\text{s]} \) is introduced:
\[
\frac{RT}{x_i} \left[ 1 + \left( \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right)_{\tau,\rho} \right] \nabla x_i = -\frac{RT}{x_i} \frac{x_j (u_j - u_i)}{D_{ij}} \quad \text{(B.13)}
\]
Rewriting this results in the expression for molar flux with respect to molar average velocity and
shows the relation between the Fick and MS diffusivities (Bird, Stewart, and Lightfoot 2007), (Rutten
1992):
\[
J_i^* = c_i (u_i - u^*) = -cD \gamma \left[ 1 + \left( \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right)_{\tau,\rho} \right] \nabla x_i = -cD \gamma \nabla x_i \quad \text{(B.14)}
\]
For ‘ideal’ mixtures, when the activity coefficient \( \gamma_i = 1 \), or when the activity is neglected both
diffusion constants are equal.
For binary mixtures the Fick diffusivity is the most convenient and widely used diffusivity, because it
is the easiest to determine experimentally compared to the MS diffusivity and the activity.
Appendix C: Extension of ideal tracer dispersion theory

(Berentsen 2003) showed that the exact spatial variance for an ideal diffusive tracer in a unidirectional velocity field reads:

\[ \sigma_{\text{c,s}}^2 = 2D_{\text{mol}}t + \sum_{n=1}^{\infty} v_n^2 \tau_n \left( t + \tau_n \left[ e^{-\frac{t}{\tau_n}} - 1 \right] \right) \]  \hspace{1cm} (C.1)

Here the \( n^{\text{th}} \) Fourier mode of the velocity field is defined by

\[ v_n = \frac{2}{H} \int_0^H v(y) \cos \left( \frac{2n\pi y}{H} \right) dy = - \frac{6v_0}{(n\pi)^2}, \quad n=1,2,... \]  \hspace{1cm} (C.2)

where the last equality is obtained for channel flow. The \( n^{\text{th}} \) modal relaxation time is

\[ \tau_n = \frac{1}{D_{\text{mol}}} \left( \frac{H}{2n\pi} \right)^2 \]  \hspace{1cm} (C.3)

And expresses the transverse mixing time for the \( n^{\text{th}} \) Fourier scale. From the Fourier modes of the velocity we can calculated the velocity variance:

\[ \sigma_v^2 = \frac{1}{2} \sum_{n=1}^{\infty} v_n^2 = \frac{1}{5} v_0^2 \]  \hspace{1cm} (C.4)

For verification, this result corresponds exactly to the derived variance in section 1.2 (equation (1.5)). The effective relaxation time is defined such that the approximate expression of the variance (1.4) matches the exact variance in the asymptotic Fickian limit, i.e.:

\[ \tau_{\text{eff}} = \frac{1}{4} \sum_{n=1}^{\infty} v_n^2 \tau_n = \frac{1}{D_{\text{mol}}} \left( \frac{H}{2n_{\text{eff}}\pi} \right)^2 \]  \hspace{1cm} (C.5)

By rewriting, this gives us the expression for \( n_{\text{eff}} \):

\[ n_{\text{eff}} = \sqrt{\frac{\frac{1}{2} \sum_{n=1}^{\infty} v_n^2 \tau_n}{\frac{1}{2} \sum_{n=1}^{\infty} v_n^2 \tau_n 4\pi^2 D_{\text{mol}}}} = \sqrt{\frac{1}{\tau_{\text{eff}} 4\pi^2 D_{\text{mol}}}} = 1.0314 \]  \hspace{1cm} (C.6)