

AN ABSTRACT OF THE THESIS OF

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Title: Preasymptotic Dispersion: A Theory that Includes Evolution from the Initial Condition

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Brian D. Wood

The objective of this study is to investigate the dispersion of solute matter introduced into a fully developed laminar flow in a circular capillary tube under preasymptotic regimes. For this purpose, we have used the method of volume averaging to upscale microscale balance equations for the case of diffusion-convection transport system while the initial condition was kept as a non-zero term. More precisely, any arbitrary space function can be considered as an initial condition for the system. Upon scaling, a non-conventional additional source term appears in one of the closure variables that accounts for the initial configuration. An important feature of this rigorous theory is that it is able to predict the effective transport properties from initial to asymptotic times. In this study, we compare the asymptotic solution for the effective dispersion tensor with that of calculated by Taylor-Aris diffusion-convection transport equation as a validation for the developed theory. The results for the effective dispersion tensor and the second moment of initial concentration is presented for a wide Péclet range.

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Preasymptotic Dispersion: A Theory that Includes Evolution from
the Initial Condition

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Ehsan Taghizadeh, Author

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Chapter 1: Introduction

1.1 Introduction to Taylor-Aris Dispersion in a Capillary Tube

Exploring the dispersion phenomena of two contacting miscible fluids under shear stress has been widely investigated in the literature [7–13]. Some potential applications of studying the dispersion state include, but are not limited to, (1) the distribution of tracers and drugs in the bloodstream, (2) conventional chromatography, (3) field flow fractionation or polarization chromatography (4) the transient behavior of tubular reactors, (5) pollutant transport in the atmosphere, and (6) material and thermal pollution of natural streams [14]. The wide applications of such dispersion phenomena was a strong motivation for early development of the dispersion theories. The first study on dispersion of a soluble matter injected into a circular capillary tube in which a fluid was moving was reported by G.I.Taylor [15,16] and Aris [17]. They theorized the convective-diffusive transport processes for a solute matter introduced into a fully developed laminar flow in a capillary tube. Later, some modifications on original theory and extensions for different applications (such as flow in rectilinear duct and channel) were added by others [2–4,18–25]. Starting from convective-diffusive description of the motion of a Brownian tracer particle through an abstract multidimensional phase space, Brenner [26–28] modified the classical Taylor-Aris rectilinear-flow dispersion problem which greatly increased the scope of application. Some examples include: sedimentation of non-spherical particles [10,29], surface transport phenomena [30], direct coupling effects [28], the transport of flexible bodies and chains of interacting Brownian particles [31], time-periodic non-unidirectional flows [32], effects of finite-size particles applied to chromatographic separation [33–35], and turbulent flow fields [36].

1.2 Introduction to Volume Averaging

The volume averaging technique can be used to derive continuum equations for multiphase systems. A multiphase system is one described by the simultaneous presence of several phases; each of which may have different flow characteristics. Continuum equations which are valid within one phase may not be valid within the other phases. The volume averaging method can express the multiphase system as a whole by means of spatially smoothing the continuum equations that are valid in one phase to produce constitutive equations that are valid everywhere. This method can also be used to analyze multiphase systems that are hierarchical in nature and have disparate length scales. The difference between the time and the length scales in most physics of interest is shown in Figure 1.1. There are four principle objectives at each step of volume averaging process [6].

- Derivation of the spatially smoothed equations
- Validation of spatially smoothed equations by applying the constraints
- Development of closure problem in order to estimate the effective transport coefficients
- Comparison between theory and experiment

In the method section (Section 3), we will explain the general volume averaging procedure by which governing point equations and boundary conditions can be spatially smoothed for a simple case of diffusion-convection transport equation. The process of spatially smoothing produces the governing equation for the local volume averaged quantities which includes the spatial deviation quantities. This process along with the four principle objectives mentioned earlier will be addressed in details.

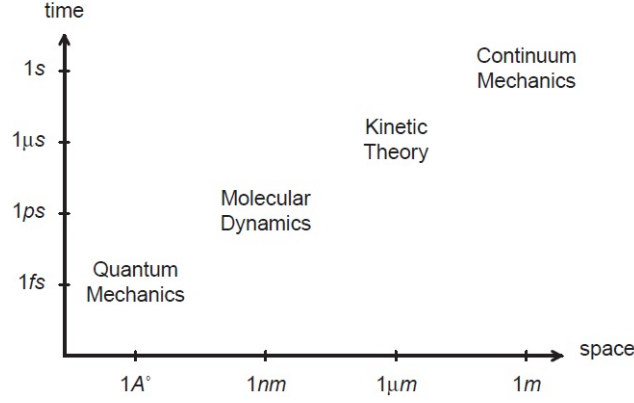


Figure 1.1: The difference between the time and the length scales for commonly used physics [1].

1.3 Introduction to Multiscale Modeling

In contrast to traditional modeling which mainly focuses on one scale, multiscale modeling is founded on modeling methods in which multiple models at different scales are simultaneously applied to characterize the complexity of systems that are hierarchical in nature. A hierarchical structure is a structure with different levels of detail associated with the different scales within the system. By simultaneously implementing models at these separate scales, one hopes to adopt an approach that shares the efficiency of the macroscopic models as well as the accuracy of the microscopic models [1]. One main assumption underlying this type of modeling is that the larger scales are at quasi-steady state compared to the microscales. Multiscale modeling aims to encompass the different scales involving physical laws at different resolutions in which the system property is critical. In such systems, a combination of the system properties at the different scales controls the overall system behavior. Oftentimes, an macroscale model which is less accurate but computationally faster to solve is combined with an microscale model to address the system behavior. The microscale model is more accurate but it usually offers too much information. Different methods (such as volume averaging) can be used to exploit the proper statistics of system

in order to eliminate such superfluous information.

1.4 Motivation

The main motivation behind this study is using the method of volume averaging to investigate the dispersion of a single species in a tube under preasymptotic regimes. The volume averaging approach can be used to upscale microscale balance equations for the case of diffusion-convection transport system. One interesting feature of the developed theory is its ability to predict the effective transport properties from initial to asymptotic times. As a result, the asymptotic solution for the effective dispersion tensor can be compared with that of calculated by Taylor-Aris diffusion-convection transport equation as a validation for the developed theory.

Chapter 2: Literature Review

Early studies of the dispersion pattern of a solute pulse introduced into a laminar or turbulent flow of a solvent in a capillary tube dates back to mid 1950s when the British fluid dynamicist Geoffrey I. Taylor published the idea that longitudinal shear stress, resulting from the parabolic velocity profile of the moving fluid, can raise the *virtual* diffusion coefficient (now usually called the *effective dispersion* coefficient) K of a species in the direction of the flow

$$K = \frac{a^2 U^2}{48 \mathcal{D}_A} \quad (2.1)$$

where U is the mean velocity of flow, a is the radius of pipe, and $\mathcal{D}_A$ is the molecular diffusion coefficient. This virtual diffusion coefficient is a combined result of the velocity gradient over the cross section of the tube and the molecular diffusion in the radial direction. More precisely, dispersion of solute matter is influenced by two separate mechanisms. A slow molecular or turbulent diffusion and a fast molecular turbulent diffusion induced by velocity shear. Taylor theoretically and experimentally explored the correlation between the longitudinal dispersion coefficient and the average concentration. He stated that the average concentration influences the virtual diffusion coefficient and the virtual diffusion coefficient determines the dispersion state. For the case of turbulent flow, the virtual diffusion coefficient was defined by

$$K = 10.1 a v_* \quad \text{or} \quad K = 7.14 a U \sqrt{\gamma} \quad (2.2)$$

where γ is the resistance coefficient and v_* is the friction velocity. Dispersion was also found to be greatly controlled by a small amount of curvature [15, 16, 37].

Aris [17] followed Taylor with the next work considered seminal for the problem of defining effective dispersion coefficients. Aris successfully eliminated the restrictions under which the Taylor analyses was valid (i.e. $\frac{4L}{A} \gg \frac{Ua}{D} \gg 6.9$, where L is the length over which observable changes in concentration happen) using the moments of solute distribution. He defined a *effective* diffusion constant (again, in more modern parlance this would be called the *effective dispersion coefficient*) as one-half of the growth rate of the variance of the solute distribution about the moving origin

$$V = \frac{1}{S} \iint_S dydz \int_{-\infty}^{+\infty} (x - Ut)^2 C(x, y, z, t) dx \quad (2.3)$$

$$\lim_{t \rightarrow \infty} \frac{1}{2} \frac{dV}{dt} = \mathcal{D} + \frac{a^2 U^2}{48 \mathcal{D}} = K \quad (2.4)$$

Here, V and K are the variance and effective diffusion constant, respectively. He also calculated that dispersion in a elliptical tube is more than that of a circular tube of the same area for a constant pressure drop.

Based upon Taylor and Aris work, which provide it with a robust scheme for the study of dispersion phenomena in convection-diffusion transport process [38], other researchers extended general Taylor dispersion theory for different applications. As such efforts, Gill and Sankarasubramanian [2] showed for the steady state, fully developed, laminar flow condition, the dispersion model used by Taylor (shown below) can be valid within any time if the dispersion coefficient also depends on time.

$$\frac{\partial C}{\partial t} + U_m \frac{\partial C}{\partial x} = k \frac{\partial^2 C}{\partial x^2} \quad (2.5)$$

where t is time, C is the area average concentration, U_m is the average velocity, x is the axial coordinate, and k is the dispersion coefficient which does not depend on x and t , but rather depends on physical parameters. For this heat equation type formula (Equation 2.5),

the center of mass of the concentration x_g and the variance σ^2 are given by

$$x_g = Ut \quad (2.6)$$

$$\sigma^2 = 2Kt \quad (2.7)$$

If one chooses units of concentration (i.e. $\int_{-\infty}^{+\infty} C dx = 1$), one possible solution for Equation 2.5 would be the Gaussian curve

$$C(x, t) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x - x_p)^2}{2\sigma^2}\right) \quad (2.8)$$

Gill and Sankarasubramanian [3] also demonstrated that an exact solution for unsteady-state convection diffusion transport equation can be obtained from first principles for the convective coefficient $K_1(\tau)$, the apparent diffusion coefficient $K_2(\tau)$ and an infinite set of time-dependent coefficient $K_i(\tau)$ for the case of non-uniform initial distribution of solute such as one depicted in Figure 2.1. Their work was able to address a larger class of physical problems.

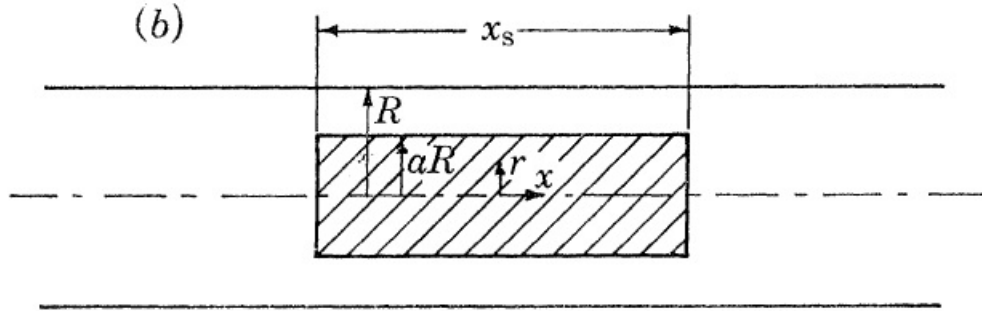


Figure 2.1: A schematic system that Gill et al. investigated in his research with uniform initial distribution [2], and with non-uniform initial distribution. Courtesy of [3].

In a later work, Gill and Sankarasubramanian [39] extended their theory of miscible dispersion to the case of system with interface transport. They specifically studied the

dispersion of a non-uniform initial distribution in time-variable isothermal laminar flow in a tube with a first-order rate process at the tube wall. As a consequence of interface transport phenomenon, a time-dependent ‘exchange coefficient’ depending on the rate of interface transport and the initial solute distribution, but with no dependency on velocity distribution, was explicitly derived. They developed only asymptotic large-time evaluations due to the complex nature of the problem. Their research provided more insight to several heat and mass transfer system such as (1) open tube chromatography (2) thermal pollution in natural streams, (3) unsteady heat transfer in double pipe heat exchangers, and (4) tubular flow reactors with heterogeneous catalysis.

Chatwin [4] studied the dispersion, as a result of diffusion and convection, of a passive solute in a straight pipe of uniform cross-section. He developed an asymptomatic series (Equation 2.9) for the concentration distribution based upon the assumption that diffusion of solute follows Fick’s law. The first term in the series contains a Gaussian function and the next terms involve asymmetries in the system as shown in Figure 2.2. For the case of $\frac{D \cdot t}{a^2} > 0.2$ (D is molecular diffusion coefficient), three terms of the series can acceptably explain the distribution of concentration in Poiseuille flow in a pipe of radius a . In the case of a turbulent open channel, there was an excellent match between the model predictions and numerical data provided by Sayre [40].

$$\frac{\partial C}{\partial t} + U_m \frac{\partial C}{\partial x} = K_2 \frac{\partial^2 C}{\partial x^2} + K_3 \frac{\partial^3 C}{\partial x^3} + K_4 \frac{\partial^4 C}{\partial x^4} + \dots \quad (2.9)$$

Later on, Chatwin [18] addressed whether the general solution of Equation 2.5 better described the observed non-Gaussian concentration profile, than Equation 2.8. For preasymptotic time, Equation 2.5 is possibly more accurate. For asymptotic times, however, Equation 2.5 is not better since all terms of order greater than two are not given by the general solution for the Equation 2.5, according to the author.

Doshi et al. [5] investigated the effect of side walls on the dispersion process for open

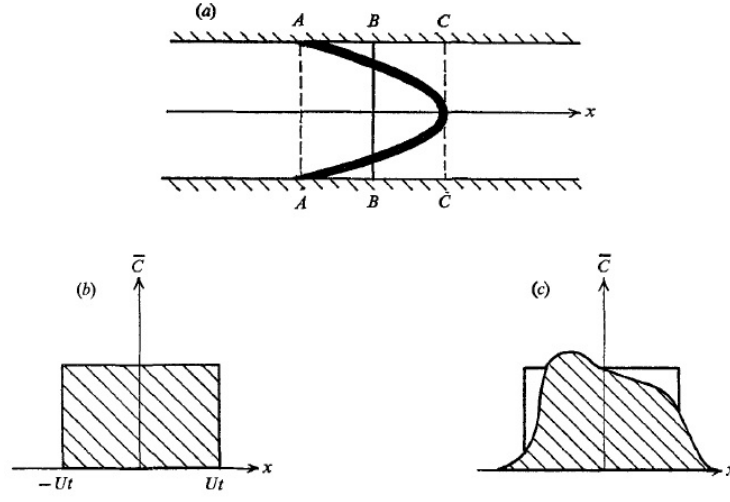


Figure 2.2: Initial dispersion state of solute in Poiseuille flow, showing the asymmetry caused by diffusion and interaction with the pipe wall. Courtesy of [4].

and closed rectangular ducts (as shown in Figure 2.3). For the laminar flow in a rectangular cross-section channel, the Taylor longitudinal diffusivity is about $8D_0$ (where D_0 is longitudinal diffusivity when all variations across the channel are neglected) as aspect ratio $\frac{b}{h}$ reaches infinity.

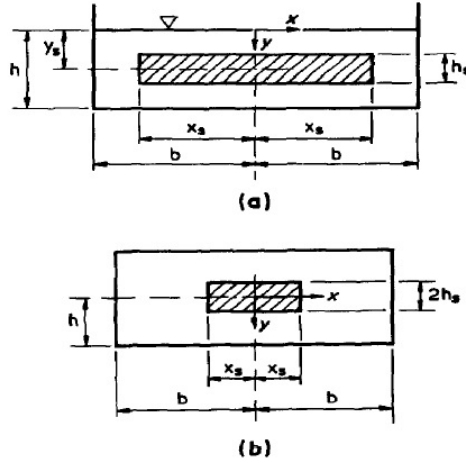


Figure 2.3: Examined geometries in Doshi et al. work. Cross section perpendicular to the flow direction for (a) open channels and for (b) closed duct. Courtesy of [5].

According to Chatwin and Sullivan [19], who analyzed the Taylor's longitudinal diffusivity in the case of turbulent flow in a flat-bottomed channel of large aspect ratio, the time necessary for the Taylor analysis to be valid in a channel with large aspect ratio should be of order of $\frac{a^2}{k}$ for laminar flow and of order $\frac{a^2}{bw_*}$ for turbulent flow; where a is channel width, b is channel height, k is molecular diffusivity, and w_* is shear viscosity. In both laminar and turbulent flow, the time must satisfy

$$\frac{Kt}{b^2} = \mathbf{O} \left(\frac{a^2}{b^2} \right) \quad (2.10)$$

in which

$$K \propto \frac{W^2 L^2}{K} \quad (2.11)$$

where W is velocity, L is the characteristic length of the cross-section, and k is a measure of the intensity of the lateral mixing of solute.

Taylor showed that after a sufficient amount of time, the longitudinal dispersion of a solute is governed by a time-constant factor in the convection-diffusion equation, making it difficult to use Taylor theory in many practical applications since there might not be sufficient time available for this asymptotic state to be reached. Smith [20] addressed this problem by introducing a delay-diffusion equation

$$\frac{\partial \bar{C}}{\partial t} + \bar{U} \frac{\partial \bar{C}}{\partial x} - \bar{k} \frac{\partial^2 \bar{C}}{\partial x^2} - \int_0^\infty \mathcal{D} \frac{\partial^2 \bar{C}}{\partial x^2} \left(x - \int_0^\tau \tilde{u}(\tau') d\tau', t - \tau \right) d\tau = \bar{q}(x, t) \quad (2.12)$$

in which $\bar{q}$ is the source strength, $\bar{U}$ is the bulk velocity, $\tilde{u}$ is a transport velocity for the free decay of cross-stream concentration variations.

Chapter 3: Method

3.1 Volume Averaging

In our analysis, we use volume averaging to coarse-grain (or upscale or aggregate) the system information. One fundamental assumption of the volume averaging technique is that the system can be characterized by more than one length scale, that is to say, volumes that are sufficiently large compared to the microscale characteristic length exist within the system [6]. For any such volume, the intrinsic volume average for a scalar field property ψ_γ is defined over the region $V(\mathbf{x})$ by

$$\langle \psi_\gamma \rangle^\gamma|_{(\mathbf{x},t)} = \int_{\mathbf{r} \in V(\mathbf{x})} w(\mathbf{x} - \mathbf{r}) \psi_\gamma(\mathbf{r}, t) dV(\mathbf{r}) \quad (3.1)$$

where w is a weighting function that is compacted in V . This definition associate every point in space with an averaging volume that is invariant with respect to time and space [6]. For a n -phase system, the averaging volume can be expressed as

$$V = \sum_{i=1}^n V_i(x) \quad (3.2)$$

where $V_i(x)$ is the volume of the i -phase contained within the averaging volume and n is the total number of phases. A representation of macroscale region and averaging volume for a solid-liquid two-phase system is illustrated in Figure 3.1. Following this notation for a two-phase system, the intrinsic average concentration and the intrinsic average velocity

are defined by

$$\langle c_{A\gamma} \rangle^\gamma = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} c_{A\gamma} dV \quad (3.3)$$

$$\langle \mathbf{v}_\gamma \rangle^\gamma = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} \mathbf{v}_\gamma dV \quad (3.4)$$

in which $V_\gamma(\mathbf{x})$ represents the volume of the γ phase contained within the averaging volume.

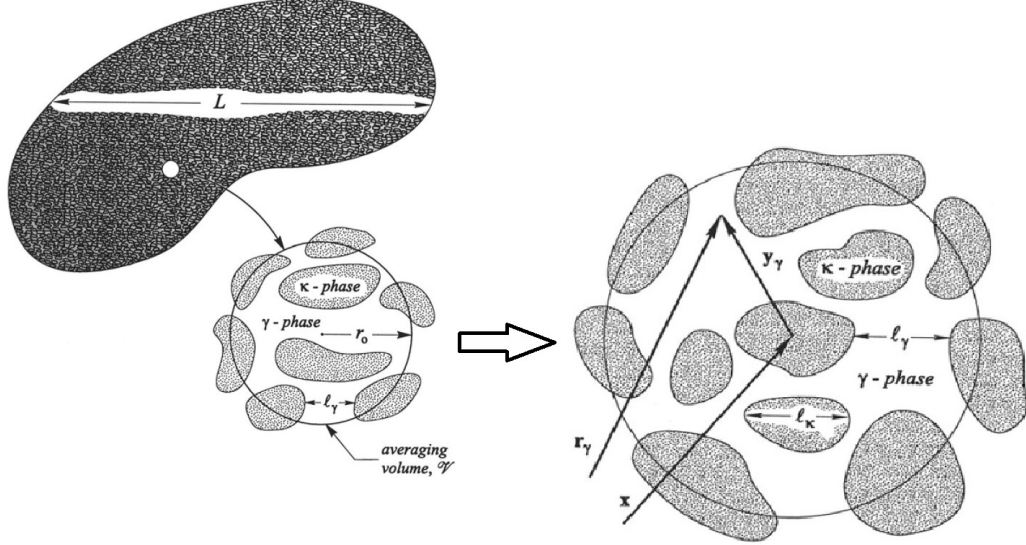


Figure 3.1: Macroscopic region and averaging volume for a two-phase system. The γ - and the κ -phase represent the liquid and the solid phase, respectively. r_0 is the characteristic length for averaging volume, l_γ is the characteristic length for liquid phase and l_κ is the characteristic length for solid phase. The position vector $\mathbf{r}_\gamma$ is used to locate any point in the γ -phase. The position vector $\mathbf{x}$ locates the centroid of the averaging volume. The relative position vector $\mathbf{y}_\gamma$ shows the location of points in the γ -phase relative to the centroid of averaging volume. Courtesy of [6].

3.2 Spatial Averaging Theorem

In the process of volume averaging one may encounter the interchanging of differentiation and integration in order to express the flux in terms of volume averaged quantities. This

can be achieved by means of the spatial averaging theorem. For a scalar field property ψ_γ and a vector field property Ψ_γ defined over the region $V(\mathbf{x})$, the spatial averaging theorem is given by

$$\langle \nabla \psi_\gamma \rangle^\gamma = \nabla \langle \psi_\gamma \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \psi_\gamma dA \quad (3.5)$$

$$\langle \nabla \cdot \Psi_\gamma \rangle^\gamma = \nabla \cdot \langle \Psi_\gamma \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot \Psi_\gamma dA \quad (3.6)$$

in which $A_{\gamma\kappa}$ defines the area of the interface between two phases [41–43]. The latter is the vector form of the spatial averaging theorem. We will repeatedly use the spatial averaging theorem for the purpose of direct interchanging differentiation and integration along with the general transport theorem which will be presented in the next section.

3.3 General Transport Theorem

General transport theorem (or Leibniz-Reynolds transport theorem) [44] is a three-dimensional representation of the Leibniz rule for interchanging differentiation and integration which can be expressed as

$$\frac{d}{dt} \int_{\Omega(t)} \psi_\gamma dV = \int_{\Omega(t)} \frac{\partial \psi_\gamma}{\partial t} dV + \int_{\partial\Omega(t)} \psi_\gamma (\mathbf{w} \cdot \mathbf{n}) dA \quad (3.7)$$

in which $\Omega(t)$ is an arbitrary, time-dependent region and $\partial\Omega(t)$ is the bounding surface of this region. The outward-pointing unit normal vector and the speed of displacement of the bounding surface is given by $\mathbf{n}$ and $\mathbf{w} \cdot \mathbf{n}$, respectively. It is clear that this formulation is very general and can be applied to a variety of applications. We will use the general transport equation for interchange of differentiation and integration for the accumulation term. With these theorems in place, we have the necessary elements to begin the volume

averaging process for the Taylor-Aris boundary value problem.

3.4 Averaging Theory for Taylor-Aris Dispersion

We examine the simplest convective transport system; a passive (i.e., no adsorption or reaction at the fluid-wall boundary or the fluid-porous interface) convection and diffusion multiscale system. We are particularly interested in distribution state of a single species in a single fluid phase inside a capillary tube. The cylindrical geometry has been chosen for this investigation since Taylor-Aris dispersion theory was first adopted for the cylindrical coordinate system. Note, the volume averaging process for the one-phase system discussed in this study can be extended for a homogeneous porous medium (i.e. a coarsened pore scale in such a way that internal boundaries are not needed to be resolved). We consider the transport phenomena of a single species A which is being carried out by the fluid phase, identified as the γ -phase, in a tube using the method of volume averaging.

3.5 Representative Elementary Volume for Taylor-Aris Dispersion Problem

For our case, the representative elementary volume (or averaging volume) within which the change in system properties can be well evaluated by a statistical description is the differential slice of the tube as shown in Figure 3.2. A further adoption of the intrinsic average concentration formulation (Equation 3.3) for the presented REV leads to

$$\langle c_{A\gamma} \rangle^\gamma = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} c_{A\gamma} d(Ah) = \frac{1}{\mathcal{A}_{\gamma e}} \int_{\mathcal{A}_{\gamma e}} c_{A\gamma} dA = \langle c_{A\gamma} \rangle_{\gamma e} \quad (3.8)$$

One might assume that the intrinsic average concentration, $\langle c_{A\gamma} \rangle^\gamma$, can be represented as an area average concentration, $\langle c_{A\gamma} \rangle_{\gamma e}$ (i.e the average concentration over a cross section

along the longitudinal axis of tube) for this specific REV. Although they are essentially the same, we use volume averaging notation for our averaging process presented in this study.

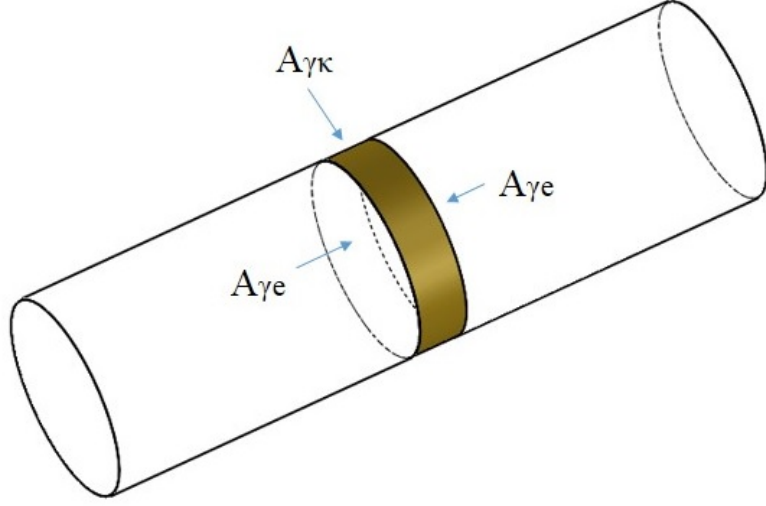


Figure 3.2: A tube with its representative elementary volume. We are interested in studying diffusion-convection transport phenomenon inside the tube. $\mathcal{A}_{\gamma\kappa}$ represents the entire interface area between the γ -phase and the tube wall contained within REV and $\mathcal{A}_{\gamma e}$ represents the area of the entrance and the exit of the γ -phase passing through the REV.

3.6 Length-Scale Constraints for Taylor-Aris Multiscale System

Before starting the volume average process for Taylor-Aris dispersion problem, it is important to point out that one may need to use the conventional length scale constraint in order to neglect some high order terms that frequently appear in the volume averaging process (such as the average or the average of an averaged scalar or vector field)

$$l_\gamma \ll r_0 \ll L \quad (3.9)$$

in which l_γ is the characteristic length for γ phase, r_0 is the characteristic length for averaging volume and L is the characteristic length for macroscopic region (these three length scales are compared in Figure 3.1). There are three length scales associated with Taylor-Aris dispersion multiscale system, similar to conventional length scale, but they have slightly different relations. For Taylor-Aris problem, the size of the macroscale length (L) is described as at least the size of the initial condition (i.e. how wide the initial condition is spread out along the tube length) while the characteristic length of γ phase (l_γ or microscale length) is of order of tube radius. The radius of the tube (r_0) represents the REV length scale leading to

$$l_\gamma \sim r_0 \ll L \quad (3.10)$$

In other words, the REV characteristic length and microscale characteristic length happened to be in same order for Taylor-Aris multiscale system in a tube. We will use this length scale constraint for the development of the averaged equation and the closure problems.

3.7 Microscale Balance Equations

We examine a single fluid phase system in a tube such as one illustrated in Figure 3.2. This system is essentially the same system that was studied originally by Taylor [15] and Aris [17]. The governing equation, the boundary conditions, and the initial condition for this multiscale system are given by

$$\frac{\partial c_{A\gamma}}{\partial t} + \nabla \cdot (c_{A\gamma} \mathbf{v}_\gamma) = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) \quad (3.11)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.12)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) = F_A(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.13)$$

$$\text{I.C.1} \quad c_{A\gamma}(\mathbf{x}, 0) = \varphi_A(\mathbf{x}) \quad \text{at } t=0 \quad (3.14)$$

in which $\mathcal{A}_{\gamma\kappa}$ represents the entire interface area between the γ -phase and the tube wall contained within the averaging volume, while $\mathcal{A}_{\gamma e}$ identifies the area of the entrance and the exit of the γ -phase passing through the averaging volume. In Equation 3.11, $c_{A\gamma}$, $\mathbf{v}_\gamma$, and $\mathbf{D}_{A\gamma}$ are concentration of species A in γ phase, fluid velocity, and mixture diffusivity of species A , respectively. One assumption that has been implemented in the diffusive mass flux equation is that the mole fraction of species A is small enough (i.e., $x_A \ll 1$). Moreover, the following reasonable assumptions has been made in order to simplify the volume averaged process: (1) the fluid flow is incompressible and steady; (2) the velocity field is symmetric cross-sectional fluid pressure at the ends of the tube is uniform, which leads to a symmetric velocity field; and, (3) the concentration field is symmetric in the angular direction, so that $\partial c_A / \partial \theta = 0$. Furthermore, it should be clear that this equation set (Equations 3.11-3.14) serves as a simple convection-diffusion system with an impermeable wall boundary condition (no flux of species A can pass through the wall), a known flux for species A along the entrance and the exit of the tube, and an arbitrary initial configuration for species A distributed inside the tube. Although the second boundary condition implies a flux at the external boundaries, keeping this term as non-zero condition adds significant complexity to the analysis without adding much in the way of additional insight. Therefore, one can treat this boundary condition as zero-flux boundary condition for a sufficiently long tube in such a way that no flux of initial configuration can exit the external boundaries.

It is also important to note that the initial condition ($\varphi_A(\mathbf{x})$) can have any arbitrary function of coordinate system and this will not affect the volume averaging process. We

will keep this initial configuration as a non-zero term, in contrast to the second boundary condition, in the volume average process.

3.8 Averaging Process (Spatial Smoothing)

The result of the spatial smoothing process is obtained by developing the intrinsic volume average (Equation 3.1) for the microscale balance equation (Equation 3.11) as follows

$$\frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} + \langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla \tilde{c}_{A\gamma} \rangle^\gamma = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) \quad (3.15)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.16)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) = \langle F_A(\mathbf{x}, t) \rangle^\gamma \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.17)$$

$$\text{I.C.1} \quad \langle c_{A\gamma} \rangle^\gamma|_{(\mathbf{x},0)} = \langle \varphi_A \rangle^\gamma|_{\mathbf{x}} \quad \text{at } t=0 \quad (3.18)$$

Here we have used the spatial decompositions for development of the balance equations

$$c_{A\gamma}(\mathbf{x}, t) = \langle c_{A\gamma} \rangle^\gamma(\mathbf{x}, t) + \tilde{c}_{A\gamma}(\mathbf{x}, t) \quad (3.19)$$

$$\mathbf{v}_\gamma(\mathbf{x}) = \langle \mathbf{v}_\gamma \rangle^\gamma(\mathbf{x}) + \tilde{\mathbf{v}}_\gamma(\mathbf{x}) \quad (3.20)$$

Here, $\tilde{c}_{A\gamma}$ and $\tilde{\mathbf{v}}_\gamma$ are the spatial deviation concentration and spatial deviation velocity. $\tilde{c}_{A\gamma}$ and $\tilde{\mathbf{v}}_\gamma$ have different length scales compared with the counterpart terms (i.e. $\langle c_{A\gamma} \rangle$ and $\langle \mathbf{v}_\gamma \rangle$). These decompositions of length scale defined in Equation 3.19 and Equation 3.20 cause the average quantities to be subjected to major changes over only large scale length (L) and the spatial deviation quantities to vary over small length scale (l). Therefore, average quantities (i.e. $\langle c_{A\gamma} \rangle$ and $\langle \mathbf{v}_\gamma \rangle$) are of the order of the macroscale length and spatial deviation quantities (i.e. $\tilde{c}_{A\gamma}$ and $\tilde{\mathbf{v}}_\gamma$) are of the order of the microscale length. Several

steps have been taken to derive Equations 3.15-3.18. We try to explain these steps in the following sections.

Using the general transport theorem (Equation 3.7) along with the fact that the volume of REV (V_γ) does not change with time justifies the direct interchange of the gradient and the averaging operations within the accumulation term. So, the accumulation term can be rewritten as

$$\left\langle \frac{\partial c_{A\gamma}}{\partial t} \right\rangle^\gamma = \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} \quad (3.21)$$

One can develop the averaging theorem for the gradient of the local concentration as

$$\langle \nabla c_{A\gamma} \rangle^\gamma = \nabla \langle c_{A\gamma} \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} dA \quad (3.22)$$

Turning our attention to the integral part of the Equation 3.22, it is evident that for the radial-symmetry initial condition (Section 3.7, assumption #3) the concentration of the species A ($c_{A\gamma}$) is independent of θ -direction for any specified r such as $r = R$

$$c_{A\gamma}(r, \theta, z, t)|_{r=R} = c_{A\gamma}(z, t) \quad (3.23)$$

Moreover, one can show that the Equation 3.25 is valid for any closed, piecewise smooth surface using the divergence theorem

$$\text{divergence theorem} \quad \int_{\partial V} \phi n_i dA = \int_V \frac{\partial \phi}{\partial x_i} dV \quad (3.24)$$

$$I_i = \int_{\partial V} n_i dA = \int_V \frac{\partial 1}{\partial x_i} dV = 0 \quad (3.25)$$

where V is a volume in three dimensional space bounded by a single continuous surface ∂V with outward unit normal vector $\vec{n}$ and ψ is a scalar function of the coordinate x_i within

the volume. Rewriting the integral part of Equation 3.22

$$\frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} dA = \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} c_{A\gamma}(z, t) n_i dA = \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} c_{A\gamma}(z, t) n_i d(Rd\theta dz) \quad (3.26)$$

At this point, it can be easily understood that for any specific value of z and t

$$\frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} c_{A\gamma}(z, t) n_i dA = 0 \quad (3.27)$$

This is illustrated in Figure 3.3. Because of the radial-symmetry of the initial configuration the circles, which are closed surfaces, represent a constant concentration for any specific z at any time. Therefore, one can conclude that the spatial averaging theorem allows the direct interchange of the gradient and averaging operations for systems where the initial condition is radially-symmetric. This can be expressed as

$$\langle \nabla c_{A\gamma} \rangle^\gamma = \nabla \langle c_{A\gamma} \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} dA = \nabla \langle c_{A\gamma} \rangle^\gamma \quad (3.28)$$

For the non-symmetry initial condition (which is beyond the scope of this thesis), one may need to calculate the integral terms appearing in the averaged equation for concentration as

$$\langle \nabla c_{A\gamma} \rangle^\gamma = \nabla \langle c_{A\gamma} \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \langle c_{A\gamma} \rangle^\gamma dA + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} dA \quad (3.29)$$

This is an active area of research. Our main focus for this thesis will remain on systems where the initial configuration is radially-symmetric. Now, we try to find a spatially smoothed equation for the diffusive transport term (the term on the right-hand-side of Equation 3.11) in order to substitute it in the microscale balance equation. For this purpose, we apply the

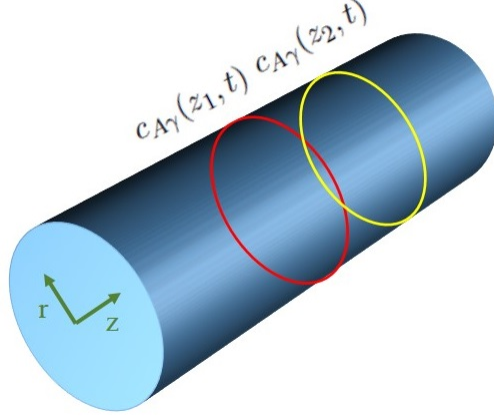


Figure 3.3: The colored circles represent a constant concentration and velocity for any specific z at any time since the initial concentration and local velocity profiles are radially-symmetric. This essentially means local concentration and velocity are independent of the θ -direction.

spatial averaging theorem on this term as

$$\langle \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) \rangle^\gamma = \nabla \cdot \langle \mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma} \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) dA \quad (3.30)$$

Recalling the first boundary condition of the microscale balance equation

$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.31)$$

the last term on the right-hand-side of Equation 3.30 is identically zero. Under this circumstances, the diffusive transport term (Equation 3.30) is reduced to

$$\langle \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma}) \rangle^\gamma = \nabla \cdot \langle \mathbf{D}_{A\gamma} \cdot \nabla c_{A\gamma} \rangle^\gamma \quad (3.32)$$

Here, we have made the assumption that the variations of molecular diffusivity ($\mathbf{D}_{A\gamma}$) within the averaging volume can be ignored since it gradually varies with pressure, temperature, and concentration [45].

Turning our attention to the convection term, we implement the fact that the velocity field is solenoidal inside the tube so that the continuity equation takes the form $\nabla \cdot \mathbf{v}_\gamma = 0$, which immediately leads to

$$\nabla \cdot \langle \mathbf{v}_\gamma \rangle^\gamma = 0 \quad (3.33)$$

$$\nabla \cdot \tilde{\mathbf{v}}_\gamma = 0 \quad (3.34)$$

Applying the spatial averaging theorem on the convective term gives us the volume averaged form for the convective term as

$$\langle \nabla \cdot (c_{A\gamma} \mathbf{v}_\gamma) \rangle^\gamma = \nabla \cdot \langle c_{A\gamma} \mathbf{v}_\gamma \rangle^\gamma + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot (c_{A\gamma} \mathbf{v}_\gamma) dA \quad (3.35)$$

The second term on the right-hand-side of Equation 3.35 is identically zero since the $A_{\gamma\kappa}$ is treated as a rigid, impermeable wall as

$$\mathbf{n}_{\gamma\kappa} \cdot \mathbf{v}_\gamma = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.36)$$

Therefore, Equation 3.35 simplifies to

$$\langle \nabla \cdot (c_{A\gamma} \mathbf{v}_\gamma) \rangle^\gamma = \nabla \cdot \langle c_{A\gamma} \mathbf{v}_\gamma \rangle^\gamma \quad (3.37)$$

It is possible to remove volume averaged quantities from within the averaging volume in order to simplify the right-hand-side of Equation 3.37 after expanding this term based on spatial deviation concentration (Equation 3.19) and spatial deviation velocity (Equation 3.20) as

$$\langle c_{A\gamma} \mathbf{v}_\gamma \rangle^\gamma = \langle c_{A\gamma} \rangle^\gamma \langle \mathbf{v}_\gamma \rangle^\gamma + \langle c_{A\gamma} \rangle^\gamma \langle \tilde{\mathbf{v}}_\gamma \rangle^\gamma + \langle \tilde{c}_{A\gamma} \rangle^\gamma \langle \mathbf{v}_\gamma \rangle^\gamma + \langle \tilde{c}_{A\gamma} \rangle^\gamma \langle \tilde{\mathbf{v}}_\gamma \rangle^\gamma \quad (3.38)$$

This is justified by the length-scale constraint $\ell_\gamma \ll L$ (more details can be found in Ap-

pendix A). We can also make the explicit assumption that $\langle \tilde{c}_{A\gamma} \rangle^\gamma \ll \langle c_{A\gamma} \rangle^\gamma$ so that variations of volume averaged quantities may be neglected in the average balance as follows

$$\langle c_{A\gamma} \mathbf{v}_\gamma \rangle^\gamma = \langle c_{A\gamma} \rangle^\gamma \langle \mathbf{v}_\gamma \rangle^\gamma + \langle \tilde{c}_{A\gamma} \rangle^\gamma \langle \tilde{\mathbf{v}}_\gamma \rangle^\gamma \quad (3.39)$$

Expanding the two terms on the right-hand-side of above formulation using Equations 3.33 and 3.34 leads to

$$\nabla \cdot (\langle \mathbf{v}_\gamma \rangle^\gamma \langle c_{A\gamma} \rangle^\gamma) = \langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \quad (3.40)$$

$$\nabla \cdot \langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \rangle^\gamma = \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla \tilde{c}_{A\gamma} \rangle^\gamma \quad (3.41)$$

The volume averaged convective transport term can be written as its final form as

$$\nabla \cdot (c_{A\gamma} \mathbf{v}_\gamma) = \langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla \tilde{c}_{A\gamma} \rangle^\gamma \quad (3.42)$$

Substitution of averaged accumulation, convective, and dispersive transport terms back into the microscope balance equation (Equation 3.11) gives us the volume averaged convective-diffusion transport equation (Equation 3.15) as

$$\underbrace{\frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} + \underbrace{\langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma}_{\text{convective transport}} + \underbrace{\langle \tilde{\mathbf{v}}_\gamma \cdot \nabla \tilde{c}_{A\gamma} \rangle^\gamma}_{\text{dispersive transport}} = \underbrace{\nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma)}_{\text{diffusive transport}} \quad (3.43)$$

One may wonder why the B.C.1 (Equation 3.16) and the B.C.2 (Equation 3.17) have different forms after averaging process. This can be justified by the fact that developing the volume averaged transport equation for the wall (Equation 3.16) does not have any physical interpretation, even though it possible to derive a mathematical expression for it, as the integral domain is a surface rather than a volume. Therefore, B.C.1 is a simple substitution of the spatial deviation concentration (Equation 3.19) into Equation 3.16. We have also developed volume averaged flux at the external boundaries (i.e. $\langle F_A(\mathbf{x}, t) \rangle^\gamma$) and volume

averaged initial condition (i.e $\langle \varphi_A(\mathbf{x}) \rangle^\gamma$) as

$$\langle F_A(\mathbf{x}, t) \rangle^\gamma = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} F_A(\mathbf{x}, t) dV \quad (3.44)$$

$$\langle \varphi_A(\mathbf{x}) \rangle^\gamma = \frac{1}{V_\gamma(\mathbf{x})} \int_{V_\gamma(\mathbf{x})} \varphi_A(\mathbf{x}, t) dV \quad (3.45)$$

3.9 Deviation Equations

To derive the boundary value problem for spatial deviation concentration, one can subtract the original average equations (Equations 3.15-3.18) from the point equations (Equations 3.11-3.14) to obtain

$$\begin{aligned} & \underbrace{\frac{\partial \tilde{c}_{A\gamma}}{\partial t}}_{\text{accumulation}} + \underbrace{\mathbf{v}_\gamma \cdot \nabla \tilde{c}_{A\gamma}}_{\text{convection}} + \underbrace{\tilde{\mathbf{v}}_\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma}_{\text{local convective source}} - \underbrace{\nabla \cdot \langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \rangle^\gamma}_{\text{non-local convection}} = \\ & + \underbrace{\nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma})}_{\text{diffusion}} \end{aligned} \quad (3.46)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma)}_{\text{source}} \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.47)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = \underbrace{\tilde{F}_A(\mathbf{x}, t)}_{\text{source}} \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.48)$$

$$\text{I.C.1} \quad \tilde{c}_{A\gamma}(\mathbf{x}, 0) = \underbrace{\tilde{\varphi}_A(\mathbf{x})}_{\text{source}} \quad \text{at } t=0 \quad (3.49)$$

Here, we have adopted the following notation

$$\tilde{F}_A(\mathbf{x}, t) = F_A(\mathbf{x}, t) - \langle F_A(\mathbf{x}, t) \rangle^\gamma \quad (3.50)$$

$$\tilde{\varphi}_A(\mathbf{x}) = \varphi_A(\mathbf{x}) - \langle \varphi_A(\mathbf{x}) \rangle^\gamma \quad (3.51)$$

Turning our attention on $\nabla \cdot \langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \rangle^\gamma$ term, it is clear that the value of the $\tilde{c}_{A\gamma}$ is evaluated throughout the entire REV rather than at the centroid of the REV and, as a result, it is a *non-local* term in nature. More simplification of the non-local convection term will be explained in the next section.

3.10 Simplification of the Closure Problems

The closure problems above are linear but nonlocal (in space) convection-diffusion problems. The solutions and properties of such problems is an active area of research. However, it can be shown that solutions exist, that the solutions depend continuously on the initial conditions, and that the nonlocal equations converge to the local ones as the nonlocal terms become small enough [46–49]. Much less information is available about the properties of even linear nonlocal equations in the presence of boundaries, although they are frequently solved numerically [50]. Fortunately, for this particular set of equations, we can make some very compelling arguments indicating that the integral terms are negligible for the purposes of the closure problems. This yields the following set of *localized* closure problem.

$$\frac{\partial \tilde{c}_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \tilde{c}_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = -\tilde{\mathbf{v}}_\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \quad (3.52)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.53)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma}) = \tilde{F}_A(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.54)$$

$$\text{I.C.1} \quad \tilde{c}_{A\gamma}(\mathbf{x}, 0) = \tilde{\varphi}_A(\mathbf{x}) \quad \text{at } t=0 \quad (3.55)$$

3.11 Integral Solutions to the Closure Problems

The simplified closure problem above is a local and linear parabolic equation. The solution to the problem for species A is a classical solution that can be represented in integral form by Polyanin [51] as

$$\begin{aligned}
 \tilde{c}_{A\gamma}(\mathbf{x}, t) = & \underbrace{\int_{\tau=0}^{\tau=t} \int_{\mathbf{y} \in \mathcal{V}_\gamma(\mathbf{x})} -G_A(\mathbf{x}, \mathbf{y}, t, \tau) \tilde{\mathbf{v}}_\gamma(\mathbf{y}) \cdot \nabla_{\mathbf{y}} \langle c_{A\gamma} \rangle^\gamma|_{(\mathbf{y}, t)} dV(\mathbf{y}) d\tau}_{\text{volume source}} \\
 & + \underbrace{\int_{\tau=0}^{\tau=t} \int_{\mathbf{y} \in \mathcal{A}_{\gamma e}(\mathbf{x})} -G_A(\mathbf{x}, \mathbf{y}, t, \tau) \tilde{F}_A(\mathbf{y}, t) dA(\mathbf{y}) d\tau}_{\text{boundary source}} \\
 & + \underbrace{\int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} G_A(\mathbf{x}, \mathbf{y}, t, 0) \varphi_A(\mathbf{y}) dV(\mathbf{y})}_{\text{initial condition source}}
 \end{aligned} \tag{3.56}$$

where $G_A(\mathbf{x}, \mathbf{y}, t, \tau)$ is the Greens function for this problem. We have already imposed the length-scale constraints $\ell/L \ll 1$, which allows us to remove average quantities from integrals. We also impose at this point the approximations that the characteristic time scale, T , associated with the average concentration gradient is much larger than the time scale, t^* , associated with the Greens function. In other words, we must have an analogous separation of time scales

$$t^* \ll T \tag{3.57}$$

This approximation is a version of the *quasi-steady* approximation, and it is described in additional detail in [52] and [53]. Although there are conditions when this approximation will clearly not be true (e.g., when the structure of the initial condition is such that it must span large distances before it is *relaxed*), the approximation is nonetheless a useful one because it allows the development of a time-localized theory. These approximations allow us to put the solution in the conventional time- and space- localized form [45]. Additionally,

when we are interested in systems where the system boundaries are far in some sense from the chemical species of interest, we can safely set the boundary conditions to zero (i.e., $\tilde{F}_A = 0$). In the following, we will adopt this assumption to keep the analysis clear. However, note that if the particular boundary conditions are *known*, then one may incorporate them into the theory with very little additional effort.

With these approximations in place, the *local* solution for the set of balance equations associated with chemical species A is given by

$$\tilde{c}_{A\gamma}(\mathbf{x}, t) = \mathbf{b}_{A\gamma}(\mathbf{x}, t) \cdot \nabla \langle c_{A\gamma} \rangle^\gamma|_{(\mathbf{x}, t)} + S_{A\gamma}(\mathbf{x}, t) \quad (3.58)$$

where $\mathbf{b}_{A\gamma}$ and $S_{A\gamma}(\mathbf{x}, t)$ are known as *closure variables* and are defined by

$$\begin{aligned} \mathbf{b}_{A\gamma}(\mathbf{x}, t) = & \int_{\tau=0}^{\tau=t} \int_{\mathbf{y} \in \mathcal{V}_\gamma(\mathbf{x})} -G(\mathbf{x}, \mathbf{y}) \tilde{\mathbf{v}}_\gamma(\mathbf{y}) \, dV(\mathbf{y}) d\tau \\ & + \int_{\tau=0}^{\tau=t} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} -G(\mathbf{x}, \mathbf{y}) \tilde{F}_A(\mathbf{y}, t) \, dA(\mathbf{y}) d\tau \end{aligned} \quad (3.59)$$

$$S_{A\gamma} = \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} G(\mathbf{x}, \mathbf{y}, t, 0) \tilde{\varphi}_A(\mathbf{y}) dV(\mathbf{y}) \quad (3.60)$$

Note that $S_{A\gamma}$ is an exponentially-decaying function of time (this can be easily seen by attempting a conventional separation of variables for $\tilde{c}_{A\gamma}$). At early times, the magnitude of this function can be significant, and can create (apparent) deviations from Fickian behavior (especially in the second moment), even though the spreading process is a Fickian one.

3.12 Closed Form

We start with the averaged equation to derive the closed form that does not depend on the spatial deviation concentration

Averaged equation

$$\frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} + \langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla \tilde{c}_{A\gamma} \rangle^\gamma = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) \quad (3.61)$$

We substitute the local solution to the balance equation (Equation 3.58) to develop the closed form of convection-dispersion transport equation as

$$\begin{aligned} \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} &= \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) - \nabla \cdot (\langle \tilde{\mathbf{v}}_\gamma \otimes \mathbf{b}_{A\gamma} \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma) \\ &\quad - \langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma - \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla S_{A\gamma} \rangle^\gamma \end{aligned} \quad (3.62)$$

To simplify the notation, we can define the following effective parameters

$$\mathbf{D}_{A\gamma}^H = -\langle \tilde{\mathbf{v}}_\gamma \otimes \mathbf{b}_{A\gamma} \rangle^\gamma \quad (3.63)$$

$$\mathbf{D}_{A\gamma}^T = \mathbf{D}_{A\gamma} + \mathbf{D}_{A\gamma}^H \quad (3.64)$$

$$S_{A\gamma}^* = \langle \tilde{\mathbf{v}}_\gamma \cdot \nabla S_{A\gamma} \rangle^\gamma \quad (3.65)$$

in which $\mathbf{D}_{A\gamma}^H$ and $\mathbf{D}_{A\gamma}^T$ identify as *hydrodynamic* dispersion tensor and the *total* dispersion tensor, respectively. As a result, Equation (3.62) can be written compactly as

$$\underbrace{\frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla \cdot (\mathbf{D}_{A\gamma}^T \cdot \nabla \langle c_{A\gamma} \rangle^\gamma)}_{\text{diffusive transport}} - \underbrace{\langle \mathbf{v}_\gamma \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma}_{\text{convective transport}} - \underbrace{S_{A\gamma}^*}_{\text{non-conventional convective source}} \quad (3.66)$$

Note that this balance equation is unusual in that it contains a non-conventional source term, $S_{A\gamma}^*$. The role of this term is to account for the evolution of the initial condition at early times. Because this term is an exponentially decreasing function of time, it will

decay toward zero as time grows large enough. The effect of this term on the early stages of diffusion-convection transport phenomenon will be discussed in the discussion section. To complete the problem, as a final step, we must evaluate the closure variables over a representative domain. This is described in the following section.

3.13 Solving for the Closure Variables

Recall the solutions for the deviation concentrations for species A is given by a linear form where each term is proportional to one of the sources in the balance equation

$$\tilde{c}_{A\gamma} = \mathbf{b}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + S_{A\gamma} \quad (3.67)$$

The linearity of the balance equation for $\tilde{c}_{A\gamma}$ allow us to separate the deviation concentrations problem into two separate problems, where each set of equations represents the contribution of one source term. It is fairly simple to show

$$\frac{\partial \tilde{c}_{A\gamma}}{\partial t} = \frac{\partial \mathbf{b}_{A\gamma}}{\partial t} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + \mathbf{b}_{A\gamma} \cdot \frac{\partial (\nabla \langle c_{A\gamma} \rangle^\gamma)}{\partial t} + \frac{\partial S_{A\gamma}}{\partial t} \quad (3.68)$$

$$\nabla \tilde{c}_{A\gamma} = \nabla \otimes \mathbf{b}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma + \mathbf{b}_{A\gamma} \cdot \nabla \otimes \nabla \langle c_{A\gamma} \rangle^\gamma + \nabla S_{A\gamma} \quad (3.69)$$

At this point, the *quasi-steady* assumption is conventionally adopted, and this allows one to neglect derivatives with respect to time, assuming that certain length-scale constraints are met. Additionally, it is usually assumed that the gradient of the average concentration can be treated as being constant, so that the second gradient of the average concentration may be neglected.

However, more recently certain schemes have been developed to investigate useful transient closure problems [54]. Under these conditions, the terms involving the second gradient of the average concentration and the time-derivative of the gradient of the concentration are neglected. Under these conditions, a set of soluble closure problems for $\mathbf{b}_{A\gamma}$ and $S_{A\gamma}$

can be developed.

Substituting Equation 3.67 into the closure problem given by Equations 3.52-3.55 yields two sets of equations as

Species A closure for $\mathbf{b}_{A\gamma}$

$$\frac{\partial \mathbf{b}_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \otimes \mathbf{b}_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = - \underbrace{\tilde{\mathbf{v}}_\gamma}_{\text{source}} \quad (3.70)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = +\mathbf{n}_{\gamma\kappa} \cdot \mathbf{D}_{A\gamma} \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.71)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.72)$$

$$\text{I.C.1} \quad \mathbf{b}_{A\gamma} = 0 \quad \text{at } t=0 \quad (3.73)$$

Species A closure for $S_{A\gamma}$

$$\frac{\partial S_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla S_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = 0 \quad (3.74)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot \nabla S_{A\gamma} = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.75)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = \tilde{F}_A(\mathbf{x}, t) = 0 \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.76)$$

$$\text{I.C.1} \quad S_{A\gamma} = \tilde{\varphi}_A \quad \text{at } t=0 \quad (3.77)$$

It is apparent that the first of these two closure problems provides information about the evolution of $D_{A\gamma}^H$ in time, whereas the second problem provides information about how $S_{A\gamma}^*$ will evolve in time.

3.14 Treatment of the Boundary Condition 2 using Periodic Boundary Conditions

Since we are not interested in solving these two closure problems over the macroscopic region, we abandon B.C.2 and replace it with a unit cell in a spatially periodic model as

Species A closure for $\mathbf{b}_{A\gamma}$

$$\frac{\partial \mathbf{b}_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \otimes \mathbf{b}_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = -\tilde{\mathbf{v}}_\gamma \quad (3.78)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = +\mathbf{n}_{\gamma\kappa} \cdot D_{A\gamma} \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.79)$$

$$\text{B.C.2} \quad \mathbf{b}_{A\gamma}(\mathbf{x} + l_i, t) = \mathbf{b}_{A\gamma}(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.80)$$

$$\text{I.C.1} \quad \mathbf{b}_{A\gamma} = 0 \quad \text{at } t=0 \quad (3.81)$$

Species A closure for $S_{A\gamma}$

$$\frac{\partial S_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla S_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = 0 \quad (3.82)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.83)$$

$$\text{B.C.2} \quad S_{A\gamma}(\mathbf{x} + l_i, t) = S_{A\gamma}(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.84)$$

$$\text{I.C.1} \quad S_{A\gamma} = \tilde{\varphi}_A \quad \text{at } t=0 \quad (3.85)$$

3.15 Treatment of the Boundary Condition 1 for $\mathbf{b}_{A\gamma}$ Closure Equation

Taking a second look at B.C.1 (Equation 3.12) of the microscale balance equation, one can conclude that the gradient of the average concentration is not a function of r and θ

direction, in cylindrical coordinate, but rather it does depend on z and t

$$\langle c_{A\gamma} \rangle^\gamma = \frac{1}{A_{\gamma e}} \int_{\gamma e} c_{A\gamma} dA_{\gamma e} \quad (3.86)$$

$$\langle c_{A\gamma} \rangle^\gamma = \frac{1}{A_{\gamma e}} \int c_{A\gamma}(r, \theta, z, t) d\theta r dr \quad (3.87)$$

$$\langle c_{A\gamma} \rangle^\gamma = f(0, 0, z, t) \quad (3.88)$$

Also, the third component of the normal unit outward vector to the wall is zero as shown in Figure 3.4.

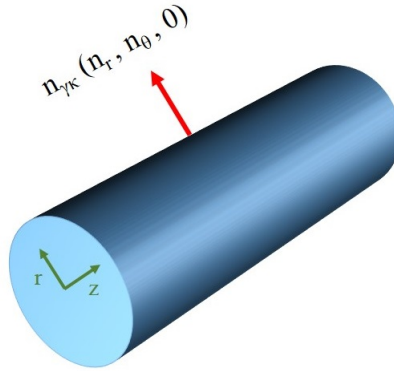


Figure 3.4: The schematic showing the components of the normal unit outward vector to the wall for a tube (red arrow). Note, the third component of normal unit outward vector is zero.

As a result, the gradient of the averaged concentration would be only a function of z

$$\nabla \langle c_{A\gamma} \rangle^\gamma = \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial r} \vec{r} + \frac{1}{r} \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial \theta} \vec{\theta} + \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial z} \vec{z} \quad (3.89)$$

$$\nabla \langle c_{A\gamma} \rangle^\gamma = \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial z} \vec{z} \quad (3.90)$$

Forming the dot product of $\mathbf{n}_{\gamma\kappa}$ and $\nabla \langle c_{A\gamma} \rangle^\gamma$

$$\mathbf{n}_{\gamma\kappa} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma = (\mathbf{n}_r, \mathbf{n}_\theta, 0) \cdot (0, 0, \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial z}) = 0 \quad \text{at } A_{\gamma\kappa} \quad (3.91)$$

We recall the simplified version of the B.C.1 for the averaged equation (Equation 3.16)

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \tilde{c}_{A\gamma} = \mathbf{n}_{\gamma\kappa} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.92)$$

Rearranging this equation leads to

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \tilde{c}_{A\gamma} = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.93)$$

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{A\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma - \mathbf{n}_{\gamma\kappa} \cdot \nabla S_{A\gamma} = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.94)$$

One can express above equations as

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{A\gamma} = 0 \quad (3.95)$$

$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla S_{A\gamma} = 0 \quad (3.96)$$

Finally, we are able to rewrite the closure problems (Equations 3.79-3.85) as

Species A closure for $\mathbf{b}_{A\gamma}$

$$\frac{\partial \mathbf{b}_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \otimes \mathbf{b}_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = -\tilde{\mathbf{v}}_\gamma \quad (3.97)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.98)$$

$$\text{B.C.2} \quad \mathbf{b}_{A\gamma}(\mathbf{x} + l_i, t) = \mathbf{b}_{A\gamma}(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.99)$$

$$\text{I.C.1} \quad \mathbf{b}_{A\gamma} = 0 \quad \text{at } t=0 \quad (3.100)$$

Species A closure for $S_{A\gamma}$

$$\frac{\partial S_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla S_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = 0 \quad (3.101)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_{A\gamma} \cdot \nabla S_{A\gamma}) = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (3.102)$$

$$\text{B.C.2} \quad S_{A\gamma}(\mathbf{x} + l_i, t) = S_{A\gamma}(\mathbf{x}, t) \quad \text{at } \mathcal{A}_{\gamma e} \quad (3.103)$$

$$\text{I.C.1} \quad S_{A\gamma} = \tilde{\varphi}_A \quad \text{at } t=0 \quad (3.104)$$

We are now left with four sets of equation to solve for Taylor-Aris dispersion problem in a tube: (1) microscale balance equations (Equations 3.11-3.14), (2) averaged equations (Equations 3.15-3.18), (3) closed equations for $\mathbf{b}_{A\gamma}$ (Equations 3.97-3.100), and (4) closed equations for $S_{A\gamma}$ (Equations 3.101-3.104). We have used the finite elements package COMSOL Multiphysics 5.3® and MATLAB R2017® for all computational analysis. The physical parameters for the simulations are reported in Table 3.1.

Table 3.1: Parameters used in the simulations

Parameter	Value	Definition
T	293.15 K	System temperature
L_t	200 cm	Length of tube
L	15 cm	Length of initial concentration
r	1 cm	Radius of tube
$\mathcal{D}_{A\gamma,0}$	$1 \times 10^{-9} \text{ m}^2/\text{s}$	Molecular diffusivity of species A
c_0	$1 \times 10^0 \text{ mol}/\text{m}^3$	Initial concentration

Chapter 4: Results & Discussion

In this chapter, our focus will remain on evaluating the total dispersion tensor and the second moment of the initial configuration for an arbitrary structure of the initial concentration using the analytical expression we already derived in Chapter 3 for the computation of the total dispersion coefficient (Equation 3.65). We extend these evaluation for Péclet numbers ranging $10^{-3} - 10^2$. We recall that the development of the closure problems were performed based on the microscale balance equations involving an arbitrary shape of initial configuration. This is one of the exciting features of our analysis in this study.

A three-dimensional representation of the initial concentration which we use for our analysis is illustrated in Figure 4.1. Note, the flow direction is left to right. This non-uniform but radially-symmetric configuration has two separate blocks of equal length ($\frac{L}{3}$) with different volumes. The left block which is located at the center of tube and initially moves faster eventually catches up with the right block which initially moves slower (located at the tube wall). The distance between these two blocks is also $\frac{L}{3}$, leaving it L as the total length of the initial configuration. We consider the length of the initial configuration as the macroscale length and the radius of the tube as the microscale length throughout this chapter. Therefore, $\frac{L}{r} = \frac{15}{1} \gg 1$ length scale constraint is automatically satisfied for analysis purpose. Because of the non-uniformity of the initial solute distribution, there should be a finite time interval for which the higher-order terms appearing at the right side of the Equation 2.9 decay in the approach to a Gaussian distribution. Since the initial relaxation time of the left block is less than that of the right block, the left block, at some point, should merge with the right block. We are concerned with the evolution of total dispersion tensor and second moment of concentration along the tube length under the preasymptotic and asymptotic regimes.

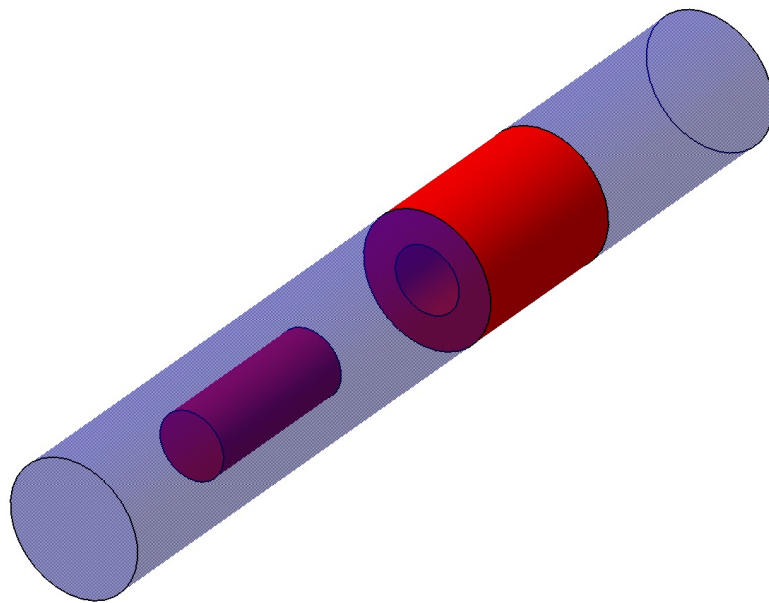


Figure 4.1: A three-dimensional representation of the initial concentration. Note, The flow direction is left to right. This initial configuration is radially-symmetric and non-uniform in nature.

4.1 Total Dispersion Tensor

As expected, the total dispersion tensor varies with time and it finally reaches an asymptotic plateau behavior for all value of Péclet number as shown in Figures 4.3-4.4. Note, the value of the total dispersion tensor is divided by diffusivity ($\mathcal{D}_{A\gamma,0} = 1 \times 10^{-9}[m^2/s]$) for comparison purpose. We recall that the total dispersion tensor is influenced by the combined actions of the diffusivity tensor and the hydrodynamic dispersion tensor

$$\mathbf{D}_{A\gamma}^T = \mathbf{D}_{A\gamma} \cdot \left(\mathbf{I} + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{A\gamma} dA \right) - \langle \tilde{\mathbf{v}}_\gamma \otimes \mathbf{b}_{A\gamma} \rangle^\gamma \quad (4.1)$$

It is easy to show that for the initial configuration shown in Figure 4.1 this tensor will reduce to a scalar if one follows the analogy provided in Section 3.15.

$$D_{A\gamma}^T = \mathcal{D}_{A\gamma} - \langle \tilde{v}_{\gamma,z} b_{A\gamma,z} \rangle^\gamma \quad (4.2)$$

in which $\tilde{v}_{\gamma,z}$ is the spatial deviation velocity in flow direction and $b_{A\gamma,z}$ is *b-field* in the z direction. Now, instead of a tensor calculation, which may be tedious, one can simply compute this scalar as the total dispersion tensor. The first term on the right-hand-side of Equation 4.2 is a constant scalar ($\mathcal{D}_{A\gamma} = 1 \times 10^{-9}[m^2/s]$). Therefore, the second term, which varies with time, should determine the overall (preasymptotic and asymptotic) behavior of the total dispersion tensor. Expanding this term leads to

$$-\langle \tilde{v}_{\gamma,z} b_{A\gamma,z} \rangle^\gamma = -\frac{1}{V_\gamma} \int_{V_\gamma} \left(v_{\gamma,z} - \frac{1}{V_\gamma} \int_{V_\gamma} v_{\gamma,z} dV \right) b_{A\gamma,z} dV \quad (4.3)$$

The only term that seems to have a dependency on time is $\mathbf{b}_{A\gamma,z}$ and this term is actually a function of both r and t (this is illustrated in Figure 4.2).

We recall the diffusion-convection transport equation for closure variable $\mathbf{b}_{A\gamma,z}$ (Equa-

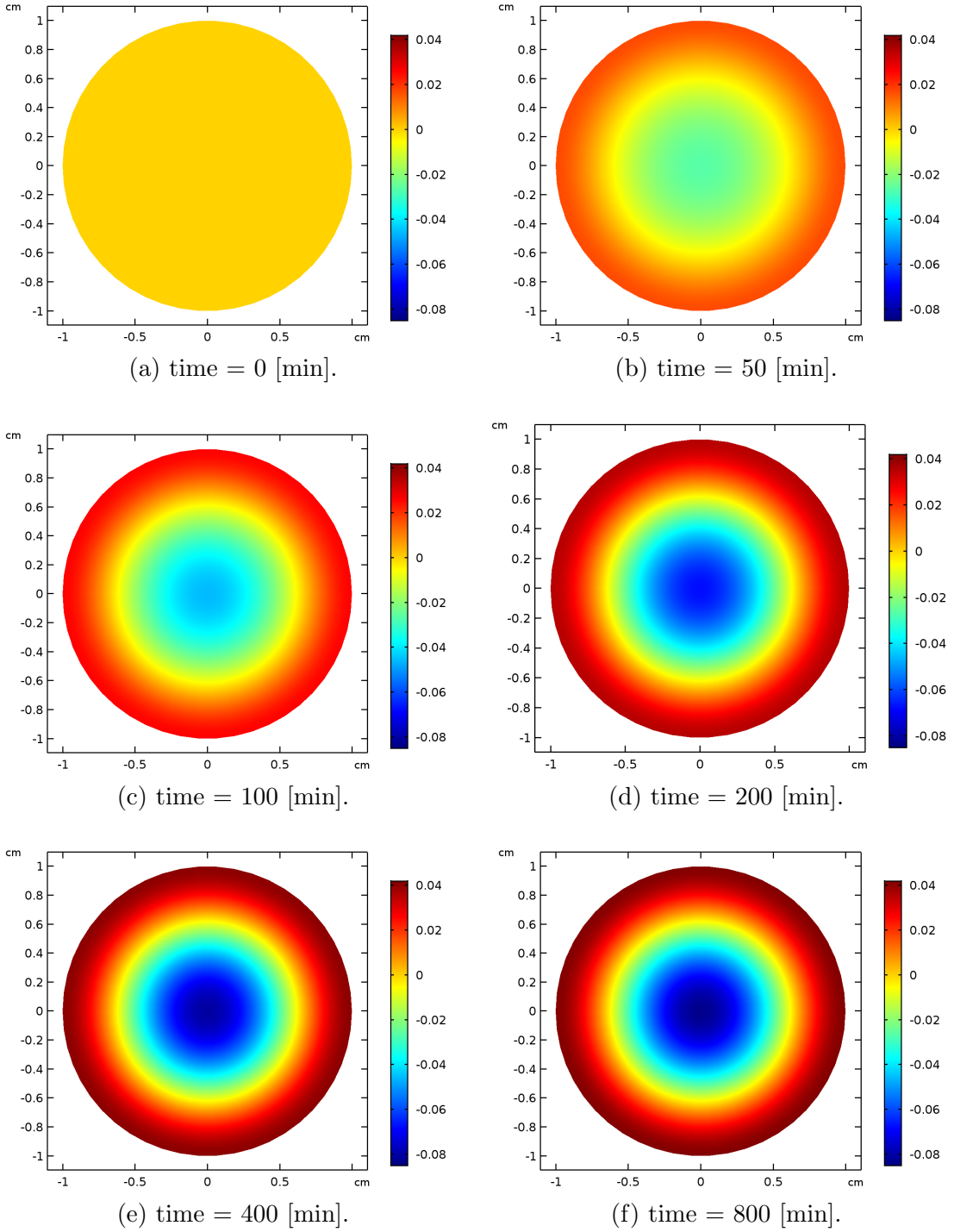


Figure 4.2: The evolution of the b-field across a plane perpendicular to the tube for $\text{Pé} = 100$. These pictures show that the b-field which is independent of z -direction is a function of radial position r and time t .

tion 3.97)

$$\frac{\partial \mathbf{b}_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \otimes \mathbf{b}_{A\gamma} - \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = -\tilde{\mathbf{v}}_\gamma \quad (4.4)$$

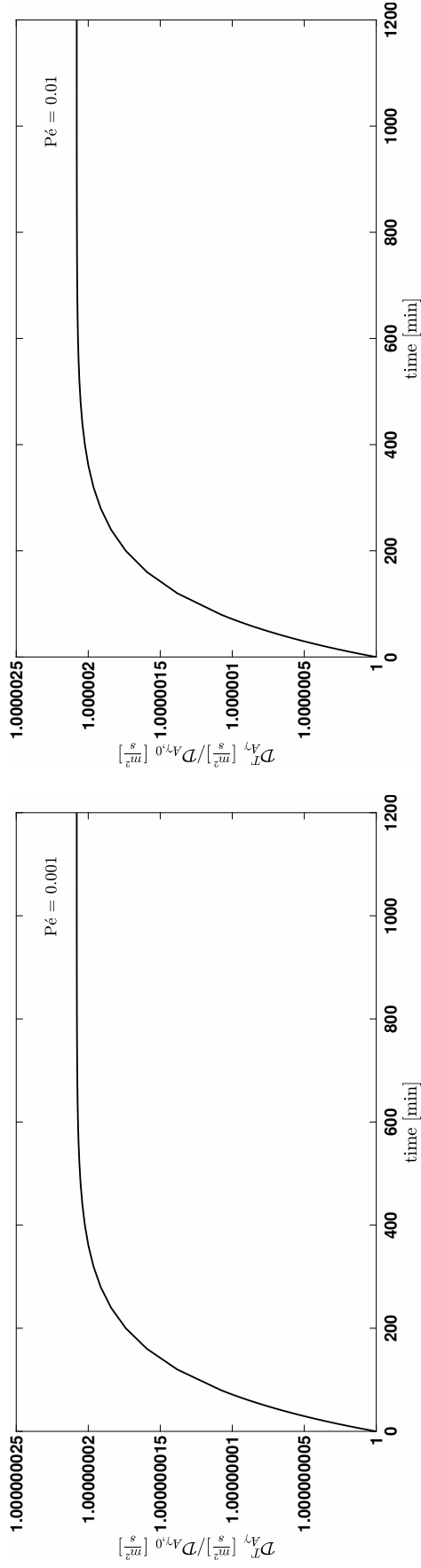
At this point, it should be obvious why the total dispersion tensor follows a transient behavior (transport equation for the closure variable $\mathbf{b}_{A\gamma,z}$ is a transient equation).

The asymptotic value of the normalized dispersion tensor increases as Pé goes up. This can be justified by the fact that dispersion induced by shear flow as a result of laminar or turbulent convection is much more effective than that of molecular diffusion process (the asymptotic value of the total dispersion tensor for Pé=200 is almost 200 times the asymptotic value of the total dispersion tensor for Pé=1).

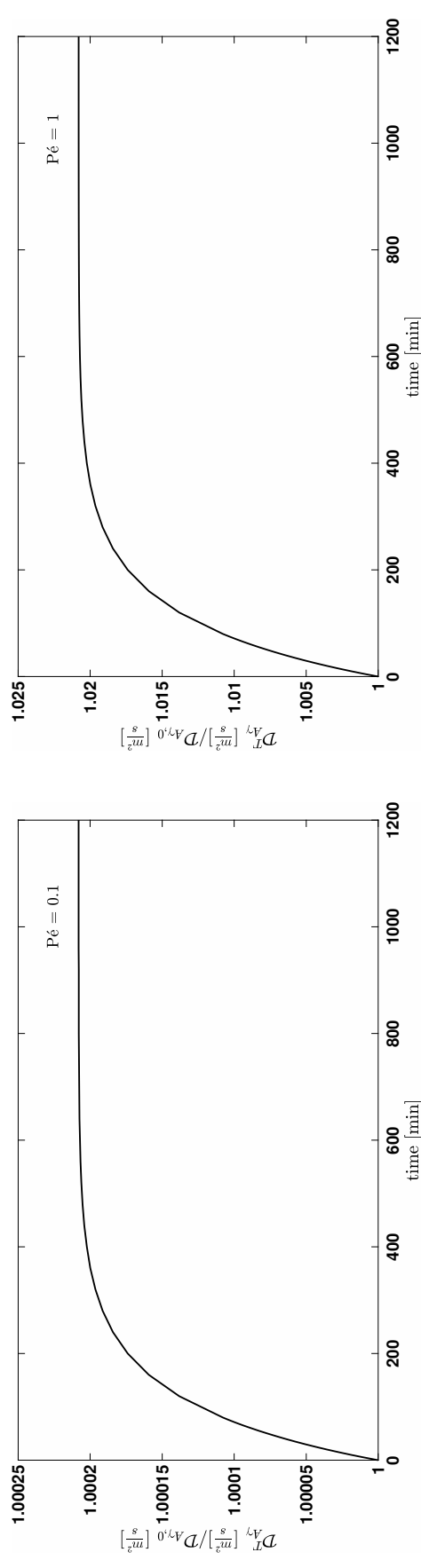
Also, the asymptotic value of the total dispersion tensor is close to the value of diffusivity ($\mathcal{D}_{A\gamma} = 1 \times 10^{-9} [m^2/s]$) for the low Péclet numbers ($\text{Pé} \leq 1$).

In order to determine the approximate time at which the total dispersion tensor reaches the asymptotic solution, the total dispersion tensor is divided by its asymptotic value (for each Pé) and plotted versus time for all Pé numbers. The results have been provided in Figure B.1. Surprisingly, the total dispersion tensor approaches its asymptotic value around 1100 [min] for all values of the Pé number. However, any possible conclusion or correlation between the characteristic time of the system (i.e. $\text{characteristic time} = \frac{\text{characteristic length}}{\text{velocity}}$) and this specific time will remain an active area of research.

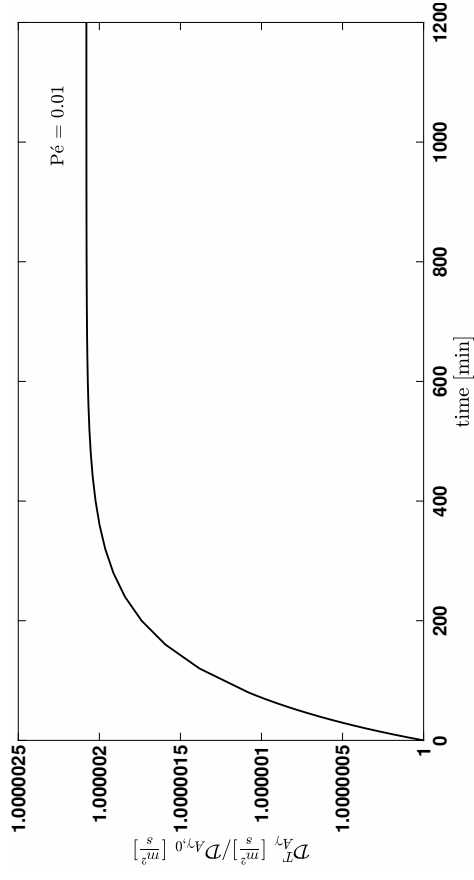
One may ask this question: How can the results obtained from the volume averaging process be validated for our system (Taylor-Aris dispersion in a tube)? The answer to this question is, to the best of the author knowledge, (1) for the zero-velocity condition (i.e. $\text{Pé} \rightarrow 0$), which is considered as a pure diffusion process, the value of the total dispersion tensor should be equal to the diffusivity since if $\mathbf{v} \rightarrow 0$, the diffusion-convection transport



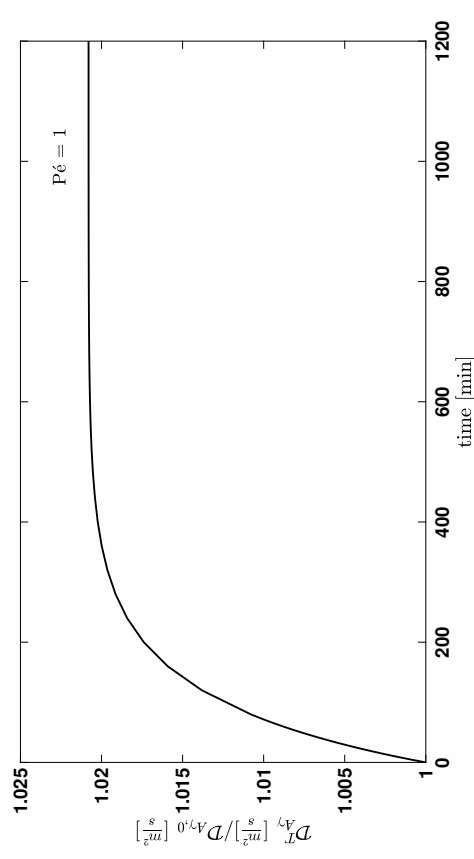
(a) Péclet number = 0.001.



(c) Péclet number = 0.1.

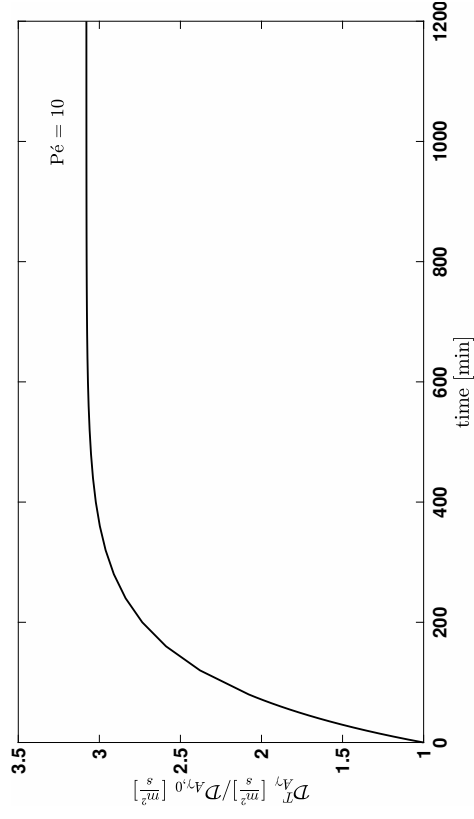


(b) Péclet number = 0.01.

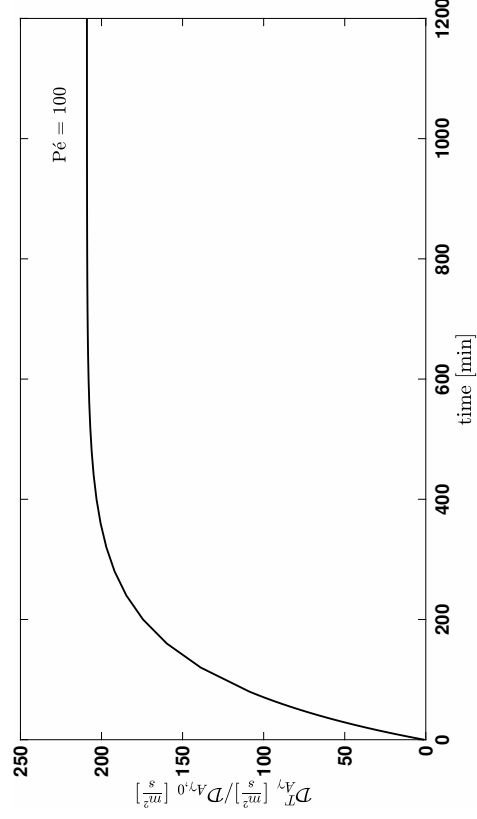


(d) Péclet number = 1.

Figure 4.3: The total dispersion tensor as a function of time for Péclet number $\in \{10^{-3}, 10^{-2}, 10^{-1}, 10^0\}$.



(a) Péclet number = 10.



(b) Péclet number = 100.

Figure 4.4: The total dispersion tensor as a function of time for Péclet number $\in \{10^1, 10^2\}$.

equation for closure variable $\mathbf{b}_{A\gamma,z}$ (Equations 3.97-3.100) is reduced to

$$\frac{\partial \mathbf{b}_{A\gamma}}{\partial t} = \nabla \cdot (\mathbf{D}_{A\gamma} \cdot \nabla \otimes \mathbf{b}_{A\gamma}) = \mathcal{D}_{A\gamma} \nabla \cdot \nabla \otimes \mathbf{b}_{A\gamma} \quad (4.5)$$

$$\text{B.C.1} \quad -\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{A\gamma} = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (4.6)$$

$$\text{B.C.2} \quad -\mathbf{n}_{\gamma\kappa} \cdot \nabla \otimes \mathbf{b}_{A\gamma} = 0 \quad \text{at } \mathcal{A}_{\gamma\kappa} \quad (4.7)$$

$$\text{I.C.1} \quad \mathbf{b}_{A\gamma} = 0 \quad \text{at } t=0 \quad (4.8)$$

Note, boundary condition 2 is written in its original form, not periodic form. Using separation of variables, one can find that the only solution that can satisfy this equation set is when $\mathbf{b}_{A\gamma} = 0$. Therefore, if $\mathbf{v} \rightarrow 0$, then $\mathbf{b}_{A\gamma} \rightarrow 0$, then, $b_{A\gamma,z} \rightarrow 0$, and, consequently, $-\langle \tilde{v}_{\gamma,z} b_{A\gamma,z} \rangle^\gamma \rightarrow 0$, which leads to $D_{A\gamma}^T \rightarrow \mathcal{D}_{A\gamma}$. It is obvious that the asymptotic solution for the case of low Péclet numbers is very close to diffusivity value of $1 \times 10^{-9} [m^2/s]$. (2) For the case of non-zero velocity condition, the asymptotic solution should match the Taylor-Aris dispersion theory [55] for all Péclet range.

$$D_{A,\text{eff}} = \mathcal{D}_A + \frac{U^2 a^2}{48 \mathcal{D}_A} \quad (4.9)$$

The results are illustrated in Figure 4.5. There is an excellent agreement between the asymptotic solution for the total dispersion tensor calculated by the volume averaged approach and that of Taylor-Aris dispersion theory. Since both condition (1) and (2) are satisfied, one can conclude that the time-dependent closure variable $\mathbf{b}_{A\gamma}$ transport equation derived based upon volume averaged process may be valid.

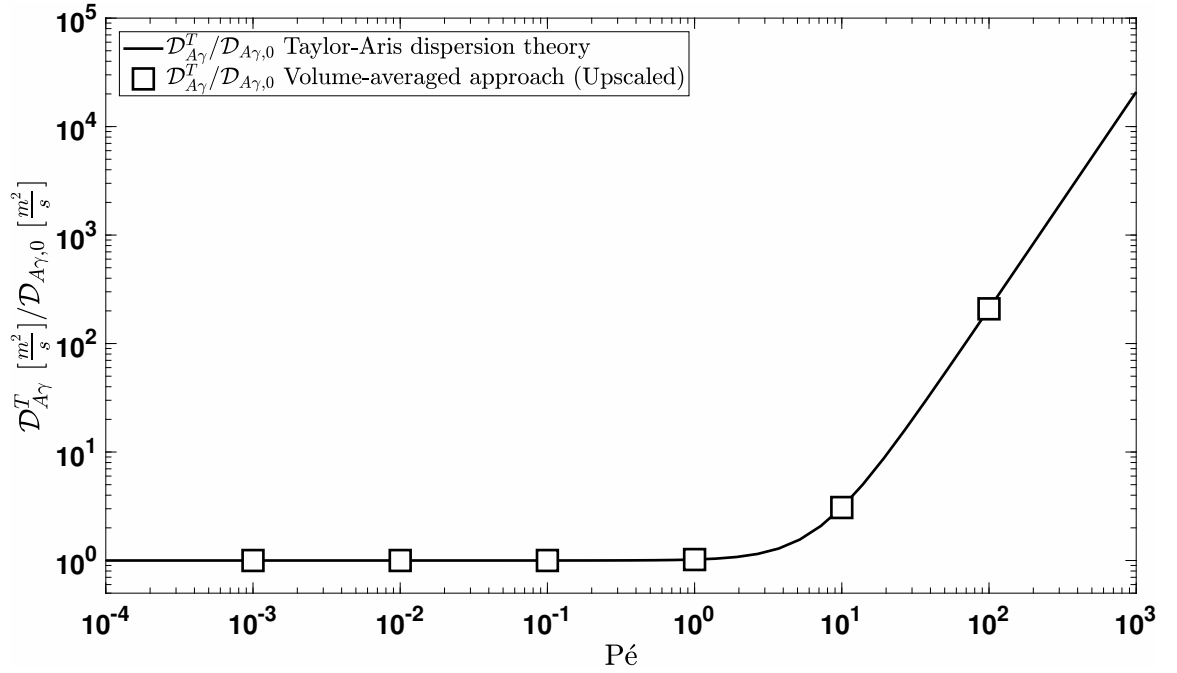


Figure 4.5: Comparison between the asymptotic total dispersion tensor calculated by volume averaged approach (black square) and the Taylor-Aris diffusion-convection transport equation. There is excellent agreement between the asymptotic solution for the total dispersion tensor calculated by the volume averaged approach and that of Taylor-Aris dispersion theory.

4.2 Total Dispersion Tensor: Volume-Averaged vs. Direct Numerical Solution

Direct numerical solution for the microscale balance equation set (Equations 3.11-3.14) leads to the distribution of the initial configuration for preasymptotic and asymptotic times. Knowing the concentration of the initial configuration, one can calculate the first and second moment of the concentration in the flow direction using the one-dimensional n-th spatial moment of the concentration distribution $c(x, t)$ as

$$m_{n,t} = \int_{-\infty}^{\infty} x^n c(x, t) dx \quad (4.10)$$

in which $m_{n,t}$ is the n-th spatial moment. Spatial moments usually describe the overall mass behavior. The zeroth moment $m_{0,t}$ shows the total mass of the initial configuration, the first spatial moment $m_{1,t}$ represents the mean location of the center of the mass, and the second spatial moment $m_{2,t}$ describes the spread of concentration deviation about its center of mass [56]. The large scale effective velocity of the solute can be defined as [57]

$$V_{eff} = \frac{d}{dt} \left(\frac{m_{1,t}}{m_{0,t}} \right) \quad (4.11)$$

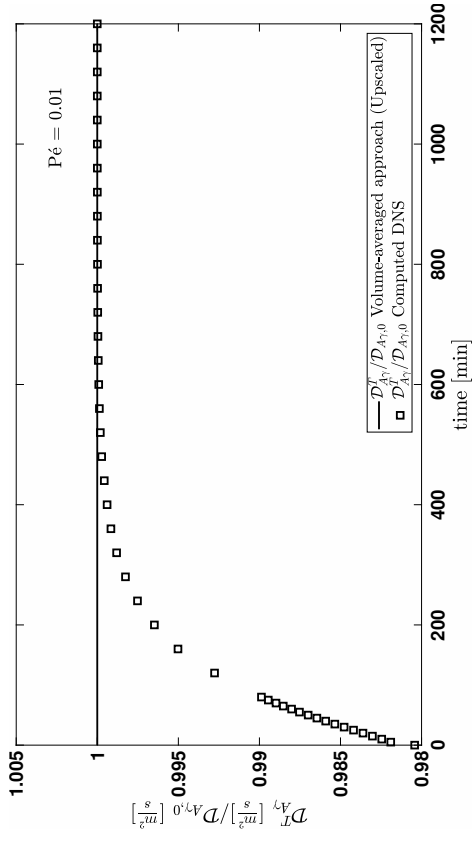
and variance as

$$\sigma^2 = \frac{m_{2,t}}{m_{0,t}} - \left(\frac{m_{1,t}}{m_{0,t}} \right)^2 \quad (4.12)$$

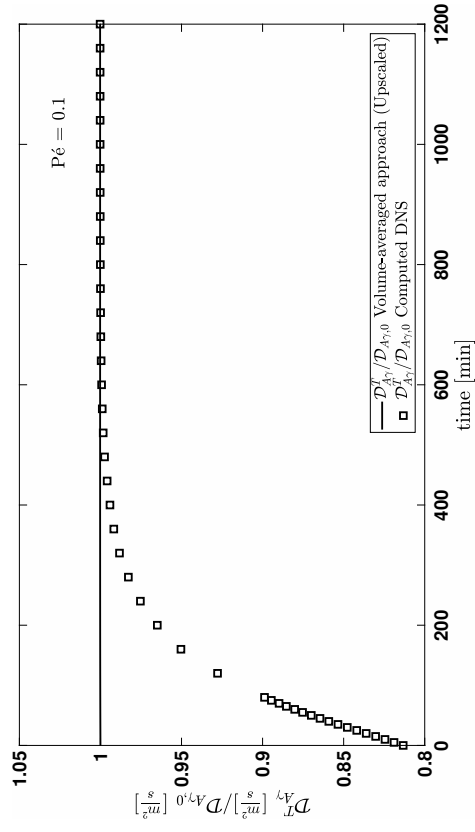
The effective dispersion coefficient may be obtained by

$$D_{eff} = \frac{1}{2} \frac{d}{dt} \sigma^2 \quad (4.13)$$

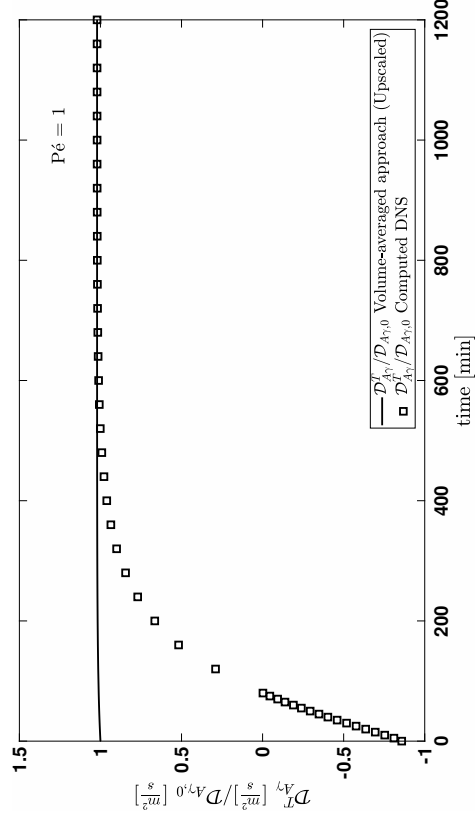
The comparison between the total dispersion tensor calculated based upon Equation 4.13 and volume-averaged total dispersion tensor are illustrated in Figures 4.6-4.7.



(a) Péclet number = 0.001.

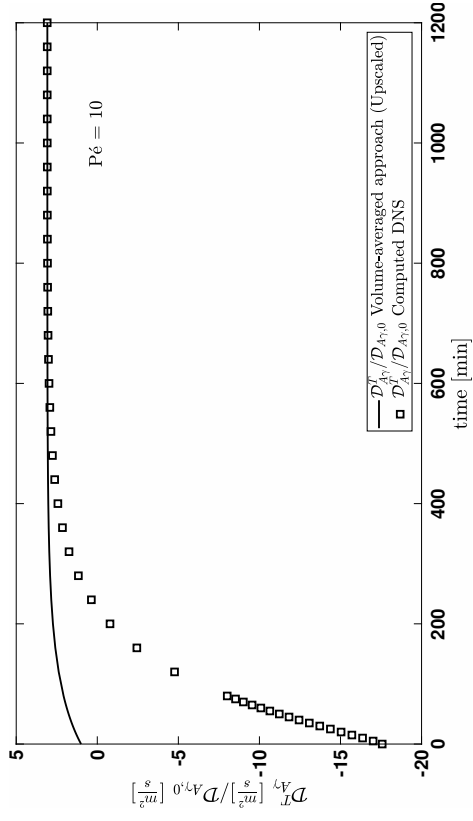


(c) Péclet number = 0.1.

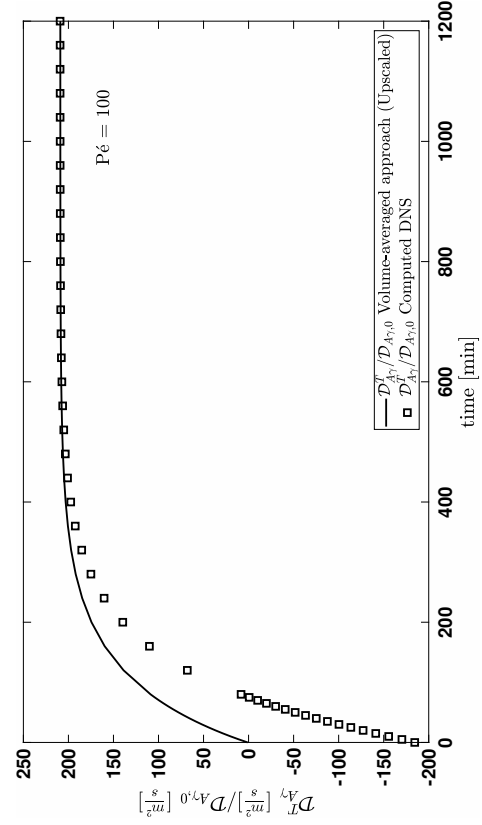


(d) Péclet number = 1.

Figure 4.6: Comparison between the total dispersion tensor calculated by volume averaged approach (black solid line) and DNS method (black square) for Péclet number $\in \{10^{-3}, 10^{-2}, 10^{-1}, 10^0\}$.



(a) Péclet number = 10.



(b) Péclet number = 100.

Figure 4.7: Comparison between the total dispersion tensor calculated by volume averaged approach (black solid line) and DNS method (black square) for Péclet number $\in \{10^1, 10^2\}$.

There are two distinct regimes: preasymptotic and asymptotic ones. The total dispersion tensor calculated by the volume averaged process eventually matches up with that of calculated by DNS approach at asymptotic time for all Pé range. This can be another indication that the volume average process can successfully evaluate the value of the total dispersion tensor for a wide range of Pé number. One may expect minor change in total dispersion tensor at low Pé numbers over time since the speed of displacement of the fluid and, consequently, the initial configuration is very slow. In this case, the center of mass of initial configuration does not significantly move along the flow direction with time. At high Pé numbers, in contrast, considerable change in the total dispersion tensor is expected. These two trends can be found in Figures 4.6-4.7 (solid black lines). In addition, the preasymptotic solution for the total dispersion tensor calculated by DNS method has negative values at Pé ranging $10^0 - 10^2$. This can not be true since the negative value for total dispersion tensor does not have physical interpretation. In general, it seems that volume averaged process is more accurate in terms of assessing the preasymptotic dispersion behavior of the solute matter.

4.3 The Second Moment

The results of the second moment for the initial configuration moving along the tube are depicted in Figure 4.8. Since the displacement speed of solute is slow at low Pé numbers, there is not much going on at the large scale and the second moments calculated by the volume averaged process and the DNS method follow the same low monotonic increment. At higher Pé number (i.e. $Pé = 100$), however, one may expect that the left block of initial configuration (Figure 4.1) can pass the right one since it moves faster.

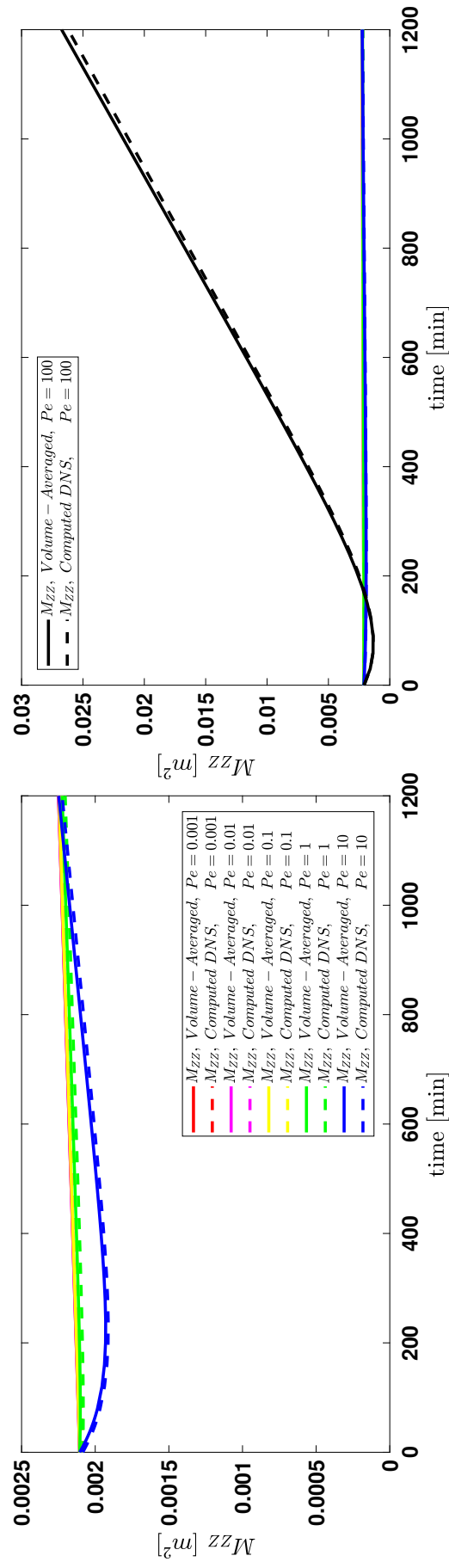


Figure 4.8: Comparison between the second moment calculated by the volume averaged approach (solid line) and the DNS method (dashed line) for Péclet numbers $\in \{10^{-3}, 10^{-2}, 10^{-1}, 10^0, 10^1, 10^2\}$ (left picture) and $Pe = 100$ (right picture).

4.4 The Evolution of the Concentration

The results of the species A concentration on a plane crossing the centerline of the tube are illustrated in Figures 4.9 and 4.10 in order to gain a better insight into how the initial configuration of the solute evolves along the tube. At low Péclet numbers (i.e. $Pé \in \{0.1, 1\}$), two separate blocks of the initial configuration does not seem to merge at all even until 1600 [min]. It is expected, however, that these two blocks will merge and form a homogeneous mixture at infinite times. They tend to radially disperse and form a relatively homogeneous mixture at radial direction due to a huge radial concentration gradient. Note, there is a concentration gradient in the longitudinal direction as well and this causes dispersion of the blocks at longitudinal direction at higher times. Dispersion phenomena will be dominated by diffusion since the convection force is not significant in low Péclet numbers. At $Pé = 100$, the left block quickly passes the right block and will remain the leading block. One may rise the question of what is the minimum point in the second moment of concentration for $Pé=100$ near 100 [min] seen in Figure 4.8. Taking a closer look at the part (b) of the Figure 4.10, the left block starts to reach and touch the right block at about 100 [min], then it will remain the tip of concentration profile. This may justify why the spread of concentration deviation about its center of mass shows a monotonic increment after a monotonic decrement. In general, it seems that the concentration profile along the tube will remain more radially-symmetric and more compact when the convection term is low, causing a low amount of concentration deviation from the center of mass. When the convective term is dominant, however, the concentration profile spreads longitudinally, and radially, leading to a high concentration deviation from the center of mass.

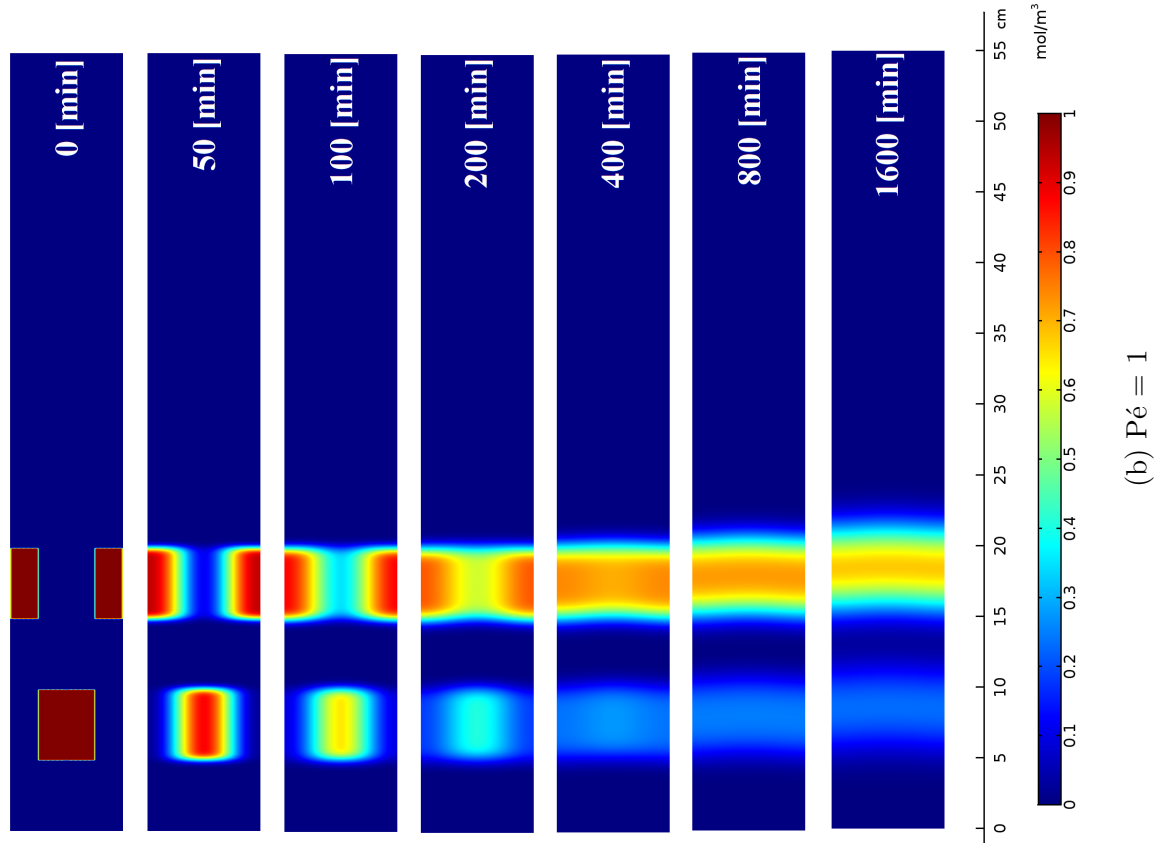
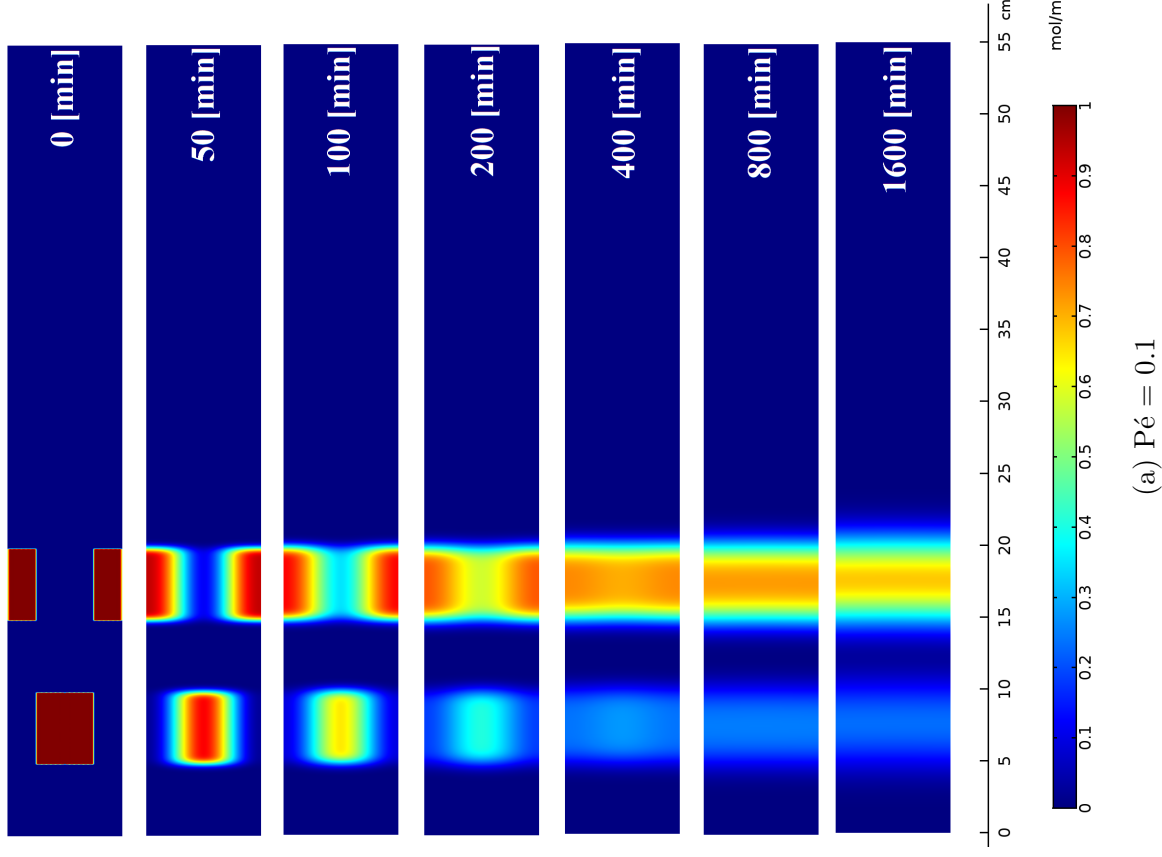
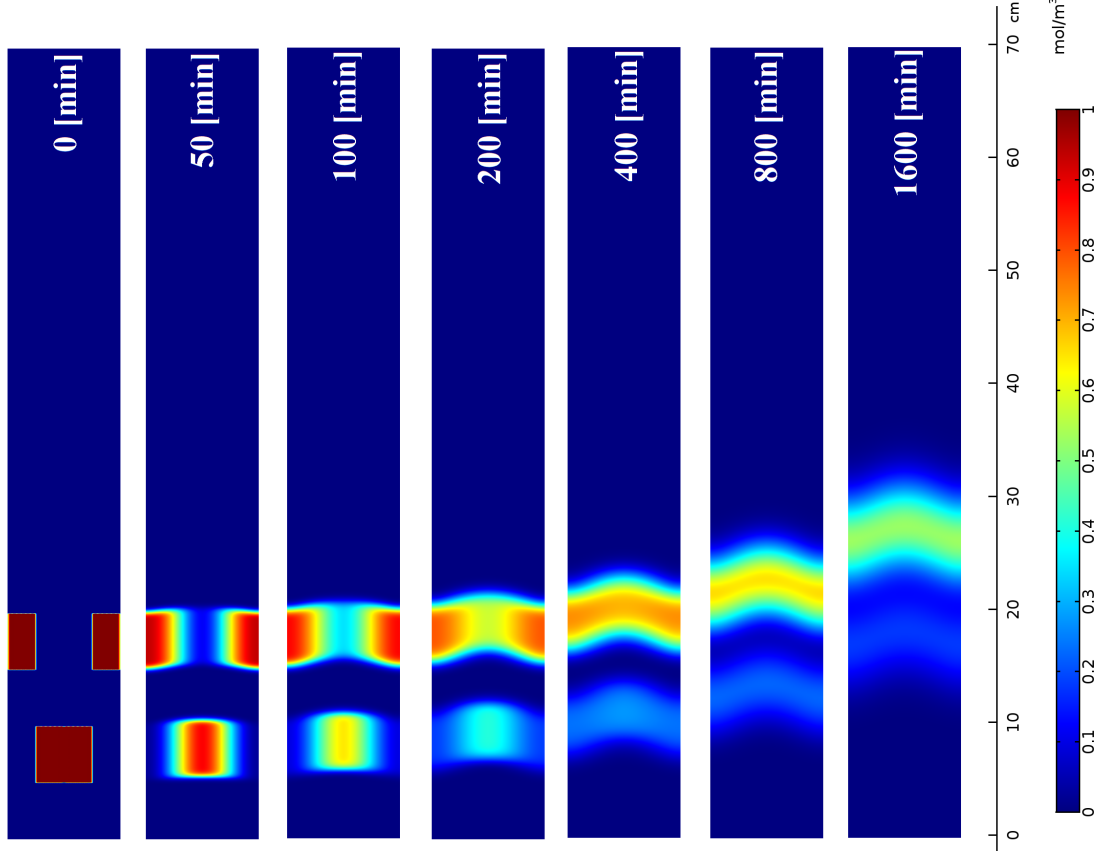
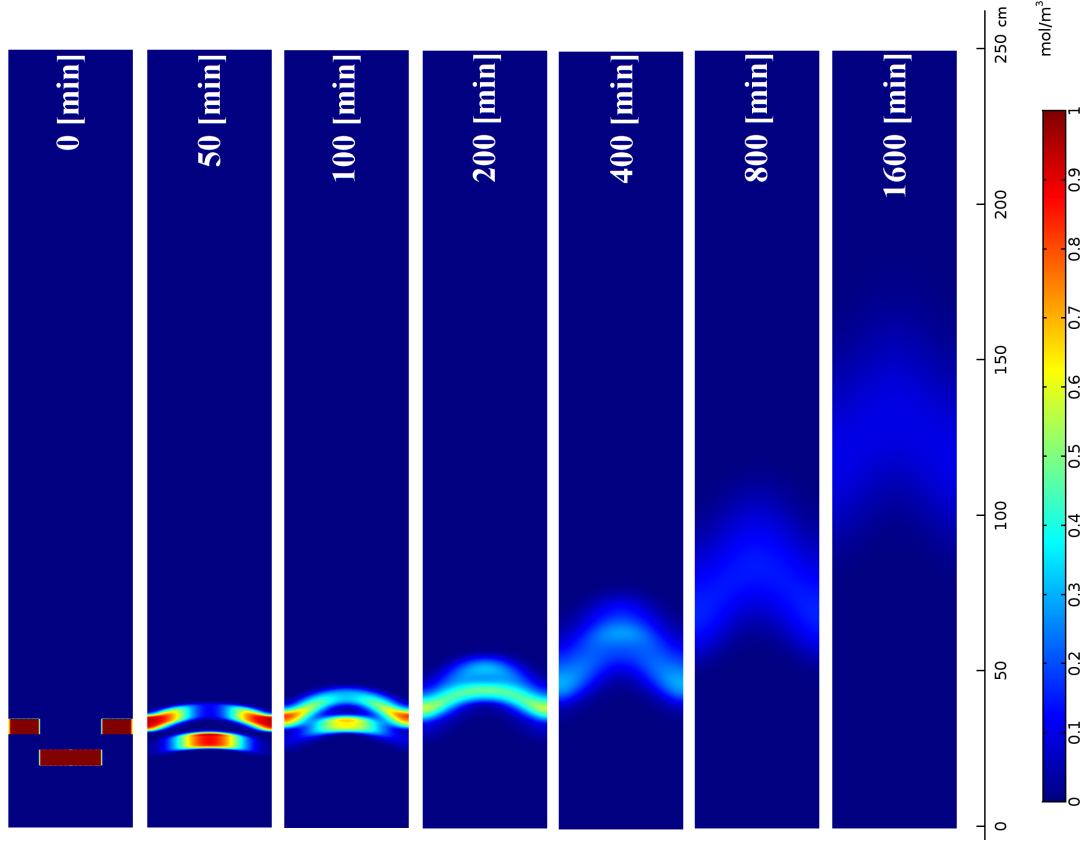


Figure 4.9: The evolution of the concentration on a plane crossing the centerline of the tube for Péclet number $\in \{10^{-1}, 10^0\}$



(a) $Pé = 10$



(b) $Pé = 100$

Figure 4.10: The evolution of the concentration on a plane crossing the centerline of the tube for Péclet number $\in \{10^1, 10^2\}$

Chapter 5: Conclusion Remarks & Future Work

The method of volume averaging was used to investigate the preasymptotic dispersion of an arbitrary initial configuration in a tube governed by diffusion-convection transport phenomena. The role of the non-conventional additional source term appearing in the averaging process was found to account for the evolution of the initial condition at early times. The term was found to exponentially decay toward zero as time increases. Upon averaging, two closure problems were derived. One of these provided information about the evolution of $D_{A\gamma}^H$ in time, whereas the other provided information about the evolution of $S_{A\gamma}^*$. One exciting feature of the developed theory is that it can accurately describe the effective transport properties from preasymptotic to asymptotic times. It was found that the volume averaged process is more accurate in calculating the preasymptotic dispersion of solute matter.

In terms of future work, one can investigate the Taylor-Aris dispersion for the case of diffusion-convection-reaction transport phenomena. Moreover, taking into account the effects of viscoelastic fluids, instead of Newtonian fluids, on the microscale balance equation will extend the applications of upscaled model to the biological systems. Furthermore, developing the averaged transport equation for the non-symmetric initial configuration will be of interest to consider.

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APPENDICES

Appendix A: Estimates of the Variance of the Deviations

The most direct way to obtain an estimate of $\langle \tilde{c}_A \rangle^\gamma$ is to follow the development of Whitaker [6].

As a second, even more conservative estimate for $\tilde{c}_{A\gamma}$, we examine the deviation balance equation directly. Multiplying the balance equation for $\tilde{c}_{A\gamma}$ by $\tilde{c}_{A\gamma}$ itself and averaging, it is fairly easy to obtain a relation for the variance of the deviation field, σ_A^2

Species A

$$\frac{\partial \sigma_A^2}{\partial t} + \mathbf{v}_\gamma \cdot \nabla \sigma_A^2 - \nabla \cdot (D_{A\gamma} \cdot \nabla \sigma_A^2) = -2 \underbrace{\langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma}_{source} \quad (\text{A.1})$$

$$B.C. \ 1 \quad -\mathbf{n}_{\gamma\kappa} \cdot (D_{A\gamma} \cdot \nabla \sigma_A^2) = 0 \text{ at } \mathcal{A}_{\gamma e} \quad (\text{A.2})$$

$$I.C. \ 1 \quad \sigma_A^2(\mathbf{x}, 0) = \underbrace{\tilde{\varphi}_A^2(\mathbf{x})}_{source} \quad (\text{A.3})$$

where $\sigma_A^2 = \langle \tilde{c}_{A\gamma}^2 \rangle^\gamma$. There are two source terms that drive this problem: (1) the volumetric source on the right-hand-side of Equation (A.1), and (2) the initial condition source given in Equation (A.3). We can get an estimate of the size of σ_A^2 by conducting a conventional order-of-magnitude analysis of the problem.

A constraint for this condition can be developed by conducting an order-of-magnitude analysis. We start by defining the following metrics for the velocity field, diffusion, and hydrodynamic dispersion tensor

$$\mathbf{O}(\tilde{\mathbf{v}}_\gamma) \sim \tilde{v}_\gamma = [\sigma_v(\tilde{\mathbf{v}}) \cdot \sigma_v(\tilde{\mathbf{v}})]^{\frac{1}{2}} \quad (\text{A.4})$$

$$\mathbf{O}(D_{A\gamma}) \sim D_{A\gamma} = (D_{A\gamma} : D_{A\gamma})^{\frac{1}{2}} \quad (\text{A.5})$$

$$\mathbf{O}(D_A^H) \sim D_A^H = (D_A^H : D_A^H)^{\frac{1}{2}} \quad (\text{A.6})$$

where $\sigma(\cdot)$ is the standard deviation operation, and the double-dot notation is defined by the contraction $\mathbf{A} : \mathbf{B} = A_{ij}B_{ji}$. Neglecting the accumulation term, a reasonable estimate of the left-hand-side of Eq. (A.1) is

$$\mathbf{v}_\gamma \cdot \nabla \sigma_A^2 - \nabla \cdot (D_{A\gamma} \cdot \nabla \sigma_A^2) \sim \mathbf{O} \left(\frac{v_\gamma \sigma_A^2}{L} + \frac{D_{A\gamma} \sigma_A^2}{L^2} \right) \quad (\text{A.7})$$

In this expression, note that the sign of the term has no role in estimating its magnitude (thus all terms are estimated by their absolute values).

For the right-hand-side, first note

$$\begin{aligned} -2\langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \rangle^\gamma \cdot \nabla \langle c_{A\gamma} \rangle^\gamma &= -2\langle \tilde{\mathbf{v}}_\gamma \cdot \mathbf{b}_{A\gamma} \rangle : \nabla \langle c_{A\gamma} \rangle^\gamma \otimes \nabla \langle c_{A\gamma} \rangle^\gamma \\ &= -2D_A^H : \nabla \langle c_{A\gamma} \rangle^\gamma \otimes \nabla \langle c_{A\gamma} \rangle^\gamma \end{aligned} \quad (\text{A.8})$$

Then, the right-hand-side can be estimated by

$$-2D_A^H : \nabla \langle c_{A\gamma} \rangle^\gamma \otimes \nabla \langle c_{A\gamma} \rangle^\gamma \sim \mathbf{O} \left[\frac{2D_A^H (\langle c_{A\gamma} \rangle^\gamma)^2}{L^2} \right] \quad (\text{A.9})$$

Equating (A.7) and (A.9) yields an estimate for the concentration deviations of the form

$$\left(\frac{v_\gamma \sigma_A^2}{L} + \frac{D_{A\gamma} \sigma_A^2}{L^2} \right) = \mathbf{O} \left[\frac{2D_A^H (\langle c_{A\gamma} \rangle^\gamma)^2}{L^2} \right] \quad (\text{A.10})$$

Solving this for σ_A^2 yields

$$\frac{\sigma_A}{\langle c_{A\gamma} \rangle^\gamma} = \left(\frac{2D_A^H/D_{A\gamma}}{\frac{v_\gamma L}{D_{A\gamma}} + 1} \right)^{\frac{1}{2}} \quad (\text{A.11})$$

In the following, we define the Péclet number by

$$Pe = \frac{v_\gamma L}{D_{A\gamma}} \quad (\text{A.12})$$

To continue, note that $D_A^H \rightarrow 0$ as $Pe \rightarrow 0$. Now we can consider two possible limits (1) $Pe \gg 1$, and (2) $Pe \ll 1$. For case (1), when $Pe \gg 1$, then $D_A^H/D_{A\gamma} \sim \mathbf{O}(\alpha_L v_\gamma/D_{A\gamma})$, where α_L is a longitudinal dispersivity. Hence

$$\frac{\sigma_A}{\langle c_{A\gamma} \rangle^\gamma} \sim \mathbf{O}\left(\frac{\alpha_L}{L}\right)^{\frac{1}{2}} \quad (\text{A.13})$$

Note that the dispersivity in this case would be approximately the same size as the small length scale, ℓ . Hence, under the length-scale constraints that we have already imposed, this condition is automatically satisfied, and we can conclude that $\sigma_A \ll \langle c_{A\gamma} \rangle^\gamma$.

Appendix B: Normalized Total Dispersion Tensor

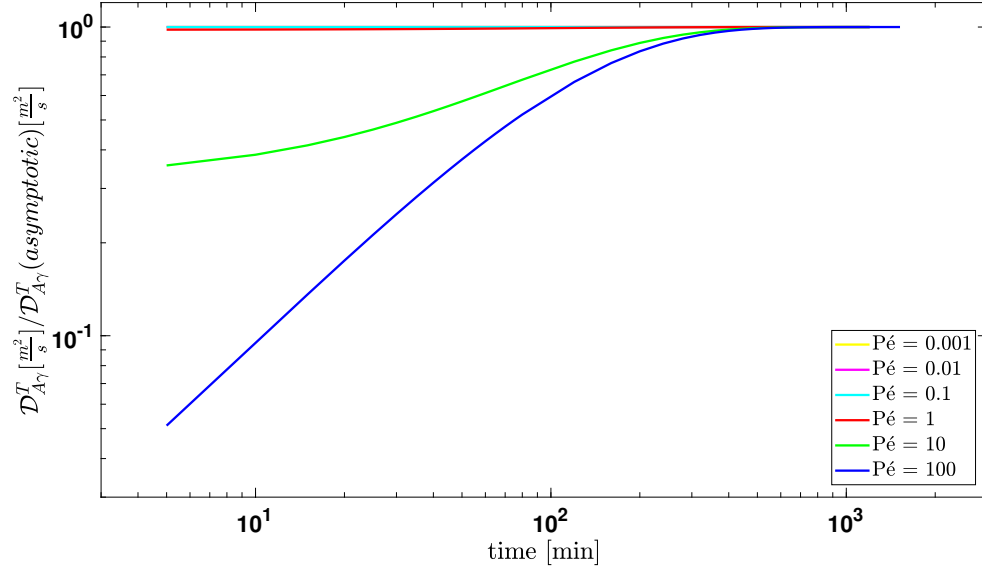


Figure B.1: Normalized total dispersion tensor for all range of Péclet number.

Appendix C: Validation of the Numerical Method

The estimation of the uncertainty associated with the numerical results becomes significant when an analytical solution is not available. The numerical solutions of this study obtained by COMSOL® has been verified for a wide range of Péclet number based upon the method originally introduced by Roache [58] for the uniform reporting of grid refinement studies known as Grid Convergence Index (GCI). The GCI is, in fact, a grid refinement error estimator based upon the theory of Richardson Extrapolation [59] also known as “ h^2 ” extrapolation. The discrete solution f are assumed to have a series representation, in the grid spacing h , of

$$f = f[exact] + g_1 h + g_2 h^2 + g_3 h^3 + \dots \quad (C.1)$$

$$f[exact] = \frac{h_2^2 f_1 - h_1^2 f_2}{h_2^2 - h_1^2} + H.O.T \quad (C.2)$$

in which functions g_1 , g_2 , etc. are defined in the continuum and do not depend on any discretization and H.O.T are high order terms. The above equation should be a valid definition for the order of the discretization. The basis idea for the second-order process is to combine two separate discrete solutions f_1 and f_2 on two different grids with uniform grid spacing h_1 (fine grid) and h_2 (coarse grid) in order to eliminate the leading order error terms. Substituting the grid refinement ratio $r = \frac{h_2}{h_1}$ into Equation C.2 leads to

$$f[exact] = f_1 + \frac{f_1 - f_2}{r^2 - 1} \quad (C.3)$$

Base upon the GCI method, one can calculate the uncertainty associated with grid convergence. The numerical solution for a variable ξ on at least three different grids with refinement ratios $r_{21} = \frac{\Delta_2}{\Delta_1}$ and $r_{32} = \frac{\Delta_3}{\Delta_2}$ is first calculated. Then, the fine (ξ_1) and medium

(ξ_2) grid solutions are interpolated to the coarse grid. The *local* apparent order of accuracy can be calculated as [60]

$$P(\mathbf{x}) = \frac{1}{\ln(r_{21})} \left| \ln \left| \frac{\epsilon_{32}(\mathbf{x})}{\epsilon_{21}(\mathbf{x})} \right| + \ln \left(\frac{r_{21}^{P(\mathbf{x})} - \text{sign}\left(\frac{\epsilon_{32}}{\epsilon_{21}}\right)}{r_{32}^{P(\mathbf{x})} - \text{sign}\left(\frac{\epsilon_{32}}{\epsilon_{21}}\right)} \right) \right| \quad (\text{C.4})$$

in which $\epsilon_{32}(\mathbf{x}) = \xi_3(\mathbf{x}) - \xi_2(\mathbf{x})$ and $\epsilon_{21}(\mathbf{x}) = \xi_2(\mathbf{x}) - \xi_1(\mathbf{x})$. By averaging $P(\mathbf{x})$ at nodes with monotone convergence (i.e. $\text{sign}\left(\frac{\epsilon_{32}}{\epsilon_{21}}\right) > 0$) the *global* order of convergence (P_G) can be calculated. Finally, the CGI of the fine grid solution is obtained by

$$CGI(\mathbf{x}) = F_s \left| \frac{\xi_1(\mathbf{x}) - \xi_2(\mathbf{x})}{1 - r_{21}^{P_G}} \right| \quad (\text{C.5})$$

in which $F_s = 1.25$ is a conservative factor of safety for a three grid refinement study [61].

Key results of the grid convergence study calculated for the total dispersion tensor is reported in Table C.1.

Table C.1: Grid convergence quantifications for the system explained in Chapter 3.

Pe	ξ	P_G	CGI[%]
100	$D_{A\gamma}$	1.32	2.56

