OSCILLATORY FLOW: EFFECT ON TRANSVERSE DIFFUSIVITY AND INERTIAL MIGRATION OF PARTICLES AND BUBBLES

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

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Notre Dame, Indiana
August 2008
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Abstract

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Oscillatory flow has numerous interesting and useful applications, many of which take advantage of oscillatory flow’s unique features. Two processes which benefit from oscillatory flow are investigated herein: the first, using oscillatory flow to enhance mass transport in a porous medium, and the second, developing separation strategies from the study of inertial migration of particles and bubbles in oscillatory flow.

The effect of oscillatory flow on mass transport in a porous medium was studied both fundamentally, in a model porous medium, and specifically, in the direct methanol fuel cell (DMFC). In the limit where the oscillatory flow could be considered quasi-steady, it was found that the transverse diffusivity of a solute could be predicted accurately using a steady flow model. The transverse diffusivity was observed to increase a factor of $10^4$ over the molecular diffusivity. Enhancement in the transverse diffusivity was observed in the DMFC, where the mass transfer resistance of the system was reduced by superimposing fluid oscillations on the anode feed. The oscillations increased the peak power density by up to 30% and the limiting current density more than twofold. An optimization study was performed which examined the effect of other variables relative to the mass transfer
resistance of the DMFC. A promising alternative use of oscillatory flow in the DMFC was discovered during this study: it assists with carbon dioxide bubble management at low steady feed rates.

Inertial migration of particles and bubbles in oscillatory tube flow was investigated in both the horizontal and vertical orientations. In the horizontal case, particle mobility was controlled by the ratio of the inertial force to the gravitational force and can be predicted using existing steady flow theories. This result suggested a particle/bubble removal technique using an asymmetric oscillatory flow. An asymmetric oscillatory flow was used to remove bubbles in the DMFC and stabilize its performance. In the vertical case, oscillatory flow was used to stabilize or reverse the net drift of non-neutrally buoyant particles. A simple asymptotic model was developed which is consistent with the experimental data and suggests a possible particle separation strategy.
DEDICATION

To Renae and my children
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\( a \) radius of sphere, fiber, particle or bubble
\( A \) amplitude of the sinusoidal pressure gradient
\( A_c \) cross-sectional area of flow conduit
\( A_{ch} \) cross-sectional area of the channel, \( 3wd \)
\( A_e \) active area of the electrode
\( c \) solute concentration
\( C', C_i \) empirical constants used to predict \( i_{lim} \)
\( Ca \) Capillary number, \( \frac{\mu \dot{u} \omega}{\sigma} \)
\( c_b \) bulk concentration
\( c_f \) feed concentration
\( c_M \) methanol concentration in the feed
\( C_o \) characteristic solute concentration
\( c_s \) scaling constant for adapting steady flow models
\( d \) depth of anode channel
\( d' \) distance of particle center to plane
\( D \) depth of packed bed
\( d_{fr} \) depth of flow reversal section
\( d_h \) hydraulic diameter of the channel
\( D_o \) molecular diffusivity of solute
\( D_{o,St} \)  molecular diffusivity calculated by Stokes’ law
\( D_L \)  axial (longitudinal) diffusivity
\( D_T \)  transverse (lateral) diffusivity
\( D_{To} \)  transverse diffusivity in absence of convection
\( D_{yy} \)  transverse diffusivity in the diffusion layer
\( f \)  friction coefficient
\( F \)  Faraday’s constant, \( 9.6485 \times 10^4 \) C/mol
\( F \)  function of \( d'/l' \) calculated by Schonberg and Hinch
\( f(r^*) \)  spatial function satisfying ODE for oscillatory flow in a tube
\( f(y^*) \)  spatial function satisfying ODE for oscillatory flow in a channel
\( f_h \)  homogeneous solution of \( f(r^*) \)
\( F_L \)  lift force acting in the lateral direction
\( f_p \)  particular solution of \( f(r^*) \)
\( g \)  acceleration due to gravity
\( \hat{G} \)  complementary complex pressure gradient
\( G(t) \)  time-varying pressure gradient
\( G_o \)  magnitude of the sinusoidal pressure gradient
\( i \)  current density
\( I_B \)  blue pixel intensity
\( I_G \)  green pixel intensity
\( i_{lim} \)  limiting current density
\( I_R \)  red pixel intensity
\( i_i^{eff} \)  effective mass transfer coefficient in the diffusion layer \( i \).
\( k_{lim} \)  rate constant at high methanol concentrations
\( k_o \)  mass transfer coefficient not due to the diffusion layer
$k_{tot}$  total mass transfer coefficient

$l$  characteristic length scale

$l'$  channel width

$L$  length of packed bed

$L_{ch}$  length of the channel

$L_{fr}$  length of the flow reversal section

$l_i$  thickness of diffusion layer $i$

$L_{t}$  length of the tube

$L_{tot}$  total anode channel length

$n$  counter in infinite series or sum

$P$  pressure

$P, P^\dagger$  adapted mobility functions

$\Delta P$  pressure drop over anode channel length

$(p_1, p_2, p_3)$  fitting coefficients for quadratic model

$\Delta P_a$  change in pressure due to actual stroke displacement

$P_{atm}$  atmospheric pressure

$\Delta P_{ch}$  pressure drop in the channel

$Pe$  Peclet number, generally $\frac{U}{D_o}$; in diffusion layer, $\frac{U_{dl}}{D_o}$

$\hat{P}e$  root mean square Peclet number

$\Delta P_{fr}$  pressure drop in the flow reversal section

$Pe_{sc}$  screening length Peclet number, $\frac{U_{sc}}{D_o}$

$\langle |\frac{\partial P}{\partial x}|\rangle$  time-averaged magnitude of the oscillatory pressure gradient

$Q$  flow rate

$Q_{an}$  anode steady feed rate

$Q_{an,min}$  minimum anode feed rate required

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$Q_c$  cathode feed rate
$Q_o$  amplitude of oscillatory flow rate
$Q_s$  steady feed rate
$Q(t)$  oscillatory feed rate
$r$  radial position
$r^\dagger$  equilibrium radial position
$r^*$  dimensionless radial position, $r/R$
$\Delta r$  fluctuation in radial position from $r^\dagger$
$R$  tube radius
$R_c$  channel Reynolds number from Schonberg and Hinch, $\frac{U_{ml}}{\nu}$
$Re$  Reynolds number, generally $\frac{U}{\nu}$
$\widehat{Re}$  root mean square Reynolds number
$\langle Re \rangle$  time-averaged Reynolds number, $\frac{\langle U \rangle d}{\nu}$
$Re_{max}$  maximum Reynolds number, $\frac{U_{max} d}{\nu}$
$Re_\omega$  frequency Reynolds number, $\frac{\omega d_s^2}{\nu}$
$Re_p$  particle Reynolds number
$R_p$  particle Reynolds number from Schonberg and Hinch
$Re_s$  sedimentation Reynolds number
$t$  time
$u$  scalar velocity
$\vec{u}$  velocity vector $(u_x, u_y, u_z)$
$\hat{\vec{u}}$  complementary complex velocity
$U$  characteristic velocity
$\overline{U}$  average velocity
$\tilde{U}$  general magnitude of oscillatory velocity
\( \langle U \rangle \)  
- time-averaged velocity

\( U_{dl} \)  
- velocity in the diffusion layer

\( U_f \)  
- fluid velocity

\( u_L \)  
- migration velocity of Vasseur and Cox

\( U_m \)  
- centerline velocity

\( U_{max} \)  
- maximum oscillatory velocity, \( \Delta V/A_{ch} \)

\( U_o \)  
- amplitude of oscillatory velocity, \( \frac{\Delta x \omega}{2} \)

\( U_p \)  
- particle velocity

\( \langle U_p \rangle \)  
- particle drift velocity

\( \langle U_p \rangle^* \)  
- dimensionless particle drift velocity: \( \frac{(U_p-U_s)}{\Delta x \omega} \)

\( \langle U_p \rangle_{max} \)  
- maximum particle drift velocity

\( U_{rms} \)  
- root-mean squared velocity

\( U_s \)  
- Stokes sedimentation velocity

\( U_{slip} \)  
- slip velocity

\( \Delta V \)  
- stroke volume

\( V_b \)  
- bubble volume

\( V_b^* \)  
- dimensionless bubble volume, \( V_b/2\pi R^3 \)

\( \Delta V_b \)  
- change in bubble volume

\( u_L \)  
- migration velocity of Segré and Silberberg

\( W \)  
- width of packed bed

\( w \)  
- width of anode channel

\( w_{fr} \)  
- width of flow reversal section

\( W_p^* \)  
- migration velocity of Schonberg and Hinch

\( x \)  
- coordinate parallel to the flow direction

\( \Delta x \)  
- stroke length
\(\Delta x^*\)  dimensionless amplitude of oscillatory tube flow
\(\Delta x_{\text{asym}}\)  stroke length of an asymmetric oscillation
\(\Delta x_f\)  displacement in the forward direction
\(\Delta x_{\text{max}}\)  maximum particle displacement
\(\Delta x_o\)  amplitude of a steady parabolic tube flow
\(\Delta x_p\)  displacement of a particle or bubble
\(\Delta x_r\)  displacement in the reverse direction
\(y\)  coordinate perpendicular to the flow direction
\(z\)  lateral coordinate across channel

**Greek letters**

\(\alpha\)  Womersley number, \((\frac{\omega}{l})^{1/2}\)
\(\alpha^*\)  dimensionless particle size for a channel, \(a/l\)
\(\gamma\)  aspect ratio, \(d/w\)
\(\gamma^*\)  dimensionless shear rate, \(\dot{\gamma}l/U_m\)
\(\dot{\gamma}_w\)  characteristic wall shear rate
\(\delta\)  open area ratio
\(\epsilon\)  absolute wall roughness
\(\epsilon_s\)  dimensionless surface roughness
\(\eta\)  small \(Pe\) coefficient from Koch and Brady
\(\kappa\)  Darcy permeability
\(\kappa_e\)  estimated theoretical permeability
\(\kappa_T\)  effective transverse diffusivity, \(D_T/D_o\)
\(\lambda\)  large \(Pe\) coefficient extracted from steady flow models
\(\hat{\lambda}\)  magnitude of \(\hat{G}\); \(\hat{G} = \hat{\lambda}e^{it^*}\)
\(\lambda_{SH}\)  constant from Schonberg and Hinch
\( \lambda_{VC} \) constant from Vasseur and Cox
\( \mu \) viscosity of the carrier/working fluid
\( \mu_f \) coefficient of friction
\( \nu \) kinematic viscosity of the carrier/working fluid
\( \rho \) density of the carrier/working fluid
\( \rho_p \) density of the particle/bubble
\( \Delta \rho \) density difference between fluid and particle/bubble
\( \sigma \) surface tension
\( \sigma^2 \) variance of \( \chi \) distribution
\( \tau_w \) wall shear stress
\( \Upsilon \) geometric/convective adjustment to diffusivity
\( \phi \) solid fraction
\( \chi \) volume fraction of red dye
\( \bar{\chi} \) volume fraction of red dye averaged over the channel width
\( \Psi \) mechanical power
\( \Psi_{min} \) minimum mechanical power density, \( \frac{\Psi}{\chi_c} \)
\( \Psi_o \) steady flow peak power density
\( \Psi_{osc} \) oscillatory flow peak power density
\( \Psi_{ph} \) power density required to pre-heat the anode feed
\( \omega \) angular frequency
\( \omega_f \) frequency or the forward stroke
\( \omega_r \) frequency of the reverse stroke
ACKNOWLEDGMENTS

First and foremost, I would like to thank my wife, Renae, for her support over the years while I’ve been continuing my education. She helped me stay focused on the prize but also supplied moments of much needed levity. My children, though they are ignorant of it all, have also been valuable sources of stress relief and daily reminders of the importance of pressing on. My parents, grandparents, and all my sisters were sources of encouragement which never wavered and constantly reminded me of where I came from.

I am very thankful to Dr. Leighton, who taught me both what to learn and how to learn it. I hope I can come to bring the same energy to the scientific process that he does. His teaching, encouragement, and support during my work were integral to my development as a scientist.

I am grateful to Dr. Paul McGinn, whose equipment I was able to use to further my study of the direct methanol fuel cell. During the course of learning the assembly and operation of the fuel cell, the assistance of Dr. Tim Hall and Brian Seger was invaluable. I am further indebted to Dr. Hall for helping me obtain SEM images when I required them. I am very appreciative of Jim Smith and Jim Kirksey’s efforts, either in helping me create some of my equipment from scratch or keeping old apparatuses in working order.

The assistance of Colin Fath in collecting some of the data in section 5.3.1.2—specifically Figure 5.17—was very helpful as I neared the end. Likewise, the use
of the DMFC equipment of Michael Lundin and Dr. Mark McCready was greatly appreciated.

I would be remiss if I didn’t mention some of my lab mates, past and present, who offered advice and helpful discussion throughout my time at Notre Dame: Arun, Mike, and Eric. Many of Dr. Chang’s students were also helpful; the lively discussions and facilitation of a symbiotic lab equipment exchange program were indispensable. There are many others, either in the department, elsewhere on campus, or in the community at large who helped me in some way over the last five years. To all of you I am grateful.

Finally, I would like to acknowledge the agency which supported my work, the United States Army CECOM RDEC through Agreement No. DAAB07-03-3-K414.
CHAPTER 1

INTRODUCTION

Oscillatory flow has been studied for many decades. Historically, most early studies on oscillatory flow, including the seminal work of Womersley where the velocity profile of oscillatory flow was first calculated [149], were concerned with modeling arterial blood flow (see also McDonald [95] or Hale et al. [51]). Since the calculation of Womersley, many applications of oscillatory flow to other engineering problems have been investigated. Examples demonstrating the widespread applicability of oscillatory flow abound: “split-energy” pumping techniques [34], studies on sea beds and tidal environments [132, 142], electrochemical reactors [16], soils [98], biofilms [97], ultrafiltration [62] and respiratory systems [43, 131].

The primary objective of this dissertation was to examine the application of oscillatory flow to two problems: transverse mass transport in porous media (and by extension, in a fuel cell) and the inertial migration of particles and bubbles (which has implications for various separation techniques).

There are many examples of mass transfer processes which have benefited from the use of oscillatory flow. After the initial theoretical development of Aris [10] for the dispersivity of tracers in an oscillatory tube flow, the potential for mass transport enhancement in separation techniques was noted [59, 60] and demonstrated experimentally for a pulsed column [75]. Later, mass transport enhancement via oscillatory flow was studied for numerous geometries: a curved tube [33], a flexible
tube [32], a tube with conductive walls [67], a periodically obstructed channel [61], wavy or grooved channels [100–102], and baffled tubes or columns [99]. Studies for specific separation processes are also abundant, including supported liquid membranes [20, 84], gas separations [63, 139], and liquid absorption columns [27, 80]. These studies are overwhelmingly concentrated on transport enhancement or separation techniques in the flow direction, and thus are concerned with the effect of oscillatory flow on solute transport in the same direction as the flow. Of specific interest in this work is the transverse mass transport enhancement obtained when an oscillatory flow is induced in a porous medium, which has several potential applications for separation and reaction processes. At the time of this writing, a study of oscillatory flow and transverse mass transport in a porous medium had not been found.

The inertial migration of particles, drops and bubbles is an interesting phenomenon with implications for a large class of fluid systems, such as suspensions, blood, and gas-liquid flows. The field has attracted a lot of interest originating with the work of Segré and Silberberg [123, 124], who found that a neutrally buoyant particle will obtain an equilibrium position in a steady flow which is roughly 3/5ths of the distance between the axis of a tube and its wall. The lateral migration of particles, which occurs regardless of its initial position, originates from an inertial lift force on the particle. The effect of the migration significantly impacts the processing of multiphase flows which contain particles, drops, and bubbles, as the rheology of the fluid will depend on its phase distribution. Experiments using oscillatory flow, such as the series on suspensions by Goldsmith, Mason and others [128, 136, 137] or the more recent work of Einav and Lee [35], illustrate some of the features of the inertial migration of particles but do not probe the limits
of the available parameter space. Studies of drops or bubbles are more limited, being confined to a set of experiments in microgravity [38] and a general theoretical development [91, 92]. Theories for either particle or bubble migration in an oscillatory flow are rare; those that do exist have been developed for geometries which do not translate to the tube geometry considered here.

Oscillatory flow studies for the two fields of interest introduced above are scarce compared to steady flow studies, which are plentiful. Recognizing this, this dissertation focuses on oscillatory flows which are well approximated by time-averaging or quasi-steady models. This approach serves two purposes: (1) much of the analysis is simplified while still describing the behavior accurately, and (2) it allows comparison with existing steady flow theories and experiments in the appropriate limits. Oscillatory flow was approximated as steady provided the stroke displacement was greater than the length scale of the geometry containing the flow. This assures that the fluid was traveling a distance greater than the relevant length scale with each stroke. In experimental systems where this was important, the specific criterion for each system will be given explicitly in the corresponding chapter.

In addition to this constraint, many of the steady flow theories are developed for the creeping flow limit. For steady flows, creeping flow occurs when the Reynolds number $Re \ll 1$; however, for oscillatory flow a second dimensionless parameter is also important: the Womersley number, $\alpha$. The generation method for the oscillatory flow in all the experiments described herein is volume displacement; therefore, the pressure gradient is unknown. A volume $\Delta V$ was displaced using a sinusoidal stroke of angular frequency $\omega$, so provided that the frequency is small compared to the viscous response time of the fluid the velocity ($i.e.$ small
α), the flow can be described by the simple expression

\[ u = \tilde{U} \sin(\omega t), \tag{1.1} \]

where \( \tilde{U} \) will be a function of \( \omega, \Delta V \), and the geometry the flow occurs in. If \( \alpha \) is not small, Equation 1.1 will not be valid; more complicated transient behavior will be present and the fluid does not simply modulate sinusoidally.

Clearly, the same considerations must be made if the flow is not creeping. In the smaller geometries considered in parts of this dissertation, the fluid velocity became quite large. As with any inertial flow, the possibility that the flow was becoming turbulent needed to be considered. The criterion for turbulence in oscillatory flow is not based upon the value of the Reynolds number alone as it is for steady flows. Instead, the critical Reynolds number for transition to turbulence is a function of \( \alpha \). Many experimental studies on oscillatory turbulence have been performed over the decades: see, for example, Yellin [37], Hershey and Im [54], Hino et al. [56], Ohmi and Iguchi [106] or Zhao and Cheng [164]. For cases where it became necessary to determine if there was an onset of turbulence, the relationship given by Walther et al. [144] was used since it synthesized several of these studies into a single criterion with validity over a wide range of \( Re \) and \( \alpha \).

The remainder of this dissertation will proceed as follows. In chapter 2, an experimental study of diffusivity in the presence of an oscillatory flow in a porous medium is described. A randomly ordered model porous medium was designed to permit observation of tracer diffusivity by image analysis. The oscillatory parameters were carefully chosen so that the stroke length was much greater than the size of the pores, and thus the flow was approximated as steady. This approximation permitted direct comparison with existing steady flow models for transverse dif-
fusivity. The agreement was found to be quite good as the Peclet number became large. Mass transport enhancement in the transverse direction was observed on the order of $10^4$ relative to molecular diffusion.

Chapters 3 and 4 are concerned with the application of oscillatory flow to performance in the direct methanol fuel cell. The fuel cell study follows directly from the results of chapter 2. The performance of a fuel cell is limited by the mass transfer resistance of the anode diffusion layer. The diffusion layer is a porous medium which is designed to improve gas management of the fuel cell and promote electrical contact between the electrode and the current collectors. In chapter 3 it will be demonstrated that superimposing an oscillatory flow on the anode steady feed reduced or eliminated the mass transfer resistance of the diffusion layer. The oscillatory flow enhanced the mass transport of methanol traveling to the anode catalyst in the direction transverse to the flow, just as was observed in the experiments of chapter 2. A simple one-dimensional model was developed to predict the limiting current density, an important measurement of fuel cell performance. The second part of the fuel cell study contained in chapter 4 focused on finding an optimum range of operating parameters where the oscillatory flow was most effective. The effect of various parameters on performance, particularly in the mass transfer limitation regime, was explored. A second benefit of using oscillatory flow in the fuel cell was discovered in the optimization study which is related to the management of carbon dioxide gas which is produced at the anode.

In chapter 5, the inertial migration of particles and bubbles in an oscillatory tube flow is examined. The migration phenomena are investigated in two parts: in the first, a tube in a horizontal orientation was considered; in the second, the tube was orientated vertically. In the horizontal tube, the mobility of
non-neutrally buoyant particles was found to have a rich behavior which was primarily a function of the ratio of the inertial force to the buoyancy force in the system. The particles behaved as they would in steady flow provided the Womersley number was small, and predictions based on steady flow models described the experimental mobilities well. Bubbles, if they were small enough, behaved in the same manner as particles. In practice this limit was difficult to access since a second drift mechanism due to bubble deformation will be important at finite Capillary number. An asymmetric oscillatory pumping method was demonstrated to have potential as a particle/bubble separation or removal technique. Vertical tube experiments with neutrally buoyant particles illustrated how the mobility changes with finite $Re$. The mobility of non-neutrally buoyant particles was observed to be a complex interaction between the lift due to the fluid inertia and the particle’s slip velocity. One result of this effect was the ability to “force” the particles to move in a direction opposite their settling velocity using a properly tuned oscillatory flow. Criteria for a potential particle separation technique using oscillatory flow in a vertical tube are discussed. Bubbles were found to be too buoyant in the vertical alignment to significant affect their mobilities.

The final chapter summarizes the major results of this dissertation and discusses future directions for research based on the investigations of the previous chapters.
CHAPTER 2

OSCILLATORY FLOW AND TRANSVERSE DIFFUSIVITY IN POROUS MEDIA

2.1 Introduction

The dispersive phenomenon that occurs when a solute is subjected to a constant pressure gradient in a cylindrical tube is well known \[9, 138\]. The spreading of a solute in the flow-direction came to be known as Taylor-Aris dispersion; later, it was extended to oscillatory flow in a tube \[10\] and channels of arbitrary cross-section \[36\]. In all these cases, it was found that the diffusivity of a solute was enhanced by the convective motion of the fluid, and, somewhat counterintuitively, depended on the inverse of the molecular diffusion coefficient \(D_o\). The enhanced diffusivity has the general form

\[
\frac{D_L}{D_o} = 1 + \Upsilon; \quad (2.1)
\]

where \(D_L\) is the diffusivity in the axial (flow) direction and \(\Upsilon\) is a function of the flow type and geometry. For steady flow in a pipe with a characteristic length scale (typically the diameter) and velocity of \(l\) and \(U\), respectively, \(\Upsilon = Pe^2/48\). The Peclet number \(Pe\) is a measure of the ratio of the convective time scale \(l/U\) to the diffusive time scale \(l^2/D_o\). Oscillatory flow in a pipe modifies \(\Upsilon\) to include a dependence on two flow parameters: the frequency \(\omega\) and the stroke volume \(\Delta V\).
Dispersion in pulsatile flow has been shown to have an additive behavior, and the steady and oscillatory flow results can be linearly combined.

It is quite clear from Equation 2.1 that $D_L > D_o$ provided $\Upsilon > 1$. This condition is easily satisfied for a wide range of systems, and liquids in particular, because $D_o$ is typically on the order of $10^{-6}$ cm$^2$ s$^{-1}$. Physically, the enhancement in $D_L$ occurs because fully developed steady pipe flow has a parabolic velocity profile. Though the solute is free to diffuse across streamlines, this process will be slow with respect to the bulk fluid flow when $\Upsilon \gg 1$, and a group of solutes which were initially highly concentrated will be spread out over time as they are convected downstream on streamlines of different velocities. The enhancement in $D_L$ when the pipe flow is oscillatory is more complicated; however, if $\Delta V/A_c \gg l$ ($A_c$ being the cross-sectional area of the pipe) and $\omega \ll l^2/\nu$, it will be similar to steady flow.

Of more interest in this chapter and the accompanying experimental work is the transverse diffusivity $D_T$. For steady or oscillatory pipe flow, $D_T$ is not governed by Equation 2.1. The flow is unidirectional in the cylindrical geometry and thus solutes can only access different radial positions in the tube by molecular diffusion alone. Since liquid systems will typically operate at conditions where $Pe \gg 1$, $D_L \gg D_T$. Enhancements in the transverse diffusivity can only arise when additional asymmetries in either the flow field or the geometry are present.

Similar experimental studies of solute diffusivity for oscillatory flow in porous media are not known at the time of this writing. Oscillatory flow in porous media has only been treated theoretically in a spatially periodic geometry by Dill and Brenner [31]. Though Dill and Brenner did note the possibility of using steady flow predictions for the diffusivity in the limit of low $\omega$, their development
will, by definition, result in a transverse diffusivity that is identically zero. The limited information that is available for oscillatory flow is concerned with the measurement of $D_L$ or similar quantities. For example, oscillatory flow has been demonstrated to improve the mass transport in a porous system along the axis of flow in packed column separations [64, 80]. Oscillatory flow has also been used to significantly improve the performance of supported liquid membranes when the mass transport is in the flow direction [20, 84]. Enhanced transverse mass transport could potentially improve performance in a wide variety of applications. One such example of transverse transport enhancement for the analogous heat transfer problem in a channel filled with metal foam has already been described [85]. However, little is known about the transverse diffusivity of passive solutes in a oscillatory flow in porous media. Understanding the transport mechanisms which govern dispersive behavior is important when designing improved fluid transport, reaction, or separation processes that occur in porous media. This motivated an experimental survey of transverse dispersivity in a porous medium in order to study the influence of relevant dimensionless quantities in the system.

The remainder of this chapter will describe the experimental study in more detail. In section 2.2, the relevant dimensionless parameters will be introduced and the merits of using existing steady flow models for oscillatory flow will be discussed. Section 2.3.1 contains a brief description of the how the experiments were performed. In section 2.3.2, the methodology for calculating $D_T$ from the experimental data is described. Section 2.4 presents the results of the study; in particular, the dependence of $D_T$ on $\omega$ and the Peclet number is discussed. The final section will summarize the conclusions of this study.
2.2 Dimensional Analysis

The primary objective of this work was to observe and describe transverse dispersion in a porous media when an oscillatory flow is present. A few experimental studies of axial dispersive phenomena have been performed for oscillatory flow [27, 59], but the case of transverse dispersivity has not been studied in detail. In this study, a randomly packed bed of spheres of diameter $2a$ were confined in a rectangular channel of dimensions $L \times W \times D$ ($L$ is the length, $W$ the width, and $D$ the depth). The dimensions are such that $L \gg W \gg D$, with $D \approx 2a$, so for mass transfer purposes the packed bed can be considered to be two-dimensional. Despite this simplification, the flow field is still three dimensional and several dimensionless parameters will be important in governing the mass transport behavior.

In the experiments the parameters which are varied are $\Delta V$ and $\omega$, and they are used to described a fluid velocity. Instead of the stroke volume, the stroke length $\Delta x$ is a more convenient parameter and is written as

$$\Delta x = \frac{\Delta V}{WD} = \int_0^\pi U_o \sin (\omega t) \, dt \quad (2.2)$$

where $U_o$ is an unknown characteristic magnitude of the velocity and $\pi/\omega$ is a half-period. Note that this is a “superficial” stroke length based on an unpacked cross-section of the channel. The true $\Delta x$ will be larger and depends on an accurate determination of the cross-sectional pore area, which is difficult in the experimental geometry and may vary with position. The stroke length as defined in Equation (2.2) was chosen in order to both simplify the analysis and to be consistent with existing steady flow theories which will be described later in the chapter.
Evaluating Equation 2.2 gives

$$\Delta x = \left| \frac{-U_o \cos(\omega t)}{\omega} \right|_0^{\pi} = - \left( \frac{U_o}{\omega} (-1) - \frac{U_o}{\omega} (1) \right) = \frac{2U_o}{\omega},$$

(2.3)

which defines the characteristic velocity as $U_o = \Delta x \omega / 2$. This, however, is not an average velocity but the amplitude of the velocity. Since the flow is oscillatory, the appropriate characteristic velocity is the root mean squared average velocity

$$U_{rms} = \sqrt{\frac{\omega}{2\pi} \int_0^{2\pi} (U_o \sin(\omega t))^2 \, dt} = \frac{U_o}{\sqrt{2}} = \frac{\Delta x \omega}{2\sqrt{2}},$$

(2.4)

In the rest of this chapter, unless stated otherwise, when reference is made to the velocity of the fluid, this velocity is the root mean squared velocity given by Equation 2.4.

Assuming the oscillatory flow is Newtonian and incompressible, the Navier-Stokes equations will govern the $\vec{u}$ (velocity) and $P$ (pressure) fields in the pores of the porous medium. In dimensional vector form, the equations of momentum and continuity are written

$$\rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla P + \mu \nabla^2 \vec{u}$$

(2.5)

$$\nabla \cdot \vec{u} = 0$$

(2.6)

where $\rho$ is the fluid density and $\mu$ the dynamic viscosity of the fluid, each of which is constant. A sinusoidal pressure gradient drives the flow, so $\nabla P = G_o \sin(\omega t)$, where $G_o$ is the amplitude of the pressure gradient. The following dimensionless
parameters are defined:

\[ \vec{u}^* = \frac{\vec{u}}{U_{rms}} \; ; \; t^* = \omega t \; ; \; \vec{\nabla}^* = \vec{\nabla} a \; ; \; P^* = \frac{P}{\mu U_{rms}/a} \; ; \]

where \( a \) is the radius of the particles packing the channel bed. Substituting these quantities into Equation 2.5 yields the dimensionless equation

\[
 \left( \frac{\omega a^2}{\nu} \right) \frac{\partial \vec{u}^*}{\partial t^*} + \left( \frac{U_{rms} a}{\nu} \right) \vec{u}^* \cdot \vec{\nabla}^* \vec{u}^* = -\sin t^* + \nabla^{2} \vec{u}^*, \tag{2.7}
\]

where \( \nu \) is the kinematic viscosity \( \mu/\rho \). The quantity \( \omega a^2/\nu \) is the square of the Womersley number (commonly denoted by \( \alpha \)) and \( U_{rms} a/\nu \) is the Reynolds number \( \hat{Re} \). The Reynolds number is the ratio of inertia and viscous forces, which characterizes the flow, and \( \alpha \) compares the time it takes for momentum to diffuse to the time it takes to generate the momentum. Equation 2.7 can be rearranged to give

\[
 \hat{Re} \left[ \left( \frac{\omega a}{U_{rms}} \right) \frac{\partial \vec{u}^*}{\partial t^*} + \vec{u}^* \cdot \vec{\nabla}^* \vec{u}^* \right] = -\sin t^* + \nabla^{2} \vec{u}^*; \tag{2.8}
\]

the quantity \( \omega a/U_{rms} \) is an important dimensionless length scale which compares the distance the fluid travels with each stroke (\( \Delta x \)) to the sphere radius. It can be thought of as the number of spheres (or more significantly, different pores) the average flow “sees” before flow reversal. If \( \omega a/U_{rms} \gg 1 \), the flow is approximately steady. If the condition \( \hat{Re} \ll 1 \) is also satisfied, Equation 2.8 reduces to the Stokes equation. Since the radius of the spherical packing \( a \) was chosen as the length scale, the flow can be locally quasi-steady and still be unsteady on a larger scale, such as the length of the packed bed \( L \). If \( \alpha^2 \) grows large, the unsteady term \( \partial \vec{u}^*/\partial t^* \) on the left hand side of Equation 2.8 will dominate the viscous terms on the right hand side and the flow will be out of phase with the pressure gradient.
Note that the flow field can be approximately steady \((\omega a/U_{rms} \gg 1)\) but still have significant inertia (finite \(\hat{Re}\)); in this case, Equation 2.8 is non-linear and simple analytical solutions for \(\vec{u}^*\) will be difficult to obtain. The preceding dimensional analysis of the Navier-Stokes equations demonstrates that both \(\hat{Re}\) and \(\omega a/U_{rms}\) are important quantities for the experimental system of this chapter.

In a mass transfer problem, the Navier-Stokes equations must be coupled with the convective-diffusive equation to fully describe the solute’s behavior. For a dilute system of solutes, Fick’s law of diffusion is assumed to be valid and the equation governing the concentration field \(c\) can be written as:

\[
\frac{\partial c}{\partial t} + \vec{u} \cdot \vec{\nabla} c = D_o \nabla^2 c .
\] (2.9)

Using the same scalings which rendered Equation 2.7 dimensionless, along with the additional dimensionless quantity \(c^* = c/C_o\), and substituting them into Equation 2.9 gives

\[
\frac{\omega a}{U_{rms}} \frac{\partial c^*}{\partial t^*} + \vec{u}^* \cdot \vec{\nabla}^* c^* = \left( \frac{D_o}{U_{rms}a} \right) \nabla^2 c^* ,
\] (2.10)

where the quantity \(D_o/(U_{rms}a)\) is the inverse of the Peclet number \(\hat{Pe}\). \(\hat{Re}\) and \(\hat{Pe}\) differ by the constant \(\nu/D_o\), which is the Schmidt number. The Peclet number, as defined, is the ratio of the convective time scale to the diffusive time scale at the microscopic (pore) level. Therefore, if \(\hat{Pe} \gg 1\), convection is the dominant mass transfer mechanism in Equation 2.10. The dimensionless parameter \(\omega a/U_{rms}\) effects the convective-diffusive equation in the same way as the Navier-Stokes equation, which must be true in a system where the dominant mass transfer mechanism is convection: if \(\omega a/U_{rms} \gg 1\), the concentration field will be approximately steady. The large \(\hat{Pe}\) limit was the target parameter range for the
oscillatory flow experiments, as it conveniently coincides with the quasi-steady
limit $\omega a/U_{rms} \gg 1$.

One measure of the convective mass transport enhancement is to calculate
the effective transverse diffusion coefficient $\kappa_T$, which for these experiments is the
ratio of the observed transverse diffusivity $D_T$ to $D_o$. As noted above, oscillatory
flow dispersive behavior in porous media should approach steady flow behavior
in the limit of large $\omega a/U_{rms}$. Steady flow dispersion in porous media has been
a field of significant historical interest, and past studies offer several models with
which the oscillatory results can be compared.

One of the first steady flow models was an asymptotic analysis at “sufficiently
small” $D_o$ developed by Saffman [113], which he later revised to include the effect
of finite $D_o$ [114]. The model considers the porous medium to be a network of
randomly orientated capillaries in which a Darcy’s law relationship between the
pressure gradient and velocity is valid. When the Peclet number based on the
length of the capillaries is large, Saffman’s expression for $\kappa_T$ is given as

$$\kappa_T = \frac{3}{16} \frac{Ua}{D_o} = \frac{3}{16} Pe.$$  \hfill (2.11)

Equation (2.11) contains an additional assumption which differs from Saffman’s
original work. It assumes that the length of a capillary pore is approximately
equal to the radius of a sphere in a packed bed, an approximation that will al-
low comparison with experiment. Saffman’s model for the transverse dispersivity
illustrates the simple relationship that is expected as $Pe \gg 1$: the dispersivity
will depend linearly on $Ua$, a phenomenon which is often called mechanical dis-
persion. Even though the model was based on flow in capillaries and $D_T \sim D_o$ in
a tube flow, $D_T$ is convectively enhanced in a porous medium. The enhancement
in $D_T$ arises from the random orientation of the capillary network, which induces perturbations in the flow field and allows the solute to sample many streamlines even if $D_o$ is small. At the time, Saffman was unable to validate Equation 2.11 due to the lack of experimentally measured values of $D_T$.

In a later work by Koch and Brady [73], agreement was obtained with experimental work both before [40, 47] and after [109] their theoretical development. Koch and Brady performed an ensemble average of the macroscopic transport equations over a random porous medium composed of discrete spheres. Again, in the limit that $Pe \gg 1$,

$$\kappa_T = \frac{63}{320} \sqrt{2\phi Pe}$$  \hspace{1cm} (2.12)$$

where $\phi$ is the solid fraction of packing in the porous media. Equation 2.12 was developed in the limit of low $\phi$ but predicted $\kappa_T$ quite well for porous media with $\phi > 0.5$. The similarity between Equations 2.12 and 2.11 is significant because they were calculated by different asymptotic approaches for random porous media but are in good agreement. A large number of other theoretical studies are available; however, the models given by Equations 2.12 and 2.11 are preferred in this study, as they were developed for random porous media, whereas other theoretical frameworks [15, 50] require the media to be periodically ordered.

For the sake of completeness, both an empirical model developed from several sets of experiments in a randomly packed bed over a wide range of flow parameters [29, 44, 46] and a correlation developed from a numerical study [14] were also compared to the oscillatory flow data. As $Pe \gg 1$, the empirical model asymptotes to

$$\kappa_T = \frac{1}{6} Pe.$$  \hspace{1cm} (2.13)$$

The correlation is a power law fit to simulations of a two-dimensional disordered
media with larger scale periodicity. The asymptotic expression which is valid when
\( Pe (1 - \phi) / \phi \geq 10 \) is:

\[
\kappa_T = 0.1699 \left( \frac{1 - \phi}{\phi} \right)^{0.90} Pe^{0.90}.
\]

Equations 2.13 and 2.14 have the same functionality as the theoretical models. The slight discrepancy of Equation 2.14 from the expected linear scaling with \( Pe \) is likely due to the construction of the numerical model; the packing used in the simulation is composed of discs instead of spheres and there is long-range order in the simulated porous medium. The asymptotic expressions described by Equations 2.11–2.14 can all be recast as \( \kappa_T = \lambda Pe \). The coefficient \( \lambda \) may be a function of \( \phi \) but for \( 0.4 \leq \phi \leq 0.6 \) (values of \( \phi \) which are consistent with “real” porous media), the models all converge to values of \( 0.1 \leq \lambda \leq 0.2 \).

As mentioned above, enhancement in \( D_T \) (i.e. \( \kappa_T > 1 \)) is not expected in an ordered system. If a porous media has a randomly distributed network of pores, previous work has shown that \( \kappa_T \sim \lambda Pe \) when \( Pe \gg 1 \) in a steady flow. Equation 2.8 illustrates that if \( \omega a / U_{rms} \gg 1 \), an oscillatory flow can be well-approximated by a steady flow at the pore scale. Based on these considerations, a quasi-steady, convection-dominated mass transfer regime was the asymptote the experimental study was designed to investigate. The effect of the porous medium’s order and variation in \( \widehat{Re} \) and \( \alpha \) on the mass transport behavior were briefly explored.
2.3 Experiment

2.3.1 Material and Apparatus

A series of experiments designed to observe the behavior of mass transfer in a porous media were performed in a rectangular flow cell depicted in Figure 2.1. The cell was composed of two transparent polycarbonate plastic plates. The bottom plate had a channel cut into it with the following dimensions: a length of 61.7 cm, \( W = 2.5 \) cm, and \( D = 0.15 \) cm. Grooves cut on each side of the channel contained O-rings that sealed the flow system. The top plate had 0.635 cm NPT fittings drilled into the ends to facilitate flow. The two plates were held together using 3.81 cm C-clamps. Before the plates were joined together, the channel was packed using 0.15875 cm white Teflon spheres. For the majority of the experiments, a random packing of spheres (example: Figure 2.2) formed the experimental porous media \((L = 25.1 \text{ cm})\). A limited number of experiments were also performed using an ordered packing (example: Figure 2.3); the smaller void fraction reduced the bed length \((L = 15.3 \text{ cm})\). The channel bottom was lined with a thin coat of glycerin to hold the spheres in place until the top plate was tightened down and sealed. An approximately 0.5 cm long section of open cell foam was placed just after the inlet flow port to promote uniform flow into the porous media. Silicone sealant was used on each end to seal the channel. Capillary tubing was threaded through the sealant and foam on the inlet side and mated with a 1 cm³ syringe. The syringe was used to introduce solutions of solute.

After the plates had set for 24-36 hours to allow the sealant to dry, the residual glycerin was washed out with the working fluid using a peristaltic pump at a flow rate of approximately 3 cm³ s⁻¹. The majority of the experiment used distilled water as the working fluid. Water was pumped through the channel continu-
Figure 2.1. Top and side view of the experimental flow cell. The arrangement of the spheres is representative and does not reflect the actual packing geometry.

Obviously for long periods of time to reduce the presence of air bubbles. For all of the experiments performed in water, a few drops of the surfactant Triton X-100 was also added to promote wetting of the Teflon spheres and further reduce bubbles. Other experiments used solutions of 50/50% water/glycerine and 25/75% water/glycerine (by weight percent). These experiments coincided with the use of an ordered packing. The ordered packing was a hexagonal close packing.

The solute was prepared by combining a small portion of the working fluid, approximately 3.0% (by weight) NaCl, and 1.0–1.5% (by volume) red food coloring. When the channel was sufficiently clear of bubbles, the peristaltic pump was turned off and the channel was placed on its side so the $y$ axis was aligned with gravity; the end with the protruding capillary injection port was raised approximately 40 cm above the other end. Approximately 0.15-0.20 cm$^3$ of the dyed salt-water solute was then injected into the channel using the capillary tube.
Figure 2.2. Captured video image of the randomly packed porous media $(1 - \phi = 0.614)$.

Figure 2.3. Captured video image of the ordered, hexagonal close packed porous media $(1 - \phi = 0.481)$. 
TABLE 2.1
OSCILLATORY FLOW PARAMETERS USED IN THE POROUS MEDIUM EXPERIMENTS

<table>
<thead>
<tr>
<th>Set</th>
<th>$\Delta V$ (cm$^3$)</th>
<th>$U_{rms}$ (cm s$^{-1}$)</th>
<th>$Re \left( \frac{U_{rms} a}{\nu} \right)$</th>
<th>$Pe \left( \frac{U_{rms} a}{D_o} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.44</td>
<td>0.05–15.4</td>
<td>0.4–127</td>
<td>9.5×10$^2$–3.2×10$^5$</td>
</tr>
<tr>
<td>B</td>
<td>0.79</td>
<td>0.09–28.5</td>
<td>0.7–235</td>
<td>1.8×10$^3$–5.9×10$^5$</td>
</tr>
<tr>
<td>C</td>
<td>0.08</td>
<td>0.01–2.8</td>
<td>0.1–24</td>
<td>1.8×10$^2$–6.0×10$^4$</td>
</tr>
<tr>
<td>D</td>
<td>0.17</td>
<td>0.02–5.8</td>
<td>0.1–48</td>
<td>3.6×10$^2$–1.2×10$^5$</td>
</tr>
</tbody>
</table>

The solution was allowed to flow by gravity along the bottom edge of the channel, thereby creating an initial distribution of the solute. The flow cell was then placed back in its original (horizontal) configuration and the video camera moved into position. The camera recorded the behavior of the red-dyed solute once the oscillatory syringe pump was turned on. The pump generated an oscillatory flow in the $x$ direction, perpendicular to the direction of the measured diffusivity ($y$). The syringe pump was capable of angular frequencies in the range $0.1$ rad s$^{-1}$ \( \leq \omega \leq 38.8 \) rad s$^{-1}$. The various stroke volumes and corresponding parameter ranges tested in these experiments are given in Table 2.1. The experiments were conducted until the experimental time was much greater than the characteristic time it takes $D_T$ to reach its long-time (diffusive) behavior: \( t \gg a/(U_{rms} \phi^{1/2}) \). The experimental time scale doesn’t involve $D_o$ because the dispersion mechanism in the porous medium is purely mechanical.
2.3.2 Description of Image Analysis Technique

The experimental mass transfer quantity of primary interest was the transverse dispersion coefficient $D_T$. The detection method for calculating $D_T$ relied on tracking the evolution of the solute via the presence of red dye. Video images from the experiments were analyzed by importing the frames as a series of JPEG images into the commercial computational software MATLAB. The presence of red dye was calibrated with dye volume fraction $\chi$ using the following diagnostic measure

$$I^*_R = \frac{I_R^2}{(I_B + I_G)^2}$$

(2.15)

where $I_R$, $I_B$, and $I_G$ are the intensities of the red, blue, and green pixels in the image at a local pixel coordinate, ranging in value from 0 (no color present) to 1 (complete saturation). For all experiments, $\chi$ and $I^*_R$ obeyed a linear relationship, valid when $\chi \leq 0.02$. The slope and intercept varied depending on the working fluid being used.

Pixel values along lines of constant $y$ were tabulated and converted to $\chi$, making $\chi$ a function of only the transverse coordinate $y$ and time $t$. The effective transverse dispersion coefficient $D_T$ was estimated from the data by satisfying the following partial differential equation:

$$\frac{\partial \chi}{\partial t} = D_T \frac{\partial^2 \chi}{\partial y^2}$$

(2.16)

subject to

$$\frac{\partial \chi}{\partial y} \bigg|_{y=0,W} = 0.$$  

(2.17)

$D_T$ is assumed to be a constant, independent of position and solute concentration. The solute is dilute, so using $\chi$ instead of the solute concentration $c$ is a
valid approximation. Equation 2.16 describes the evolution of the volume fraction distribution as \( t \to \infty \), where a purely diffusive relationship (i.e. the solute spreads linearly with time) is expected to hold. The general solution of Equation 2.16 is an infinite eigenvalue expansion of the form

\[
\chi(y, t) = \sum_{n=1}^{\infty} A_n \cos \left( \frac{n \pi y}{W} \right) \exp \left( -(n \pi)^2 \frac{D_T}{W^2} t \right),
\]

where \( A_n \) is a series of infinite constants that depend on the integer \( n \). The variance \( \sigma^2 \) of the volume fraction distribution can be derived using Equation 2.18:

\[
\sigma^2 = (\chi - \chi) = 2 \sum_{n=1}^{\infty} A_n^2 \left[ \exp \left( -(n \pi)^2 \frac{D_T}{W^2} t \right) \right]^2; \tag{2.19}
\]

where \( \chi \) is the volume fraction averaged over the channel width. Equation 2.19 should decay to zero as \( t \to \infty \), representing the solute becoming well-distributed in solution by mass transport mechanisms.

The analysis can be further simplified by considering only the first mode of the solution \( (n = 1) \) and linearizing the equation. Higher order modes decay to zero at faster rates and thus the first mode dominates as \( t \to \infty \). Here, infinite time is considered to be approached when \( t \gg \frac{a}{(U_{rms} \phi^{1/2})} \), the characteristic convective time. The expression which results upon manipulation of Equation 2.19 is

\[
\ln(\sigma^2) = \ln(2A_1^2) - \frac{2\pi^2}{W^2} D_T t. \tag{2.20}
\]

For each sequence of images, \( \ln(\sigma^2) \) was calculated and then plotted as a function of \( t \). An example is shown in Figure 2.4. It is clear from Figure 2.4 that the \( t \to \infty \) asymptote can be reached with minimal effort. \( D_T \) is calculated from the slope of the linear portion of the curve as shown in Figure 2.4.
Figure 2.4. Representative plot of $\ln \sigma^2$ versus $t$ for an oscillatory flow experiment ($\Delta V = 0.17 \text{ cm}^3$, $\omega = 26.9 \text{ rad s}^{-1}$). $D_T$ is calculated using Equation 2.20 and the linear regression indicated by the solid line. Note the vertical lines indicating when the experiment has reached $10^2 \times a/\left(U_{rms} \phi^{1/2}\right)$ and $10^3 \times a/\left(U_{rms} \phi^{1/2}\right)$. 
### TABLE 2.2
ESTIMATED MOLECULAR DIFFUSIVITY OF 2-NAPHTHALENESULFONIC ACID AT 25 °C

<table>
<thead>
<tr>
<th>Fluid (% by weight)</th>
<th>$D_o$ (cm$^2$ s$^{-1}$)</th>
<th>$D_{o,St}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>$3.84 \times 10^{-6}$</td>
<td>$4.07 \times 10^{-6}$</td>
</tr>
<tr>
<td>50/50% glycerine/water</td>
<td>$7.58 \times 10^{-7}$</td>
<td>$7.12 \times 10^{-7}$</td>
</tr>
<tr>
<td>75/25% glycerine/water</td>
<td>$1.52 \times 10^{-7}$</td>
<td>$1.40 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

2.4 Results and Discussion

The first experiments were performed in the absence of oscillatory flow, in order to measure $D_o$ and compare it to a value calculated from theory. The Wilke-Chang equation, which has an expected error of $\pm$ 10%, was used in the theoretical calculation $^{[146]}$. Despite the fact that the solute was actually a salt-water mixture, the measured diffusivities were collected by the image analysis technique described in the section above, and thus the value of $D_o$ for the red dye was the most relevant. The primary component of the red dye was 2-naphthalenesulfonic acid (Red-40), with the molecular formula $C_{18}H_{14}N_2O_8S_2Na_2$ and a formula weight of 496.43 g mol$^{-1}$. The estimated molecular diffusivity $D_o$ for the dye in each working fluid is given in Table 2.2 along with the value obtained from a Stokes' law calculation $D_{o,St}$, which was used to validate the estimation. Agreement between the Stokes’ law calculation and the Wilke-Chang equation is expected for 2-naphthalenesulfonic acid given its size. As Table 2.2 indicates, the two methods only differed by approximately 5%.

The calculated values of $D_o$, however, were not observed in convection-free
TABLE 2.3
OBSERVED TRANSVERSE DIFFUSIVITY IN THE ABSENCE OF FLOW AT 25 °C

<table>
<thead>
<tr>
<th>Fluid (% by weight)</th>
<th>$D_{To}$ (cm$^2$ s$^{-1}$)</th>
<th>$D_{To}/D_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>3.43×10$^{-4}$</td>
<td>89.3</td>
</tr>
<tr>
<td>50/50% glycerine/water</td>
<td>1.90×10$^{-4}$</td>
<td>251</td>
</tr>
<tr>
<td>75/25% glycerine/water</td>
<td>0.84×10$^{-4}$</td>
<td>550</td>
</tr>
</tbody>
</table>

experiments in the porous medium. The observed values of the transverse diffusivity $D_{To}$ were greater by a few orders of magnitude. The observed values for each carrier fluid are given in Table 2.3. The large disparity in the observed and expected values is very likely due to the composition of the solute. As mentioned in section 2.3.1, the solute had a density which was slightly greater than that of the carrier fluid due to small amounts of NaCl. The density difference was necessary to promote penetration of the solute into the packed bed and so obtain an initial distribution of solute which was concentrated near one wall. However, in the absence of oscillatory flow, the fluid will not be quiescent due to the density gradient between the solute and the carrier fluid. The denser fluid settled across the depth of the packed bed and was replaced by the lighter carrier fluid. Though the density difference was small, this density-driven convection current will still have a characteristic time scale which is much greater than the diffusive time scale. For the water system, the ratio of the convection current time scale to the diffusive time scale approaches 10$^3$.

After this observation, additional indirect evidence of a secondary current due
to a density gradient was collected. Tilting the flow apparatus at a small angle reduced the magnitude of $D_{To}$; the same was found when the experimental time was doubled. It was concluded that observed values of $D_{To}$ did not represent pure diffusion, which remains the same regardless of orientation or time in a quiescent fluid. The experimental system would not permit accurate measurement of $D_o$ without significant redesign, and thus $D_{To}$ was regarded as the detection limit of the technique. Despite this limitation, the primary objective of observing transverse diffusivity in the limit of large $\hat{Pe}$ and $\omega a/U_{rms}$ was unaffected; in this limit the inequality $D_T \gg D_{To}$ is still satisfied.

Intuitively, $D_T$ should increase as $\omega$ becomes larger. A greater values of $\omega$ means that the fluid is begin displaced $\Delta x$ and then $-\Delta x$ more often per unit time. If the stroke is at least as large as the circumference of a half a particle, then the solute has the opportunity to sample, at minimum, two locations where fluid elements are converging i.e. the front and back of a particle. The more frequently a solute arrives at the intersection of streamlines, the greater the possibility it will diffuse onto a new streamline and arrive at a different vertical location. Figure 2.5 supports this intuitive argument. As $\Delta V$ becomes larger, the relationship between $D_T$ and $\omega$ becomes approximately linear. This was expected because as $\Delta V$ increases in magnitude $\omega a/U_{rms} \gg 1$, and the oscillatory flow is approximately steady. The data in Figure 2.5 also illustrates that $D_T$ is not a function of $\omega$ or $\Delta V$ alone but must depend on some combination of the two parameters.

The evidence that $D_T$ increases with both $\omega$ and $\Delta V$ suggests that a combination of the two parameters may further collapse the data. An appropriate combination of $\omega$ and $\Delta V$ has already been described: $U_{rms}$. Varying $U_{rms}$ over the ranges presented in Table 2.1 resulted in experimental data over several orders
Figure 2.5. Transverse diffusivity as a function of $\omega$ for four stroke volumes ($0.08 \text{ cm}^3$, (■); 0.17 cm$^3$, (○); 0.44 cm$^3$, (▼); 0.79 cm$^3$, (△)) in a randomly packed bed.
of magnitude of both $\hat{Pe}$ and $\hat{Re}$. The important features of all the data is summarized in Figures 2.6 and 2.7. Figure 2.6 shows how $\kappa_T$ evolves over several orders of magnitude of $\hat{Pe}$. At very large $\hat{Pe}$ ($\hat{Pe} > 5 \times 10^4$), the agreement between the oscillatory data and previously described steady flow models is quite good. Only the models from Equations 2.12 and 2.14 are shown in Figure 2.6 since they most closely represent the experimental packed bed that was used in the oscillatory flow experiments. The agreement is obtained even though the steady flow models were developed for creeping flow and $\hat{Re} \gg 1$ for many of the experiments, but the same convective transport mechanism described in the theories will be important provided the flow remains stable.

For $\hat{Pe} < 5 \times 10^4$, $\kappa_T$ falls below the steady flow predictions, indicating that the oscillatory transverse diffusivity is smaller than the steady flow transverse diffusivity. As $\hat{Pe}$ continues to decrease, the oscillatory flow data crosses back over the steady flow predictions ($\hat{Pe} \sim 2 \times 10^3$) and appears to become constant. If this were a true asymptote the value of $\kappa_T$ as $\hat{Pe} \ll 1$ would be approximately $10^2$.

The severity of the deviation from steady flow theory at lower Peclet number is sharpened upon examination of Figure 2.7. Here, $D_T$ has been normalized by $U_{rms}a$. According to steady flow theories, $D_T/Ua$ will be constant when $\hat{Pe} \gg 1$. For $\hat{Re} \gtrsim 1$, $D_T/U_{rms}a$ matches the steady flow predictions quite well at the largest values of $\hat{Re}$, and then drops to a lower but approximately constant value of $D_T/U_{rms}a$ at intermediate $\hat{Re}$. When $\hat{Re} \lesssim 1$, there is a significant departure from steady flow theory.

The behavior of $\kappa_T$ as $\hat{Re} \to 1$ (or equivalently, as $\hat{Pe} < 10^3$) was to be expected based on the initial measurements of the transverse diffusivity when the
Figure 2.6. Observed effective transverse diffusivity (●) as a function of the experimental Peclet number $\hat{Pe}$. Two theoretical steady flow predictions are compared to the data: the models of Koch and Brady [73] (solid line) and Buyuktas and Wallendar [14] (dashed line).
Figure 2.7. Observed transverse diffusion coefficient normalized by the convective term $U_{rms}a$ (○) for experimental values of $\tilde{Re}$. The steady flow predictions are that of Saffman [114] (dashed line), Koch and Brady [73] (solid line), and the empirical correlation given in Equation 2.13 (dotted line).
oscillatory flow was absent \((D_{To})\). Ordinarily the value of \(\kappa T\) would continue to decrease with \(\hat{Pe}\) until it reaches the pure diffusion asymptote when \(\hat{Pe} \ll 1\). The asymptotic value will be a function of the porous medium geometry but will be approximately unity. However, in these experiments a density-driven secondary current is present; as \(\hat{Pe}\) decreases the secondary current will become the dominant mass transport mechanism instead of molecular diffusion. This was a significant limitation of the experimental methodology and, consequently, \(D_T\) could not be detected accurately as \(\hat{Pe} \to 1\). It is no surprise, therefore, that the value of \(D_{To}/D_o\) given in Table 2.3 is similar to the apparent asymptote in Figure 2.6.

A truer asymptote was examined by substituting the value of \(D_{To}\) for \(D_o\), i.e. \(D_{To}\) is taken to be the molecular diffusion coefficient. Figure 2.6 was rescaled with respect to this lower bound of detection and the result is shown in Figure 2.8. Since this adjustment reduces \(\hat{Pe}\) by a couple orders of magnitude, comparison with the \(Pe \gg 1\) asymptote from steady flow is no longer appropriate. In the previously mentioned work of Koch and Brady [73], a theoretical treatment of the same problem is performed when \(Pe \sim 1\). Koch and Brady calculated the following expression for the effective transverse diffusivity:

\[
\kappa_T = \frac{1 + \frac{63}{320} \sqrt{2\phi} Pe + \frac{21}{80} \sqrt{2\phi}}{1 - \frac{9}{80} \sqrt{2\phi}}.
\] (2.21)

The expression for \(\kappa_T\) in Equation 2.21 reduces to Equation 2.12 when \(Pe\phi^{1/2} \gg 1\). The prediction for \(\kappa_T\) described in Equation 2.21 fits the adjusted experimentally data reasonably well. The data as \(\hat{Pe} \to 1\) appears to be approaching a value of \(\kappa_T \sim (O) 1\) and the deviation from the steady flow model is less pronounced. Unfortunately, the validity of this analysis was difficult to confirm. Experimental measurements when \(\hat{Pe} < 1\), though possible, involved velocities which were on
Figure 2.8. Observed effective transverse diffusivity (●) as a function of the experimental Peclet number \( \hat{Pe} \). Both the effective transverse diffusivity and \( \hat{Pe} \) are relative to \( D_{To} \) instead of \( D_o \). A extension of the model of Koch and Brady to lower \( \hat{Pe} \) values which is given by Equation 2.21 is provided as a reference (solid line).

the order of the secondary currents produced by the density gradient.

The limited ability of the experimental technique to isolate the effects of convection due to oscillatory flow as \( \hat{Pe} \rightarrow 1 \) makes quantitative analysis of the differences between oscillatory flow and the steady flow model difficult. Qualitatively, the difference is not surprising for a couple of reasons. It occurs at values of \( \hat{Pe} \) where \( U_{rms}/\omega a \) is approaching unity. Consequently, the solute may be not be exposed to enough streamlines before flow reversal to result in an effective transverse diffusivity comparable with steady flow, where flow reversal is not present. Additionally, the porous medium is not infinite; the walls will af-
fect the distribution of spheres near the boundaries, thus modifying the velocity profile, a phenomenon known as channeling e.g. Vortmeyer and Schuster [143] or Cheng and Vortmeyer [21]. An important feature of the porous medium’s design that permitted video analysis was restricting the packed bed to be a monolayer of spheres; the absence of additional sphere layers reduces the convective transport near the top and bottom (z-direction) of the packed bed where the fluid must satisfy the no-slip condition. These limitations were mitigated at high $\hat{Pe}$ because the oscillatory velocity is of sufficient magnitude to be the dominant influence on solute transport.

The effect of the packing order and density was briefly explored. Experiments in a ordered porous medium which had a hexagonal close packing were performed at one stroke volume ($\Delta V = 0.44 \text{ cm}^3$) over the entire range of frequencies. Comparison of effective transverse dispersivity for the random and ordered medium are presented in Figure 2.9. The stroke volume used in the ordered porous medium experiments satisfied the condition that $\frac{\omega a}{U_{rms}} \gg 1$; rather surprisingly, the experiments performed in water mirror the results obtained for the random porous media for this parameter range. When the viscosity was increased (a solution of 50/50 wt% glycerin/water), the measured dispersivities are not in agreement; in fact, $\kappa_T$ is reduced significantly for the same $\hat{Pe}$. If $\hat{Pe}$ is rescaled by the empirically determined limit of detection $D_{To}$, the disparity between the effective transverse diffusivities is still present. The experiments with a 75/25 wt% glycerin/water were ineffective because the value of $D_{To}$ continued to rise and interfere with observational precision.

It is interesting to note that Equation 2.12 was developed for a random porous media, and yet the dispersivities of the ordered porous media are in good agree-
Figure 2.9. Observed effective transverse diffusivities as a function of the experimental Peclet number $\hat{Pe}$ for the random porous media in water (●) and the ordered porous media in water (○) and 50/50 wt% glycerin/water (□). The model of Koch and Brady given by Equation 2.12 is provided as a reference (solid line).
ment with the theory. As mentioned, spatially periodic porous media do not significantly enhance the transverse diffusivity. The reason the ordered porous medium used in this study behaves in a manner similar to that of a random porous medium is not clear. It is possible that in the $\hat{Pe}, \hat{Re} \gg 1$ limit, nuances of geometry do not play as significant a role in determining mass transport behavior because the flow field is more complex. Recall that this is not accounted for in the steady flow theories, which were all developed for creeping flow. Anecdotal evidence supporting this hypothesis was encountered upon examination of the experiments performed in the higher viscosity fluid. The measured dispersivities of those experiments are closer to what would be expected in a spatially periodic media; that is, much larger Peclet numbers need to be achieved before the same enhancement in $\kappa_T$ which was observed in a random porous media is reached.

2.5 Conclusions

In this chapter, a methodology for measuring the effective transverse diffusivity of a solute in a random porous medium in the presence of an oscillatory flow as a function of the relevant dimensionless parameters was described. It was expected that the oscillatory flow would be fundamentally different than steady flow, but as $\omega a/U_{rms} \gg 1$ the oscillatory flow would behave in an approximately steady manner. In this limit, it was shown that steady flow theories which were developed for steady flow in porous medium predict the experimental values of $\kappa_T$ quite well when $\hat{Pe} \gg 1$.

In general, deviation from steady flow theory at lower values of $\hat{Pe}$ corresponded to values of $\omega a/U_{rms} \sim 1$. The nuances of geometry and the flow field may also play a significant role but this was not verified. The measurement tech-
nique was limited by the presence of a secondary current induced by the difference in density between the solute and the carrier fluid. The secondary current prevented accurate study of transport behavior as $\widehat{Pe} \to 1$ and distorted the value of the experimental Peclet number. Interestingly, experiments with the same carrier fluid in an ordered porous medium yielded similar values of $\kappa_T$ compared to those performed in a random porous medium. The similarity vanished when a higher viscosity carrier fluid was used in the ordered porous medium.

The enhancement in $D_T$ when an oscillatory flow is induced in a porous medium represents an increase which is several orders of magnitude larger than $D_o$. The enhancement was observed to be comparable with what is expected from steady flow theory and experiment. For a porous medium of a given thickness and depth, a steady flow with an average velocity $U = U_{rms}$ will require a much greater length of medium to achieve the same enhancement than an oscillatory flow. In a confined or small geometry where mass transport enhancement is desirable, then, using oscillatory flow would be more advantageous than a steady flow. An oscillatory flow can also be superimposed on a steady flow if a net throughput in the system is desired. In the next two chapters, the use of oscillatory flow in one such system which possesses similar characteristics to the experimental porous medium of this chapter is investigated in detail.
CHAPTER 3

OSCILLATORY FLOW AND TRANSPORT ENHANCEMENT IN THE DIRECT METHANOL FUEL CELL

3.1 Introduction

Direct methanol fuel cells (DMFCs) are a promising alternative to hydrogen-fed fuel cells, having the advantages of a simpler overall design and a fuel that is easier to store and distribute. The basic reactions and operation principles of a DMFC have been studied extensively \[8, 118\] and are illustrated in Figure 3.1. Several technical challenges with DMFCs still remain unresolved, including maximum power densities that are typically only a fraction of hydrogen-fed cells, cross-over of methanol through the membrane to the cathode, and management of evolved carbon dioxide gas in the anode fuel stream.

Another problem which typically arises during DMFC operation is the poor mass transport of methanol to the DMFC anode at high current densities. The poor mass transport is indirectly due to the phenomenon of methanol cross-over. Methanol permeates across the membrane and produces a mixed potential at the cathode, inhibiting the oxygen reduction reaction and resulting in a drop in the power output of the DMFC \[53\]. To avoid experiencing significant methanol cross-over and the corresponding efficiency loss, the feed concentration of methanol is kept low (typically < 2 mol L\(^{-1}\)). Consequently, at high current densities when the
Figure 3.1. General schematic and reactions of the DMFC.

OVERALL REACTION: \( \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \)
reaction rate at the anode is fast enough to instantaneously consume any methanol that arrives at the catalyst surface, DMFC performance is limited by the inability of methanol to diffuse to the surface fast enough. Similarly, carbon dioxide diffuses slowly away from the catalyst surface, which tends to restrict methanol’s access to reaction sites.

The effect of poor mass transport is evident when the current-voltage behavior of a DMFC is examined. The DMFC operates in three different regimes depending on the current density. The general features of this behavior are illustrated in Figure 3.2. At low current densities (region 1), kinetic limitations of the cell dominate. An approximately linear voltage-current relationship (region 2) occurs at moderate current densities. At high current densities (region 3), the mass transport resistances of the system limit performance. Eventually, these resistances become dominant and the cell voltage drops to zero at the limiting current density \( i_{lim} \). Mass transport limitations are often explained as a combination of two phenomena: the presence of greater amounts of carbon dioxide (CO\(_2\)) gas in the anode flow channel and diffusion layer at high current densities, and the diffusion of methanol into and through the porous diffusion layer. Bubbles of CO\(_2\) both physically block access to the catalyst surface and hydrodynamically influence the movement of liquid methanol fuel into pores \[122\]. The tendency for CO\(_2\) gas to evolve and then coalesce into long slugs at high current densities and reduce \( i_{lim} \), has been verified by analytical modeling \[78\] and visualization experiments \[90\] \[160\]. Separate work \[48\] \[103\] \[119\] \[120\] \[122\] has suggested that the slow diffusion of methanol to the catalyst surface is also an important mass transport limiting mechanism, particularly when the methanol concentration is low. Despite these studies, how these two mass transfer limiting mechanisms interact with one
Figure 3.2. An example of a polarization curve obtained during this study at a cell temperature of 70 °C that illustrates the three typical regions of behavior observed in DMFCs.

An operational technique used to counter mass transfer limitations is to increase methanol concentration in the feed, thereby increasing the concentration gradient across the porous diffusion layer. This practice is undesirable because it results in a higher rate of methanol cross-over at lower current densities [28, 53]. Another common approach is to increase the anode feed rate. This has been shown to both positively [41, 154] and negatively [122, 160] affect the performance of a DMFC in the mass transfer limiting regime, depending on other operating conditions. In general, however, this practice is also not preferable because the increased flow rates reduce the cell temperature (if the anode feed is not pre-heated) and
poorly utilize the fuel. Since methanol cross-over is a more serious performance limitation in the DMFC, increasing the flow rate while keeping the methanol concentration below 2 mol L\(^{-1}\) is currently the best operational strategy to reduce mass transfer limitations.

In addition to operational changes, work has been performed which studies the effect of either the geometry of the anode flow field \([4, 155, 159]\) or the porous diffusion layer \([104, 105, 151, 156, 163]\). In the case of the flow field, it was found that an optimum channel depth and orientation exists \([4]\) and that a serpentine channel performed best in a DMFC \([159]\). Even in a case where a modified serpentine flow field improved DMFC mass transfer behavior, significant mass transfer limitations were still present \([155]\). For the diffusion layer, it was found that treating diffusion layers with Teflon did not improve performance beyond that of an untreated diffusion layer \([104, 127, 156, 163]\), but that the thickness and microstructure of the layer does affect performance, especially at low methanol concentrations \([105, 151, 156]\). A good indicator of mass transfer behavior in the DMFC is the limiting current, and in general, improvements in the limiting current density were not significant in any of these studies.

In this chapter, the effect of superimposing oscillatory flow on the steady feed to the anode of a DMFC is examined. It was concluded from the work of Chapter 2 that oscillatory flow can enhance mass transport in small or confined geometries where steady flow may not. Oscillatory flow is an attractive alternative to increasing the steady feed rate for other reasons: it does not require additional fuel or preheating to maintain operating temperatures. Based on the work of the previous chapter, it was expected that inducing an oscillatory flow would generate a pressure gradient throughout the porous anode, thereby inducing convection within
its pores. Convection in the pores will promote increased sampling of streamlines by solutes and significantly improve mass transfer. The DMFC anode and flow field is a similar system, with the important distinction that the oscillatory flow in these experiments is not generated directly in the porous medium (the diffusion layer) itself, but rather tangentially in the anode flow channel. Hence, convective enhancement of mass transfer rates in the transverse direction should result in improvements in DMFC performance at high current densities.

In the next section, a framework is developed for understanding how fluid oscillations affect mass transfer in an idealized DMFC. The theoretical and empirical considerations will lend themselves to the construction of a predictive model for the limiting current density. In the third section, the experimental system and the methods used to measure DMFC performance are described. In the fourth section, the data from the experiments is presented. In the fifth section, an argument is made for methanol diffusion being the primary mass transport limiting mechanism in our experiments and the model is compared to the data. Finally, some concluding remarks are made about the implications of this work for DMFC operation.

3.2 Theory and Calculations

3.2.1 Model Description and Development

In order to enhance mass transport in the diffusion layer without significantly altering operational and geometric variables in the DMFC, it is necessary to induce convection in the pores of the diffusion layer. Just as in the experiments of Chapter 2, convection is induced by displacing a known volume $\Delta V$ of fluid at a frequency $\omega$, which forces an oscillatory flow. Inducing an oscillatory flow in the
anode of a DMFC will affect momentum, mass, and energy transfer in the system. Characterizing these changes, however, is difficult because the transport behavior is complex. For instance, the anode geometry is complicated: the flow channel only exposes approximately 60% of the active catalyst area, and thus methanol transport may not be strictly one-dimensional and could be augmented by seeping through the porous diffusion layer underneath the ribs of the flow channel \[154\] \[161\]. Additionally, in typical operation, the methanol/water solution is fed at ambient temperature and the cell temperature is more than 30 °C higher, so temperature gradients are present in the fluid. Furthermore, due to the evolution of CO\(_2\) gas, the solution becomes multiphase, most significantly at high current densities. Many efforts have been made to model the complexities of the transport behavior in the DMFC anode \[107\], but for the purposes of this study, a simplified model that still captured the essence of the transport behavior at low methanol feed concentrations was desirable.

The following assumptions were made to isolate the effect of fluid oscillations on DMFC performance:

1. Steady state, in the sense that the oscillatory flow is purely sinusoidal and all other transients are small in magnitude;

2. Transport of methanol through the channel, porous medium, and catalyst layer is approximated as one dimensional;

3. The system is isothermal at the cell temperature;

4. The anode feed solution is dilute in methanol;

5. Fluid properties (\(\mu, \rho\)) at the anode are constant;
Figure 3.3. Simplified geometry of a DMFC anode used to develop a predictive model for the mass transport of methanol when an oscillatory flow $Q(t)$ is superimposed on a steady flow $Q_s$ in the channel. The fluid properties $\mu$ and $\rho$ along with the geometric properties of the diffusion layer ($\kappa, \phi, a$) are all considered to be constant. The time-averaged magnitude of the pressure gradient is the same in both the channel and the diffusion layer.

6. All carbon dioxide present in the porous diffusion layer is dissolved in solution.

With these assumptions, a simplified geometry of the DMFC anode such as the one presented in Figure 3.3 was used as the starting point for the model developed in the following pages.

As indicated by Figure 3.3, the anode channel has a depth $d$ and the interaction of the fluid with the side walls is neglected, which reduces the important physical mechanisms to two: unidirectional flow in the $x$ direction and diffusion of solutes in the $y$ direction. The assumption of one-dimensional diffusion through the diffusion and catalyst layers requires the fluid in the open anode channel to be regarded as well-mixed at the inlet feed concentration. This will be correct provided the
feed rate is sufficient to avoid significant methanol depletion over the length of the channel. In the experiments described in the next section, the maximum total consumption of methanol was less than 3% of the feed, thus this approximation was well satisfied.

The combination of an imposed steady feed rate $Q_s$ and oscillatory feed rate $Q(t)$ will result in a pressure gradient in the flow channel. The pressure gradient has been written as $\langle |\partial P/\partial x| \rangle$ since it represents the time-averaged magnitude of the pressure gradient; it is anticipated that time-dependent components will be averaged and may be out of phase with one another. For the time being, the model will be developed assuming $\langle |\partial P/\partial x| \rangle$ is known. Upon completing a description of the model, the methodology used to determine the pressure gradient for the experiments will be discussed.

In the model system of Figure 3.3, a pressure gradient is also present in the porous diffusion layer, but it produces a velocity which is smaller than the velocity in the channel by several orders of magnitude due to the small length scales of the pores. For unidirectional flow, the same $\langle |\partial P/\partial x| \rangle$ in the channel is also distributed throughout the porous diffusion layer, and thus the velocity in the diffusion layer can be estimated from Darcy’s law:

$$U_{dl} = -\frac{\kappa}{\mu} \langle \left| \frac{\partial P}{\partial x} \right| \rangle,$$  \hspace{1cm} (3.1)

where $\kappa$ is the permeability of the porous diffusion layer. In general, the permeability of a “real” porous medium is anisotropic. For the diffusion layers used in this study $\kappa$ has been reported by the manufacturers only in the thin (transverse) direction. Assuming the medium is approximately isotropic, however, we may use these reported permeabilities to calculate the tangential velocity $U_{dl}$ via Equation
once the pressure gradient is known.

If the flow within the open volume of the porous diffusion layer was steady, the convective-diffusive behavior of methanol could be predicted using a steady flow model for a random fibrous porous medium such as that of Koch and Brady [74]. The model of Koch and Brady follows directly from the model of Koch and Brady discussed in Chapter 2 [73], with the distinction that the former is for a fibrous porous medium while the latter is for a packed bed of spheres. Provided the amplitude of the oscillatory flow is sufficiently large that memory is lost during each half-period of oscillation, the model should also apply for oscillatory flows. This occurs if the condition $U_{dl}/\omega a \gg 1$ is satisfied (again, note the similarity to the steady condition in Chapter 2). In the majority of the experiments, $U_{dl}/\omega a \geq 10$; consequently, it is assumed that the theory of Koch and Brady will be valid for oscillatory flow as well.

The Koch and Brady model calculates the effective diffusivity as a function of the flow regime present in the porous medium. The flow regime is determined by two related dimensionless quantities: the Peclet number ($Pe$) and the screening length Peclet number ($Pe_{sc}$), which are defined as

$$Pe = \frac{U_{dl}a}{D_o} \quad \text{and} \quad Pe_{sc} = \frac{U_{dl}K^{(1/2)}}{D_o};$$

(note that in contrast to Chapter 2, $a$ is the radius of the fibers in the porous diffusion layer. Koch and Brady also present an implicit method for estimating the permeability for fibrous porous media, which was originally derived by Speilman
and Goren [134]. For the isotropic case,

\[
\frac{1}{\kappa_e} = -\frac{\phi}{\pi a^2 \mu} \left[ \frac{2}{3} f_\perp + \frac{1}{3} f_\parallel \right] + O \left( \frac{\phi}{a^2 \left( \ln \left( \frac{1}{\phi} \right) \right)^2} \right),
\]

(3.3)

where

\[
f_\perp = -4\pi \mu \left[ a\kappa_e^{-1/2} \frac{K_1(a\kappa_e^{-1/2})}{K_0(a\kappa_e^{-1/2})} + \frac{1}{2} a^2 \kappa_e^{-1} \right],
\]

\[
f_\parallel = -2\pi \mu a\kappa_e^{-1/2} \frac{K_1(a\kappa_e^{-1/2})}{K_0(a\kappa_e^{-1/2})},
\]

and \( \kappa_e \) is the estimated permeability of the porous medium, and \( K_0(x) \) and \( K_1(x) \) are the modified Bessel functions of order zero and one. Values of \( \kappa \) and \( \kappa_e \) are presented in Table 3.1 along with additional geometric information on the diffusion layers used in the experiments. For the carbon fiber papers, the agreement between \( \kappa \) and \( \kappa_e \) is excellent, but the permeability of the carbon cloth is overestimated by a factor of four. The isotropic calculation of Equation 3.3 should be accurate for the carbon fiber papers given their high porosities and random fiber orientations (Figure 3.2.1). The carbon cloth, however, is a woven material composed of aligned bundles of fibers which overlap one another and the permeability is likely to be anisotropic. More significantly, however, examination of SEM images of the carbon cloth (Figure 3.2.1) shows that much of the open area is obstructed by particulate material, decreasing the expected permeability. Thus, in our analysis, the measured permeabilities \( \kappa \) were employed for all diffusion layers.

Koch and Brady determined the effective diffusivity in the limit of low \( \phi \) for several different flow regimes defined by \( Pe \) and \( Pe_{sc} \). In this case, as was the case in the experiments of Chapter 2, the diffusivity in the direction transverse to the
Figure 3.4. Scanning electron microscope images of: (a) Toray carbon paper TGP-H-060 and (b) E-TEK ELAT carbon cloth. Both diffusion layers are composed of carbon fibers with an approximate mean diameter of 8 microns. An SEM image of Toray carbon paper TGP-H-030 was not included, as its microstructure is very similar to that of the other carbon paper shown above.
TABLE 3.1
REPORTED AND CALCULATED PERMEABILITIES OF THE
DIFFUSION LAYERS USED IN EXPERIMENTATION

<table>
<thead>
<tr>
<th>Diffusion Layer*</th>
<th>φ</th>
<th>κ (cm²)</th>
<th>κe (cm²)</th>
<th>η</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELAT CC LT 1200-W</td>
<td>0.30</td>
<td>4.90×10⁻⁹</td>
<td>2.18×10⁻⁸</td>
<td>0.929</td>
<td>0.8222</td>
</tr>
<tr>
<td>Toray CP TGP-H-030</td>
<td>0.20</td>
<td>1.05×10⁻⁷</td>
<td>1.05×10⁻⁷</td>
<td>0.917</td>
<td>0.2688</td>
</tr>
<tr>
<td>Toray CP TGP-H-060</td>
<td>0.22</td>
<td>8.00×10⁻⁸</td>
<td>8.49×10⁻⁸</td>
<td>0.915</td>
<td>0.2803</td>
</tr>
</tbody>
</table>

* The fiber radius \( a \) was determined to be 4×10⁻⁴ cm for all three diffusion layers using SEM images. The abbreviations ‘CC’ and ‘CP’ stand for carbon cloth and carbon paper, respectively.

flow (i.e. the \( y \) direction) is the value of interest. For \( Pe \equiv 0 \) and fibers which do not interact with the solute this diffusivity is given as

\[
D_{yy} = \left( \frac{1}{1 - \phi} - \frac{5}{3} \phi \right) D_o . \tag{3.4}
\]

The other asymptote for the transverse diffusivity, described by the criteria \( Pe \gg 1 \) and \( Pe_{sc} \gg 1 \), is given as:

\[
D_{yy} = \left( \frac{9}{6400} \pi^3 \frac{a}{\kappa^{3/2} \phi} Pe \right) D_o , \tag{3.5}
\]

which is purely mechanical dispersion due to the stochastic nature of the porous medium. A series of intermediate flow regimes are also described by Koch and Brady, but as an approximation the two asymptotes in Equation 3.4 and Equation
are combined into the following

\[ D_{yy} = (\eta + \lambda Pe) D_0, \quad (3.6) \]

where

\[ \eta = \left( \frac{1}{1 - \phi} - \frac{5}{3} \phi \right), \]
\[ \lambda = \left( \frac{9}{6400} \pi^3 \frac{a}{\kappa^{1/2} \phi} \right), \]

and the values of \( \eta \) and \( \lambda \) for each diffusion layer are given in Table 3.1. This simplification of the full theory captures the exact behavior of \( D_{yy} \) to within 10% over the entire range of \( Pe \).

Predicting the transverse dispersivity \( D_{yy} \) is essential to development of a DMFC performance model because it is well known that the limiting current density \( i_{lim} \) is proportional to a total mass transfer coefficient \( k_{tot} \) which is a complex function of the geometry of the DMFC anode and the operating conditions \[49, 122, 145, 154\]. In accordance with this observation, the following simple model is proposed:

\[ \frac{1}{i_{lim}} = \frac{C}{k_{tot}} = C \left( \frac{1}{k_o} + \sum_{i=1}^{n} \frac{1}{k_{eff}^i} \right), \quad (3.7) \]

where \( C \) is a constant of proportionality, \( k_{eff}^i \) is the effective mass transfer coefficient in diffusion layer \( i \), \( n \) is the number of different diffusion layers in the fuel cell anode, and \( k_o \) is the sum of the mass transfer limitations from the other components or mechanisms in the system. This model is equivalent to considering the anode as a series of mass transport resistances, of which the diffusion layer is one part, and is capable of handling composite layers such as those used in these
experiments. Isolating $k_i^{eff}$ from the other resistances in the system permits use of Equation 3.6 to estimate transverse mass transport in the following manner:

$$k_i^{eff} = \frac{\delta (1 - \phi_i) D_{yy,i} l_i}{(1 - \phi_i) D_{o\eta_i} l_i} (1 + \lambda_i' Pe), \quad (3.8)$$

where $l_i$ is the thickness of porous diffusion layer $i$, $\delta$ is the open area ratio, and $(1 - \phi_i)$ adjusts for the void fraction of diffusion layer $i$. Note that the constant $\lambda_i' = \lambda_i/\eta_i$. Combining Equation 3.7 and Equation 3.8 yields the expression

$$\frac{1}{i_{lim}} = C' + \sum_{i=1}^{n} \frac{C_i}{1 + \lambda_i' Pe}, \quad (3.9)$$

where the constants $C' = C/k_o$ and each $C_i$ can be determined empirically. The limiting current density should thus vary between two asymptotes: a $Pe \ll 1$ limit where convective mass transport enhancement is absent (i.e. $C' + \sum C_i$) and a $Pe \gg 1$ limit where diffusional limitations in the porous diffusion layer are eliminated (i.e. $C'$). The transition between these limits, however, may be predicted without further adjustable parameters.

A modification of Equation 3.9 can be made which reduces the number of empirically determined constants to one. Though $k_o$ is an unknown combination of all the mass transport coefficients in the system besides the diffusion layer, it can be estimated from the experimental asymptote $C'$. The constant $C$ is determined by a methanol flux balance to be $(6F c_b)^{-1}$, where $F$ is Faraday’s constant and $c_b$ is the concentration of methanol in the bulk. In practice, the conversion of methanol is quite small; therefore, the approximation $c_b \approx c_f$ (the feed concentration) is
used. The model for the limiting current density then becomes

\[ \frac{1}{i_{\text{lim}}} = \frac{1}{6F_c f_k o} + \sum_{i=1}^{n} \frac{C_i^*}{1 + \lambda_i Pe}, \]

(3.10)

where

\[ C_i^* = \frac{l_i}{6F_c f_0 \delta (1 - \phi_i) \eta D_o}, \]

and \(k_o\) can be estimated from the \(Pe \gg 1\) asymptote. It now remains only to determine \(\langle|\partial P/\partial x|\rangle\) for oscillatory flow in the anode channel.

3.2.2 Oscillatory Flow in the Anode Channel

In order to determine the pressure gradient, the detailed anode flow plate geometry must be considered. The geometry used in our experiments is depicted in Figure 3.5. It consists of three square parallel channels of width \(w\), measured by a caliper to be 0.081 cm, and depth \(d\). The channels have a length of 1.97 cm before expanding into flow reversal sections which are deeper \((d_{fr} = 0.162\) cm) and wider \((w_{fr} = 0.162\) cm). It was expected that the actual channel depth would deviate from its nominal depth when the DMFC was sealed because there is evidence which suggests that compressing the components of a fuel cell distorts the structure of the diffusion layer and causes it to occupy a fraction of the open area of the channel \[87\]. This hypothesis was confirmed upon examination of the diffusion layer post-experiment. As Figure 3.6 shows, the diffusion layers had ridges from being deformed in the DMFC anode and protruding into the channel.

Since the actual channel depth is not directly measurable when the DMFC is fully assembled and sealed, it was determined indirectly from measurement of the pressure drop-flow rate relationship. A series of experiments were performed
Figure 3.5. Graphite anode flow plate used in DMFC experiments.

Figure 3.6. Overhead view of a diffusion layer after use in the DMFC. Note the evenly spaced ridges which indicate deformation of the layer consistent with the spacing of the ribs and channels of the anode flow field.
Figure 3.7. The relationship between pressure drop and flow rate, where the pressure drop is normalized by the ratio of the viscosity of water to the viscosity of the solution $\mu_w/\mu$, for the DMFC anode. Experiments were performed at ambient temperature with the three diffusion layers used in experimentation. The fluids used were water (closed symbols) and 90 wt% glycerin/10 wt% water (open symbols). Lines of slope = 1 are provided as a reference.

where a known static head of fluid was applied to the assembled and sealed DMFC and the resulting flow rate in the DMFC was measured. This was done for all three diffusion layers and using fluids of two different viscosities: water and a solution of glycerin and water (90% glycerin by weight). The results of the measurements are presented in Figure 3.7.

For laminar flow at low Reynolds number the ratio of the pressure drop in the
flow reversal section to that in the channels is approximately given by

$$\frac{\Delta P_{fr}}{\Delta P_{ch}} = \left( \frac{QL_{fr}}{2w_{fr}d_{fr}^3} \right) \times \left( \frac{QL_{ch}}{3wd^3} \right)^{-1} \approx 0.02,$$

(3.11)

where \(Q\) is the flow rate, \(\Delta P_{fr}\) and \(L_{fr}\) are the pressure drop and length of the flow reversal sections, respectively, and \(\Delta P_{ch}\) and \(L_{ch}\) are the pressure drop and length of the channel sections, respectively. The ratio in Equation 3.11 is much less than one for the system of this study, principally due to the greater depth of the flow reversal regions. Since this was the case, all sources of pressure loss were considered negligible compared to the pressure loss in the channels.

If the pressure drop is solely distributed along the anode channel length and the interface between the flow channel and the diffusion layer is assumed to act as a rigid wall, the velocity has a well-known analytical solution[12] which is a function of the unknown aspect ratio \(\gamma = d/w\). Upon integrating the velocity to determine the flow rate, the following expression is obtained:

$$Q = \frac{w^4 \Delta P}{\mu L} \left( \sum_{n=1}^{\infty} \frac{8 \sin^2(\lambda_n) \tanh(\lambda_n \gamma)}{\lambda_n^5} + \frac{4}{3} \gamma \right),$$

(3.12)

where the discrete eigenvalues \(\lambda_n = \pi(n - 1/2)\). The expression in Equation 3.12 can be used in conjunction with the relationship between \(Q\) and \(\Delta P/L\) to solve for \(\gamma\). The corresponding values of \(d\) are given in Table 3.2. The values of \(d\) calculated using this method demonstrate, somewhat surprisingly, that the diffusion layer occupies between 40 to 50% of the nominal anode channel depth.

Once the actual channel depth was known, the behavior of oscillatory flow in the anode flow plate was examined. The maximum amplitude of the velocity due to the fluid oscillations can be written as \(U_{max} = \Delta V \omega / A_{ch}\), where the total cross-
TABLE 3.2

COMPOSITION OF THE DIFFUSION LAYERS USED IN THE DMFC EXPERIMENTS

<table>
<thead>
<tr>
<th>DL †</th>
<th>Component 1</th>
<th>$l_1$ ‡</th>
<th>Component 2</th>
<th>$l_2$ ‡</th>
<th>$d$ ‡</th>
<th>$d_h$ ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ELAT cloth</td>
<td>0.027</td>
<td>–</td>
<td>–</td>
<td>0.0463</td>
<td>0.0589</td>
</tr>
<tr>
<td>B</td>
<td>ELAT cloth</td>
<td>0.027</td>
<td>TGP-H-030 paper</td>
<td>0.011</td>
<td>0.0500</td>
<td>0.0618</td>
</tr>
<tr>
<td>C</td>
<td>ELAT cloth</td>
<td>0.027</td>
<td>TGP-H-060 paper</td>
<td>0.019</td>
<td>0.0430</td>
<td>0.0562</td>
</tr>
</tbody>
</table>

† The channel depth $d$ and hydraulic diameter $d_h$ were dependent on the diffusion layer composition.
‡ All lengths ($l_1$, $l_2$, $d$, and $d_h$) are in cm.

sectional area of the anode flow channels (three channels in parallel) is $A_{ch} = 3wd$.

To characterize the oscillatory flow in the anode channels, a laminar-turbulent transition criterion which summarized a large body of previous experimental work [144] is used. The transition criterion, in terms of the critical values (subscript $c$) of the relevant dimensionless parameters, is written as

$$Re_{max,c} \approx 400 \, Re_{\omega,c}^{1/2}, \quad (3.13)$$

where $Re_{max} = U_{max}d_h/\nu$ and $Re_{\omega} = \omega d_h^2/\nu$. The correlation given in Equation 3.13 was developed for tubes and uses the hydraulic diameter $d_h$ as the length scale. The anode channel is a rectangular duct and the hydraulic diameter is easily calculated. Values of $d_h$ are given in Table 3.2. Since all geometric parameters are known, the criterion of Equation 3.13 can be compared against values of $Re_{max}$ and $Re_{\omega}$ from the oscillatory flow experiments. The result of this analysis is presented
in Figure 3.8. It is interesting to note that the majority of the oscillatory flow experiments were in the turbulent regime; it was necessary to reach the turbulent regime before pressure gradients large enough to induce significant mass transfer enhancement were achieved.

3.2.3 Determination of the Pressure Gradient

For laminar flow, given that the pressure gradient has the form $G_\omega \sin(\omega t)$, the analytical solution for a channel is well known [79]. The solution can be written
in dimensionless form as

\[ u^* = \Im \left\{ \frac{\exp(it^*)}{\alpha^2} \left[ 1 - \frac{\cosh \left( \frac{\alpha y^*}{i} \right)}{\cosh \left( \frac{\alpha}{i} \right)} \right] \right\} \]  

(3.14)

where \( u^* = (4u\mu)/(G_o d^2) \), \( y^* = 2y/d \), \( t^* = \omega t \), and \( \alpha = Re_{\omega}^{1/2}(d/2d_h) \). This relationship was expanded, integrated in space and time, and rearranged to solve for the time-averaged magnitude of the pressure gradient (see Appendix A for the detailed calculation):

\[ G_o = \frac{2\mu \Delta V}{3 wd^3} \left[ \left( \frac{2}{\alpha^2} \right) \left( 1 - \frac{\sin(\sqrt{2} \alpha) + \sinh(\sqrt{2} \alpha)}{\sqrt{2} \alpha \left( \cos(\sqrt{2} \alpha) + \cosh(\sqrt{2} \alpha) \right)} \right) \right]^{-1}. \]  

(3.15)

The value of \( G_o \) calculated by Equation 3.15 is equivalent to \( \langle |\partial P/\partial x| \rangle \) and was used in Equation 3.1 to determine the velocity in the porous diffusion layer for all laminar oscillatory flow experiments in the DMFC.

For the more important turbulent flow case, obtaining the pressure gradient is decidedly more challenging. For fully developed turbulent flow in a tube, the following unsteady momentum equation applies:

\[ \frac{\partial P}{\partial x} = \rho \frac{\partial u}{\partial t} + \frac{4 \tau_w}{R} \]  

(3.16)

where \( \tau_w \) is the wall shear stress and \( R \) is the tube radius. The first term is due to the acceleration and deceleration of the fluid, and can be calculated using the reasonable assumption that the spatially averaged velocity has the form \( u = U_o \sin(\omega t) \). The second term is more difficult to calculate. If the flow is steady, \( \tau_w \) can be determined using a friction coefficient \( f \). In the oscillatory case, this is complicated by the scarcity of available correlations for fully turbulent oscillatory
flow in a channel. However, similarities between the flow regimes of oscillatory turbulence and steady turbulence, including agreement between the Blasius correlation for steady turbulent flow and measurement of wall-friction velocities in oscillatory turbulent flow have been observed [3]. Therefore, the approach taken in this study was to estimate the oscillatory friction coefficient using an available correlation for steady turbulent flow. To calculate the friction coefficient, $Re_{\text{max}}$ is not the appropriate dimensionless quantity; instead a Reynolds number is defined which accounts for the time-average of the flow:

$$\langle Re \rangle = \frac{\langle U \rangle d}{\nu}.$$  \hspace{1cm} (3.17)

where $\langle U \rangle = \frac{\Delta V \omega}{3 wd \pi}$

that is, $\langle U \rangle$ is the time-averaged velocity. The maximum experimental value of $\langle Re \rangle$ approached $10^4$.

Upon expansion of the terms in Equation (3.16), the approximate expression for the turbulent oscillatory pressure gradient becomes

$$\frac{\partial P}{\partial x} \approx -\rho \omega U_o \cos (\omega t) - 2f \rho U_o^2 \frac{d}{d} \sin (\omega t),$$  \hspace{1cm} (3.18)

where the amplitude of the velocity $U_o = (\pi/2) \langle U \rangle$, which differs slightly from the $U_o$ given in Equation (2.3). The friction coefficient depends on the roughness of the walls and $\langle Re \rangle$. In this case, the bottom wall of the channel is a layer composed of carbon fibers, many of which are likely protruding into the flow area. Assuming these protrusions are on the order of the pore radii, an available correlation for $f$...
can be used
\[ \frac{1}{f^{1/2}} = -4 \log \left[ \frac{0.27\epsilon}{d_h} + \left( \frac{7}{\langle Re \rangle} \right)^{0.9} \right], \quad (3.19) \]

where the absolute roughness \( \epsilon \) was taken to be \( 1.0 \times 10^{-3} \) cm. It should be noted that a few correlations for oscillatory turbulent flow in a pipe do exist \[106, 164\], but the parameter ranges in which they are valid coincide with only a few experiments performed in this work. In those select experiments, the values of \( f \) calculated using the correlation of Ohmi et al. for oscillatory turbulent flow \[106\] were compared to the values of \( f \) obtained using Equation 3.19; they were in good agreement, with a maximum deviation of 10%. The work of Ohmi et al. is based on a quasi-steady state approach for oscillatory turbulence that is appropriate when \( \langle Re \rangle \gg 700\alpha \). This condition, in general, was satisfied by the oscillatory turbulent experiments of this work; based on this information it was surmised that using Equation 3.19 to calculate \( f \) is a reasonable approach for this system.

The two contributions to the pressure gradient given by Equation 3.18 are \( \pi/2 \) radians out of phase with one another. Because the Darcy’s law flow in the porous diffusion layer is both laminar and low Reynolds number, the time-average magnitude of the pressure gradient is the quantity of interest. This is simply \( 2/\pi \) times the amplitude of the oscillatory pressure gradient, and this amplitude is the root mean square of the out of phase contributions in Equation 3.18. Thus,

\[ \langle \left| \frac{\partial P}{\partial x} \right| \rangle = \frac{2}{\pi} \left[ (\rho \omega U_o)^2 + \left( 2f \rho U_o^2 \frac{\alpha}{d} \right)^2 \right]^{1/2}, \quad (3.20) \]
which can be further simplified using the definition of $U_o$:

$$
\left\langle \left| \frac{\partial P}{\partial x} \right| \right\rangle = \frac{\rho \omega^2 \Delta V}{3\pi wd} \left[ 1 + \left( \frac{f \Delta V}{3wd^2} \right)^2 \right]^{1/2}.
$$

(3.21)

For the parameter ranges of the experiments, the magnitude of $(f \Delta V/3wd^2)$ varied from 1.0 to 38.7. In the turbulent oscillatory experiments, therefore, the friction at the channel walls was the dominant contributor to the time-averaged turbulent pressure gradient.

To review, the estimate of the time-average magnitude of the pressure gradient given either by Equation 3.15 or Equation 3.20—depending on the flow regime in the anode channel—was used in Equation 3.1 to solve for the velocity in the porous diffusion layer. Since the oscillatory flow has sufficient amplitude to be considered steady, $D_{yy}$ was computed using Equation 3.6 for all the experiments. With this information, the models given by Eqs. 3.9 and 3.10 were used to predict the limiting current density and compared to experimentally observed values.

### 3.3 Experimental Method

Recent work [18] has indicated that high-throughput electrocatalyst screening systems are a good barometer of expected DMFC performance. To validate that the oscillatory technique had promise enough to warrant further study in a DMFC, preliminary experimentation was performed using the multi-array high throughput electrocatalyst screening system NUV100P (Nuvant Systems, Inc., Crown Point, IN) with a Johnson-Matthey 50:50 Pt-Ru catalyst on carbon black. The diffusion layer was carbon paper TGP-H-060 (Toray Industries, Inc., Decatur, AL). A solution of 0.5 M CH$_3$OH in water was fed to the anode at 8 cm$^3$ min$^{-1}$. Humid-
ified H₂ at 60 °C was fed to a common counter electrode at 180 cm³ min⁻¹. The cell temperature was held constant at 80 °C. An oscillatory syringe pump with a manually variable stoke volume (0.01 cm³ < ΔV < 0.90 cm³) and frequency (1.32 rad s⁻¹ < ω < 38.83 rad s⁻¹) was positioned in-line just after the methanol feed pump with a tee junction. First, a series of transient experiments were performed. The voltage was forced to be constant, the oscillatory pump was activated, and the response of the cell was measured. Second, linear sweep voltammetry (LSV) tests were performed, with a scan rate of 6 mV s⁻¹ from 0.0 to 1.0 V versus the dynamic hydrogen electrode.

All DMFC experimentation was performed in a single cell (ElectroChem, Inc., Woburn, MA) with an active area A_e = 5 cm² (2.236 cm × 2.236 cm). The cell contained two gold-plated copper end plates, two graphite current collectors with the previously described flow field (Figure 3.5), and two Teflon gaskets sandwiched around the membrane electrode assembly (MEA). The cell was secured by eight bolts tightened to 6.2 N·m with a torque wrench. The MEA used was a commercially available product from www.fuelcellstore.com (Boulder, CO). It consisted of a Nafion 117 membrane with 4.0 mg cm⁻² Pt/Ru (1:1 atomic ratio) and 2.0 mg cm⁻² Pt as the catalyst loadings on the anode and cathode, respectively. The diffusion layer (DL) on both the anode and cathode was composed of different composites of varying structure and thickness l_i. The three different composites used are summarized in Table 3.2.

Experiments were performed using a gas distribution system (Teledyne Medusa RD), a 890C methanol flow control unit (Scribner Associates, Southern Pines, NC), and a 890C-100W fuel cell test load (Scribner Associates). The three units were controlled and monitored by the software package Fuel Cell® for Windows
(Scribner Associates). The gas distribution system was used to deliver humidified hydrogen at a cell temperature of 50 °C and a flow rate of 100 cm³ min⁻¹ to pre-treat the MEA. The hydrogen was delivered for a period of 10 hours to both the anode and the cathode. After the MEA pre-treatment, the anode and cathode inlets and outlets were connected to the 890C-MeOH flow control unit. The oscillatory syringe pump described previously was placed in-line with the anode feed using a tee junction. The majority of experiments were performed at a cell temperature of 70 °C and ambient pressure. The anode feed solution was 1.0 M methanol in distilled water, and the cathode feed was pure oxygen. The flow rates of the anode and cathode were 12 cm³ min⁻¹ and 500 cm³ min⁻¹, respectively. The open circuit potential (OCP) was allowed to stabilize at these flow rates.

Performance measurements were made by scanning the voltage, controlled by the 890C-100W fuel cell test load and the accompanying software, at a rate of five seconds per data point from the OCP to zero. Before any measurements were taken with the oscillatory syringe pump in operation, the DMFC was heat treated by varying the cell temperature. During the heat treatment of the DMFC, the voltage scan was also reversed back to the OCP; no significant hysteresis was observed. After the heat treatment, the DMFC was returned to the cell temperature of interest (typically 70 °C). A baseline voltage scan was performed, in which the anode feed rate had only a steady flow component. This was followed by a series of voltage scans with an oscillatory flow component superimposed upon the steady flow using the syringe pump. At a particular stroke volume, experiments were performed across the range of available frequencies. Each experiment was performed a minimum of twice to verify the observed behavior. This procedure was repeated at several other stroke volumes.
3.4 Results

As mentioned, initial experimentation was performed using the NUV100P. Since no cathode reaction was taking place, measurements taken in the NUV100P isolated the behavior of the anode. Though it does not perfectly mirror what occurs in a full cell DMFC since several of the factors affecting DMFC performance are coupled with one another, it does eliminate the possibility of mass transfer limitations being affected by activity at the cathode, as well as eliminating the effect of methanol cross-over. Non-standard behavior resulting from these experiments is certain to be due solely to changes in mass transport behavior in the anode flow field and porous diffusion layer.

A typical transient current density response is given in Figure 3.9. It is clear that inducing fluid oscillations has an appreciable effect on the current-voltage behavior of the anode. Three important characteristics of the anode’s response when oscillatory flow is induced can be recognized from the experiment: the current density improves instantaneously, the improvement remains stable for as long as the oscillations are present, and it is reproducible (that is, improvements can be recovered again by reinstating the fluid oscillations).

The LSV tests, such as the series performed at a constant stroke volume in Figure 3.10, demonstrate the other important characteristic of the anode’s response to oscillatory flow. There is no observed difference between steady and oscillatory flow experiments when the potential is \(\lesssim 0.6\) V. At these potentials, the response of the anode is due to kinetics and membrane conductivity. At potentials above 0.6 V, the anode is limited by mass transport and there is significant improvement when oscillatory flow is present. The improvement increases with the oscillation frequency. At the highest frequencies, the power density improved by greater than
Figure 3.9. The transient response of a standard DMFC anode catalyst in the NUV100P to induced fluid oscillations. The cell potential was held constant at 1.0 V vs. the dynamic hydrogen electrode, the cell temperature was 80 °C, the steady feed rate was 8 cm³ min⁻¹, and the stroke volume was 0.17 cm³.
Figure 3.10. Current density response of a standard DMFC anode catalyst in the NUV100P to a LSV test. The cell temperature was 80 °C, the steady feed rate was 8 cm³ min⁻¹, and the stroke volume was 0.44 cm³.

30% at high cell potentials.

Additional verification that oscillatory flow was affecting mass transport in the NUV100P was obtained when the flow was in the presence of an electro-kinetically poor catalyst. A less active catalyst may never experience mass transfer limitations, as the reaction rate never becomes fast enough to consume all the methanol and water at the surface. Oscillatory flow did not enhance the performance of these catalysts. One example is shown in Figure 3.11, where it is clear that the current density in the voltage range where mass transfer limitations occur did not vary with oscillation frequency.

The results from the NUV100P motivated further experimentation in the DMFC. A summary of the essential features of the DMFC experiments is pre-
Figure 3.11. Current density response of a DMFC catalyst which is considerably less active than the catalyst of Figure 3.10 in the NUV100P to a LSV test. The cell temperature was 80 °C, the steady feed rate was 8 cm$^3$ min$^{-1}$, and the stroke volume was 0.44 cm$^3$. 
sented in Figure 3.12. Each column in the figure corresponds to a different stroke volume, while each row corresponds to a different diffusion layer. Visual comparison of these graphs with one another yields several qualitative observations concerning the mass transfer behavior of the DMFC when the anode is exposed to an oscillatory flow.

First, from a comparison of the polarization curves obtained when the anode feed was steady, it was observed that $i_{lim}$ increased with decreasing diffusion layer thickness. Since all experimentation was performed at the same cell temperature, this is to be expected if the limiting current is indeed proportional to a total mass transfer coefficient. Despite the complexity of the geometry and flow field, decreasing the distance over which a solute must diffuse will increase the flux of solute through the medium, provided the driving force remains the same.

Second, the polarization curves distinctly demonstrate that the oscillatory flow improves mass transport in the DMFC anode once a critical amplitude is achieved. There is no observed difference between steady flow operation and oscillatory flow operation in either the kinetically-limited region or the ohmic region of the polarization curves. Deviation from steady flow experiments occurred only at high current densities when saturation of the current density had begun (i.e. region 3 in Figure 3.2). Thus, fluid oscillations did not affect membrane resistance or reaction kinetics in the DMFC, as would be expected.

Third, experiments performed with Diffusion Layer A (see Figures 3.12(a), 3.12(d), 3.12(g)) illustrate that the potential for enhancement in the mass transfer limiting region is only accessible when the amplitude of the oscillations are large; that is, the combination of $\Delta V$ and $\omega$ results in large values of $U_o$. The requirement that the value of $U_o$ be large is also observed to a lesser extent in the experiments
Figure 3.12. DMFC polarization curves obtained at 70 °C for: (a)-(c) \( \Delta V = 0.17 \text{ cm}^3 \), (d)-(f) \( \Delta V = 0.44 \text{ cm}^3 \), (g)-(i) \( \Delta V = 0.79 \text{ cm}^3 \). The stroke volumes were 0.17, 0.44, and 0.79 cm\(^3\) for the first, second, and third columns, respectively. The anode feed rate was 12 cm\(^3\) min\(^{-1}\) and the cathode feed rate was 500 cm\(^3\) min\(^{-1}\).
using Diffusion Layer B (Figures 3.12(c), 3.12(f), 3.12(i)). In the case of Diffusion Layer C (Figures 3.12(b), 3.12(e), 3.12(h)), enhancement in $i_{lim}$ is present even at smaller values of $U_o$; this is not unreasonable because layer C, which is thicker, had a greater degree of mass transfer limitation in the absence of oscillations.

Fourth, the magnitude of the improvement in experimental values of $i_{lim}$ suggest significant enhancement in mass transport. Typical improvements in limiting current density range from 50% – 80%. In a few cases the improvement is greater than 100%. This suggests that the total mass transfer coefficient was improved by as much as a factor of two.

Finally, enhancement in peak power density was also observed during experimentation. Such improvement was possible only in cases where the performance decay which is characteristic of mass transfer limitations occurred before the peak value was reached in the steady flow baseline experiment. In these experiments, one example of which is Figure 3.12(c), the peak power density was increased up to a maximum of 30%.

Additional experiments were performed in the DMFC using Diffusion Layer A and a syringe pump capable of accessing frequencies up to 251 rad s$^{-1}$. Investigation in this parameter range was motivated by the results presented in Figures 3.12(a), 3.12(d), and 3.12(g). It was desirable to see if DMFC performance with Diffusion Layer A could be enhanced more significantly than was possible using the initial frequency range. The results of this investigation appear in Figure 3.13. Despite the reduced cell temperature, it is evident from the experiments that mass transport was enhanced significantly in the cloth diffusion layer when the frequency was increased to a sufficient magnitude.

There are a few items to note from experimentation in the higher frequency
Figure 3.13. DMFC polarization curves obtained at $50 ^\circ C$ for $\Delta V = 0.17 \text{ cm}^3$ using Diffusion Layer A. The anode feed rate was 12 cm$^3$ min$^{-1}$ and the cathode feed rate was 500 cm$^3$ min$^{-1}$. 
range. First, the stroke volume that was used is the same as in Figure 3.12(a). This is significant because a diffusion layer which appeared to have a resistance that negated the effect of oscillatory flow did in fact have capacity for mass transport enhancement when higher frequencies were used. Second, we observed the instantaneous nature of the transition between oscillatory flow performance and steady flow performance in the experiment where $\omega = 94.6 \text{ rad s}^{-1}$. When the oscillations were discontinued during the voltage scan, the current density quickly reverted back to align with the behavior observed during steady flow operation. Lastly, the experiments suggest that there is a trade-off between frequency (or more precisely, $U_o$) and performance, in the sense that above a frequency threshold ($\sim 125 \text{ rad s}^{-1}$ in this case) only minimal gains in $i_{lim}$ were observed. This is not surprising because other mass transfer resistances will ultimately dominate the overall resistance.

3.5 Discussion

Experimental observations show that inducing oscillatory flow in the anode of a DMFC enhances performance at high current densities. At some operating conditions, the enhanced performance not only manifested as an appreciable gain in limiting current density, but also larger peak power densities. This enhancement was due to a significant decrease in overall mass transfer limitations. As previously mentioned, mass transfer limitations have traditionally been attributed to two mechanisms: physical blockage of the diffusion layer pores by CO$_2$ gas and the inability of the solutes (in particular, methanol) to diffuse quickly enough to the catalyst surface.

In previous work where evolved CO$_2$ gas was directly observed to correspond
with reduced performance at high current densities [160], the steady flow rates to the anode were low (that is, < 8 cm$^3$ min$^{-1}$) for a cell of similar size. In those experiments, nearly all CO$_2$ bubbles were removed at steady flow rates > 4 cm$^3$ min$^{-1}$ at the expense of reduced performance. It has also been demonstrated that performance can be recovered by significantly increasing the flow rate if the anode feed is preheated [5, 6]. In these experiments, however, the anode feed was at ambient temperature and increasing the flow rate negatively affected the performance by decreasing the overall cell temperature, as shown in Figure 3.14. Increasing the flow rate from 12 cm$^3$ min$^{-1}$ to 50 cm$^3$ min$^{-1}$ did not affect the limiting current density; the peak power density, however, was decreased significantly. Increasing the flow rate an additional factor of five to 250 cm$^3$ min$^{-1}$ further decreased the peak power output. The slight increase in $i_{lim}$ at this flow rate is not surprising: its magnitude is comparable to that of the oscillatory flow where mass transport enhancement was first observed in Figure 3.12. Therefore, an anode flow rate of 12 cm$^3$ min$^{-1}$ appeared to be sufficient to sweep out a large portion of the CO$_2$ bubbles, but not so large as to significantly cool the cell. All experiments depicted in Figure 3.12 were performed at this flow rate.

The dependence of the limiting current density on the molecular diffusion coefficient of methanol is presented in Figure 3.15(a). $D_o$ was varied by changing the cell temperature from room temperature up to 80 °C. The cell temperature also influences other variables in the DMFC, such as reaction rate, membrane properties, and liquid-gas equilibria, making it difficult to isolate the effect that the diffusion of methanol has on limiting current. For the temperature range considered in Figure 3.15(a), $i_{lim} \sim D_o^{3/2}$. The limiting current density clearly has a dependence on the diffusion rate of methanol; that the relationship is not
Figure 3.14. The effect of increasing the steady feed rate on DMFC performance. The cell temperature was 70 °C and the cathode feed rate was 500 cm³ min⁻¹ using Diffusion Layer A.
linear is probably due to the temperature dependence of other mechanisms in the DMFC. The issue can be further resolved if the methanol concentration in the feed is varied, as it is in Figure 3.15(b). When the methanol concentration is reduced by two, $i_{lim}$ is also reduced by a factor of two. This proportionality would not be expected if carbon dioxide was playing a significant role in the mass transport behavior at high current densities. It appears reasonable, therefore, to conclude that the dominant mass transfer resistance when the DMFC is operated at high flow rates and low methanol feed concentrations is the diffusion of methanol.

The simplified mass transfer model developed in Section 3.2 was compared to the oscillatory flow experiments to test this hypothesis. The model given by Equation 3.9 has two or three empirical constants depending on the diffusion layer. It is presented along with experimental data in Figure 3.16. As Figure 3.16 shows, the model is in good quantitative agreement with observed limiting current densities. The transition between the two asymptotic regions ($Pe \to 0$ and $Pe \to \infty$) is captured quite well. The model isolates the mass transfer resistance of the diffusion layer and is a function of $Pe$ only. It is significant that the improvements in $i_{lim}$ observed experimentally rapidly increase when $Pe \gtrsim 1$; this is consistent with the assumption that the diffusion of methanol was convectively enhanced by the fluid oscillations.

The modified model of Equation 3.10 was in reasonable agreement with the experimental data, but it overestimated the mass transfer resistance of the diffusion layers. As Table 3.3 shows, the values of $k_{tot}$ as $Pe \to 0$ calculated using Equation 3.10 are smaller than the values of $k_{tot}$ from the experimental data by 45 to 55%. The smaller values of $k_{tot}$ are more than likely a result of the simplicity of the model, which only considers methanol transport in the $y$ direction. It
Figure 3.15. (a) The relationship of the limiting current to the molecular diffusion coefficient of methanol in the DMFC. The experiments were performed using an anode feed rate of 12 cm$^3$ min$^{-1}$, a cathode feed rate of 500 cm$^3$ min$^{-1}$, and Diffusion Layer C. The cell temperatures used were 25, 30, 50, 60, 70, and 80 °C. The solid line is provided as a reference; it is a line of slope = 3/2. (b) DMFC polarization curves obtained at 70 °C and the same conditions as (a), with the exception of the methanol feed concentration. Note that the limiting current density increases by a factor of two as the methanol feed concentration is increased by two.
Figure 3.16. Model (solid lines) described by equation Equation 3.9 compared to limiting current densities measured in DMFC experiments (open symbols) as a function of $Pe$. 
TABLE 3.3
TOTAL MASS TRANSFER COEFFICIENTS OF THE DIFFUSION LAYERS AT THE TWO EXTREMA OF THE EXPERIMENTS

<table>
<thead>
<tr>
<th>DL</th>
<th>$k_{\infty}^{\text{tot}}$ (cm s$^{-1}$)</th>
<th>$k_{0}^{\text{tot}}$ (cm s$^{-1}$)</th>
<th>Pred. $k_{0}^{\text{tot}}$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.31×10$^{-3}$</td>
<td>9.09×10$^{-4}$</td>
<td>4.54×10$^{-4}$</td>
</tr>
<tr>
<td>B</td>
<td>1.51×10$^{-3}$</td>
<td>8.43×10$^{-4}$</td>
<td>3.81×10$^{-4}$</td>
</tr>
<tr>
<td>C</td>
<td>1.17×10$^{-3}$</td>
<td>5.48×10$^{-4}$</td>
<td>3.11×10$^{-4}$</td>
</tr>
</tbody>
</table>

a The superscripts refer to the corresponding Pe asymptote. Refer to Table 3.2 for the compositions of each layer.

b The predicted value as $Pe \to 0$ is calculated using Equation 3.10.

ignores the potential for methanol to diffuse under the ribs of the anode channel, thereby reacting at more catalyst sites, and the influence of carbon dioxide gas. Qualitatively, however, the mass transfer behavior of the DMFC—in particular the transition between the two $Pe$ asymptotes—was captured by Equation 3.10 for all three diffusion layers.

Inducing oscillatory flow also improved the peak power density of the cell in some experiments. The technique will not be advantageous, however, if the power required to induce the oscillations eclipses the observed enhancements in power density. The mechanical power, neglecting losses, can be estimated as

$$\Psi \approx Q_o \Delta P,$$  \hspace{1cm} (3.22)

where $\Psi$ is the power, $\Delta P$ is the pressure difference over the length of the anode channel and $Q_o$ is the amplitude of the oscillatory volumetric flow rate. Equa-
tion 3.22 represents the minimum power required to generate fluid oscillations independent of the methodology that is used. Improvements in the peak power density were observed for \( \langle Re \rangle \gtrsim 10^3 \). Consequently, the flow was turbulent and the pressure contribution due to friction at the walls given by the second part of Equation 3.18 was the dominant source of pressure loss. To simplify the analysis, the pressure gradient in the channel is assumed to be represented by the frictional source only, so \( \Psi \) can be written as

\[
\Psi \approx Q_o \left( \frac{\partial P}{\partial x} \right)_F L_{tot} = \frac{\Delta V \omega L}{2} \frac{2 \rho_f}{d} U_o^2 = \frac{1}{36} \frac{\rho_f L_{tot}}{w^2} \left( \frac{\omega \Delta V}{d} \right)^3,
\]

where \( L_{tot} \) is the total length of the channel in the anode flow plate and the subscript \( F \) denotes the frictional portion of Equation 3.18. To signify that Equation 3.23 is estimating the minimum power required to drive the oscillations, it was as \( \Psi_{\text{min}} = \Psi / A_e \), which is a power density. In this form it can be directly compared to measured power densities from the experiments. The ratio of the power density in an oscillatory experiment \( \Psi_{\text{osc}} \) normalized by the power density in the corresponding steady flow experiment \( \Psi_o \) is presented in Figure 3.17 against \( \Psi_{\text{min}} \), which is also normalized by \( \Psi_o \). The relationship \( \Psi_{\text{osc}} / \Psi_o = 1 + \Psi_{\text{min}} / \Psi_o \) was added to the figure for reference; it is the break even point at which the oscillatory flow produces more power than it requires. It is clear from examining Figure 3.17 that for the DMFC tested the energy dissipated in the fluid exceeded the gain in power output for nearly all conditions.

To use fluid oscillations to efficiently increase power output it is necessary to alter the properties of the diffusion layer, specifically reducing the pressure gradient required to achieve the Darcy’s law flow which produces the mass transfer enhancement. For example, the relationship between pressure drop and the diffu-
Figure 3.17. The peak power density in an oscillatory flow experiment \( \Psi_{osc} \) for the three diffusion layers plotted against the minimum power density required to induce the oscillatory flow \( \Psi_{min} \). Each quantity is normalized by the peak power density in the corresponding steady flow experiment \( \Psi_o \). The power requirement break even point is represented by the solid line. Scatter in the data points is due to different means of generating oscillatory flow in the diffusion layer (e.g. \( \omega \) or \( \Delta V \)).
sion layer velocity is already known from Equation \ref{3.1}, and using the limit of the isotropic permeability defined in Equation \ref{3.3} when $\phi$ is small,

\begin{equation}
U_{dl} \sim \frac{a^2 \ln (\phi^{-1})}{\phi \mu} \left\langle \left| \frac{\partial P}{\partial x} \right| \right\rangle. \tag{3.24}
\end{equation}

The scaling suggested in Equation \ref{3.24} can be combined with the definition of the Peclet number to yield

\begin{equation}
Pe \sim \frac{a^3 \ln (\phi^{-1})}{\phi \mu D_o} \left\langle \left| \frac{\partial P}{\partial x} \right| \right\rangle, \tag{3.25}
\end{equation}

which indicates that if $a$ is doubled while the solid fraction $\phi$ remains the same, the pressure gradient required to produce the same $Pe$ is reduced by a factor of 8.

The same type of analysis can be extended using the definition of power in Equation \ref{3.22}, again assuming that the turbulent oscillatory pressure gradient is only due to friction. Darcy’s law can be used to relate $U_o$ to $U_{dl}$ along with the relationship of Equation \ref{3.24} to give the following:

\begin{equation}
U_o = \left( \frac{U_{dl} \mu d}{2 \kappa f \rho} \right)^{1/2} \sim K \left\langle \left| \frac{\partial P}{\partial x} \right| \right\rangle^{1/2}, \tag{3.26}
\end{equation}

where $K$ is a collection of geometric and fluid property constants. Combining Equation \ref{3.26} with the scaling given in Equation \ref{3.25} yields:

\begin{equation}
\Psi \sim \frac{Pe^{3/2}}{a^{9/2}}, \tag{3.27}
\end{equation}

which suggests that increasing $a$ by a factor of two will reduce the minimum power requirement to drive the fluid oscillations at fixed $Pe$ by more than a factor of 20.
This would have the effect of shifting the data points in Figure 3.17 to the left by a factor of 20, leading to efficient enhancement of the peak power density, at least for thicker diffusion layers.

3.6 Conclusions

In this chapter, an oscillatory flow was superimposed upon the steady feed to the anode of a DMFC. It was demonstrated that performance improvements can be obtained using this technique, even without optimization of the system parameters; in particular, significant increases in the limiting current density (up to 100%) and peak power density (up to 30%) were observed. A mass transfer model was developed using an existing theory of dispersion in a fibrous porous medium to predict the observed limiting current densities as a function of the Peclet number in the diffusion layer of the anode. The steady flow condition (i.e. \( U_{dl}/\omega a \gg 1 \)) was satisfied in these experiments, and the theoretical prediction was in good agreement with experiments performed using three different diffusion layers. The limiting current was found to increase rapidly as \( Pe \gtrsim 1 \), which suggests that the diffusion of methanol is convectively enhanced in the direction transverse to the oscillatory flow. The primary mass transfer resistance in the DMFC anode at high current densities for the operating conditions of this study is the diffusion of methanol to the catalyst surface.

There are several ways in which an appropriately designed DMFC could take advantage of the results of this study. For example, it is not always desirable to operate at the high current densities where the technique is effective, for reasons of both catalyst utilization and gas removal. In such situations, oscillations in the anode feed are unnecessary. However, if a greater power output or a higher
current density were required, fluid oscillations could be induced, leading to an instantaneous increase in accessible power densities and limiting currents.

A DMFC with an implemented oscillatory flow generation method could also take advantage of using a thicker diffusion layer, provided the diffusion layer has an open structure. A thicker diffusion layer would permit the use of higher methanol concentrations in the anode feed, and thus better performance at low current densities because the methanol cross-over will be reduced. At high current densities, oscillatory flow would be used to eliminate the resistance of the diffusion layer by improving the mass transfer in the porous medium. This approach is investigated in detail in Chapter 4.

In regard to catalyst utilization, the DMFC is typically loaded with $\leq 4 \text{ mg cm}^{-2} \text{ Pt:Ru}$ at the anode. The DMFC is not optimized for high loadings as mass transfer limitations result in inefficient use of catalyst. Reducing such limitations would improve catalyst utilization at high current densities.

Given the prohibitive power requirements which were presented in Figure 3.17, however, using oscillatory flow as a diagnostic tool is its most promising application. The present study has shown that if appropriate values of $\Delta V$ and $\omega$ are chosen, the oscillations will produce an enhancement in the mass transfer which is easily observable as an increase in limiting current density. It has also been observed that MEAs which are not kinetically active enough to reach the mass transport limitation regime are not affected by the oscillations and the polarization curve is unchanged. Generating oscillations would be a simple technique to determine if mass transport limitations do exist in a particular DMFC or for a particular MEA, and if they do, to estimate the relative magnitude of the limitations. Additionally, oscillatory flow could be used to permit other elements of the
DMFC, such as anode kinetics or membrane transport, to be studied without the interference of mass transport limitations.

There are other design or operational variables which were unexplored in this experimental study but will have effect on the mass transport behavior of methanol in the DMFC anode. Notably, neither the effect of the concentration of methanol in the anode feed nor the steady flow rate upon which the oscillatory flow is superimposed were studied. The effect of these variables and an optimization of the oscillatory technique and flow field geometry is examined and discussed further in Chapter 4. Regardless, this work has demonstrated that oscillatory flow enhances mass transport and has the potential to significantly improve performance in an appropriately designed DMFC.
CHAPTER 4

OPTIMIZED USE OF OSCILLATORY FLOW IN THE DIRECT METHANOL FUEL CELL

4.1 Introduction

In Chapter 3 an oscillatory flow method for improving mass transfer in the direct methanol fuel cell was described. The improvement in the DMFC is directly observable as an increase in the limiting current density and, if conditions are such that the DMFC is mass transfer limited before the peak power density is achieved, there will be an enhancement in the maximum power density of the cell. Based on a combination of theoretical and empirical considerations (see Section 3.2), a model was developed to predict the limiting current density of the DMFC when oscillatory flow was present. The experimental study of Chapter 3 was designed to observe the effect of oscillatory flow in a typical DMFC and no attempt was made to optimize the system to take advantage of the benefits of oscillatory flow. In this chapter, the experimental approach used in Chapter 3 is extended to consider optimal use of oscillatory flow in the DMFC.

In one sense, since DMFC technology is still in early stages of development, most studies of DMFC operation to date are concerned with optimization. The definition of “optimization” will vary, but in general most studies are concerned with either: (1) achieving a maximum power density in the cell, or (2) designing
a DMFC that makes the best possible use of required fuel and energy. Since the early days of DMFC development, many of the greatest power densities have been achieved in optimized cells running at cell temperatures $\gtrsim 100 \, ^\circ C$ \cite{7, 110}. This is not ideal for many of the DMFC’s possible applications as it is susceptible to higher rates of methanol cross-over and requires higher rates of heat transfer i.e it will be inefficient with respect to the second category of optimization. Recent optimization studies in the second category include investigating the dynamic control of methanol concentration \cite{126, 153} and the efficiency of energy use in the DMFC \cite{150}. The goal of this optimization study was to maximize DMFC performance using oscillatory flow, with only post-experimental consideration of the operation efficiency.

The previous study did not examine the effect of several operational parameters that affect DMFC performance; of specific interest are parameters which control the magnitude of the mass transfer resistance of the DMFC anode. The relevant operational parameters with respect to mass transport behavior are the steady anode feed rate $Q_{an}$, the methanol concentration in the feed $c_M$, and the cell temperature. The effect of these parameters was briefly discussed in Section 3.1 of the previous chapter. It was concluded that, in general, both a higher feed rate and a higher concentration will reduce mass transport limitations; however, the DMFC is a complex electrochemical system and simply increasing $Q_{an}$ and $c_M$ will also have adverse effects. Therefore, the optimal choice of $Q_{an}$ and $c_M$ is not obvious and must be considered carefully. The cell temperature is an important variable but its effect was not thoroughly explored, primarily to keep the parameter space of this study manageable. Operational variables on the cathode side are significant but have a smaller effect on mass transfer at the anode. These include
the composition of the cathode feed (air, pure oxygen, etc.), the cathode feed rate $Q_c$, and the application of back pressure. A handful of experiments considered the effect of cathode variables to insure the DMFC would be operated at optimum conditions for this study.

The anode geometry was also unoptimized in the work of Chapter 3. The term “geometry” refers to the anode flow field, the diffusion layer-channel interface, and the composition and microstructure of the diffusion and catalyst layers. Though a properly designed catalyst layer would significantly affect the mass transport limitations of the anode, it has been a subject of extensive research (for an example of one such study, see Kim et al. [70] or for a recent review, see Liu et al. [89]) and was not considered in this study. Eliminating the catalyst layer as a variable (or more precisely, the entire MEA) conveniently expunges another complication from the analysis: the sensitivity of DMFC performance to the procedure used to prepare the electrode, which has been well-documented [88, 111, 133]. For the similar reasons, the effect of the polymer membrane was not considered in these experiments.

The anode flow field and diffusion layer both have a significant role in the determination of mass transfer resistance in the DMFC, which was described in detail in the previous chapter. A significant amount of effort has gone into designing the anode flow field [4, 125, 155, 159]. For these experiments, the same flow field (see Figure 3.5) was used since it had been characterized in previous work. A similar number of studies have been performed for the anode diffusion layer [108, 140, 152, 157], but it was observed in Chapter 3 that the diffusion layer is the primary mass transfer resistance in the DMFC and thus careful choice of the diffusion layer will be important for this optimization study.
The strategy for optimization in this chapter was to attempt to balance two competing effects: methanol cross-over, which increases as $c_M$ and $Q_{an}$ increases and is detrimental to performance at lower current densities, and the mass transfer resistance of the anode, which increases as $c_M$ and $Q_{an}$ decreases. It is similar in concept to recent work performed in passive DMFC which used a thick porous carbon plate to prevent methanol from reaching the catalyst surface and permit the use of very high methanol concentrations ($> 16 \text{ mol L}^{-1}$) [1, 2]. Because this work was concerned with a active DMFC, it was not anticipated that the use of such extreme concentrations would be possible; however, the use of the diffusion layer as a barrier to methanol diffusion will have a similar effect.

The experimental work in this chapter is described briefly in the next section. The results of the study are presented in the third section, which focuses on how $Q_{an}$, $c_M$, and the diffusion layer affected DMFC performance with and without oscillatory flow. In the fourth section, a discussion of the general trends of DMFC performance, the applicability of the model of Chapter 3, and experimental reliability is presented. Finally, the feasibility of an optimized oscillatory flow DMFC is examined.

4.2 Experimental Method

The DMFC experimental apparatus used in this study was identical to the system which were described in Section 3.3. Likewise, the MEAs had the same catalyst loadings, ELAT carbon cloth diffusion layers, and Nafion 117 membranes as before. In this study, the cathode diffusion layer was always carbon paper TGP-H-060 regardless of the type of diffusion layer used on the anode. Several different diffusion layers were used on the anode and they are presented in Table 4.1 below.
TABLE 4.1
PROPERTIES OF THE DIFFUSION LAYERS USED IN THE
OPTIMIZATIONS STUDY

<table>
<thead>
<tr>
<th>Diffusion Layer</th>
<th>$l$ (cm)</th>
<th>$\phi$</th>
<th>$a$ (microns)</th>
<th>$\kappa$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELAT carbon cloth</td>
<td>0.027</td>
<td>0.30</td>
<td>8</td>
<td>$4.90 \times 10^{-9}$</td>
</tr>
<tr>
<td>Toray CP TGP-H-060</td>
<td>0.019</td>
<td>0.22</td>
<td>8</td>
<td>$8.01 \times 10^{-8}$</td>
</tr>
<tr>
<td>Toray CP TGP-H-120</td>
<td>0.037</td>
<td>0.22</td>
<td>8</td>
<td>$6.30 \times 10^{-8}$</td>
</tr>
<tr>
<td>Toray CP TGP-H-090 (2x)</td>
<td>0.056</td>
<td>0.22</td>
<td>8</td>
<td>$7.14 \times 10^{-8}$</td>
</tr>
<tr>
<td>316SS wire cloth (2x)</td>
<td>0.032</td>
<td>0.44</td>
<td>66</td>
<td>—</td>
</tr>
</tbody>
</table>

Note that the ‘2x’ on Table 4.1 refers to the diffusion layer being a double layer of the same material.

A few minor alterations were made to the experimental system as follows. First, a second tee junction was introduced after the tee junction which combines the steady and oscillatory flows. This tee junction housed a ‘K’-type thermocouple which was part of a pre-heating control loop on the anode feed line. The heat was provided by heat tape controlled by a microprocessor temperature controller (Dwyer Instruments, Michigan City, IN). Second, the cathode outlet was connected to a back pressure regulator capable of up to 50 psi instead of venting directly to the atmosphere. This also required the use of a moisture trap on the cathode outlet line so water vapor did not enter the regulator. Third, the heating coil on the fuel cell was replaced with a new 40W heater so the heat could be supplied more evenly across the cell. Finally, the oscillatory syringe pump motor was replaced by a motor capable of a larger range of frequencies (up to 251 rad
s\(^{-1}\)) with a digital display of the rotation speed. This is the same motor which was used to obtain the data in Figure 3.13.

The measurement of DMFC performance was undertaken using the same approach that was used in the previous chapter. A series of experiments were designed to isolate one parameter of the following: \(Q_{an}, c_M, Q_c, \) the diffusion layer, cell temperature, \(\omega, \) or \(\Delta V.\) In the cases where \(Q_{an}, c_M, Q_c, \) or cell temperature were being investigated, the DMFC responded dynamically to the change in the parameter of interest. To preserve confidence in the experimental observations, the OCP was required to remain stable for a minimum of 15 minutes after a parameter change before the first measurement was begun. If the diffusion layer was being changed, which required discontinuing the flow of fuel and heat while the cell was dismantled and then reassembled, the DMFC was run at OCP conditions for a minimum of 1 hour.

4.3 Results

The subsections appearing below represent a series of many experiments which attempted to isolate certain parameters in the DMFC, and only representative data is provided for each case. As has been mentioned previously, the DMFC is a complex electrochemical system with several coupled reaction and transport processes. This makes it difficult to perform analysis of a quantitative nature without sophisticated models. Analysis is further complicated by the performance decay of the DMFC over time as the catalyst poisons and the feed concentration fluctuates. One example of the rate of decay is shown in Figure 4.1. Consequently, the phenomena observed in this work are discussed qualitatively.

One aspect of DMFC performance which was noted in Chapter 3 was the
Figure 4.1. Deterioration of DMFC performance with operating time. The operating conditions were as follows: cell temperature of 70 °C, $Q_{an} = 12$ cm$^3$ min$^{-1}$ of 1.0 mol L$^{-1}$, $Q_c = 500$ cm$^3$ min$^{-1}$ of pure O$_2$, and the diffusion layer was carbon paper TGP-H-060.
Figure 4.2. Transient current density response of the DMFC at a cell potential of 0.1 V. The letters A-E refer to the following oscillatory stroke volumes (cm$^3$) and frequencies (rad s$^{-1}$): A) 0.17 and 38.9, B) 0.44 and 38.9, C) 0.79 and 38.9, D) 0.44 and 8.92, and E) 0.44 and 38.9. The cell temperature was 70 °C, $Q_{an} = 12$ cm$^3$ min$^{-1}$, $Q_c = 500$ cm$^3$ min$^{-1}$, and $c_M = 1.0$ mol L$^{-1}$.

The instantaneous response of the DMFC to the fluid oscillations. This had been observed in the NUV100P directly (Figure 3.9) and inferred from the results of an experiment where the oscillations were discontinued during a voltage scan (Figure 3.13). Experiments were run to verify these observations before the optimization study was begun, in which the voltage was held constant at a cell potential that was in the mass transfer limiting regime. The transient experiments, such as the example given in Figure 4.2, confirmed that the fluid oscillations elicit an instantaneous and reproducible response in the DMFC.
4.3.1 Cell Temperature

The effect of cell temperature was not studied in great detail. It is a complex variable to study, as the kinetics, phase equilibria, and transport properties are all a function of the temperature. The performance of the DMFC as a function of several cell temperatures is shown in Figure 4.3. Unsurprisingly, the performance clearly improves as temperature increases, which is why DMFCs have typically been "optimized" at high temperatures. Of course, this performance improvement comes at an energy cost. The limiting current density and peak power density both increase with increasing temperature for the experiments of Figure 4.3. A different diffusion layer (carbon paper TGP-H-030) reveals a similar relationship between cell temperature and performance; however, the performance characteristics change at a different rate. This is clear from examining the slopes of the two data sets in Figure 4.4, which compares the limiting current densities measured in the DMFC as a function of temperature for two different diffusion layers. Figure 4.4 is an example of how the effect of temperature in the DMFC is difficult to isolate experimentally. With the exception of a few other experiments described below, the rest of the optimization study was conducted at a cell temperature of 70 °C.

The cell temperature influences the performance in another notable way. If the anode fuel is fed at ambient conditions, it will transfer heat away from the MEA until it reaches the cell temperature. Most importantly, this will locally reduce the reaction rate of the catalyst. A less active catalyst will suffer from reduced temperature more significantly than a more active catalyst. At high cell temperatures, even the fluid oscillations can contribute to this cooling effect and reduce performance, as shown in Figure 4.5. Note that the MEA at the
Figure 4.3. DMFC performance as a function of the cell temperature. The diffusion layer was carbon paper TGP-H-060, $Q_{an} = 12 \text{ cm}^3 \text{ min}^{-1}$, and $Q_c = 500 \text{ cm}^3 \text{ min}^{-1}$. 
Figure 4.4. The limiting current density of two diffusion layers as a function of cell temperature: carbon papers TGP-H-030 (■) and TGP-H-060 (○).
cell temperature of 90 °C was not very active, as there was no mass transfer limiting regime in the polarization curve. The same poor catalyst was “forced” to experience mass transfer limitations by significantly dropping the cell temperature and the cooling effect was negated. The magnitude of the mass transfer limitations at low temperatures was such that only minor improvements in performance occur when fluid oscillations are present. This is illustrated in Figure 4.6 for a series of experiments at ambient temperature. Ultimately, if the cell temperature was used to drive the DMFC into a mass transfer limited regime for any MEA and diffusion layer combination, the improvement due to inducing fluid oscillations did not compensate for the poor kinetics.

4.3.2 Methanol Concentration

From experiments in the previous chapter (see Figure 3.15(a)), it was already understood that $i_{\text{lim}}$ will be approximately proportional to $c_M$ at concentrations $\leq 1.0 \text{ mol L}^{-1}$. The majority of DMFC literature, both theoretical and experimental, agrees that the ideal value of $c_M \approx 1.0 \text{ mol L}^{-1}$, depending on other operating conditions (see, for example, the experimental work of Scott et al. [121] and the corresponding theoretical calculation by Kulikovsky [77]). This study sought to locate the proper balance between the diffusion resistance of the anode and $c_M$ to operate at concentrations greater than 1.0 mol L$^{-1}$.

The effect of concentration is presented for three different diffusion layers in Figure 4.7 at 1.0, 2.0, and 4.0 mol L$^{-1}$. Curiously, the performance of the thinnest diffusion layer studied (ELAT carbon cloth, Figure 4.7(a)) did not suffer at higher $c_M$ as expected. At 1.0 mol L$^{-1}$ it was mass transfer limited. The polarization curves for 2.0 & 4.0 mol L$^{-1}$ reduce and eliminate the mass transfer limitations,
Figure 4.5. DMFC polarization curves obtained at 90 °C for a carbon paper TGP-H-060 diffusion layer, $Q_{an} = 12$ cm$^3$ min$^{-1}$, and $Q_c = 500$ cm$^3$ min$^{-1}$. The power density (■) and cell potential (—■—) of a steady flow experiment is compared to the power density (○) and cell potential (—○—) of an oscillatory flow experiment with the following parameters: $\Delta V = 0.44$ cm$^3$ and $\omega = 26.9$ rad s$^{-1}$. 
Figure 4.6. DMFC polarization curve obtained at room temperature for a poor catalyst. The diffusion layer was carbon paper TGP-H-060, $Q_{an} = 12 \text{ cm}^3 \text{ min}^{-1}$, $Q_c = 500 \text{ cm}^3 \text{ min}^{-1}$, and $\Delta V = 0.44 \text{ cm}^3$. 


respectively, but there is no evidence of methanol cross-over at lower current densities.

The TGP-H-060 (Figure 4.7(b)) and TGP-H-120 (Figure 4.7(c)) diffusion layers are 1.7 and 2.4 times thicker than the ELAT carbon cloth, respectively. Consequently, the mass transfer limitations are much more pronounced when $c_M$ was 1.0 mol L$^{-1}$. In both cases, $i_{lim}$ roughly doubled when $c_M$ was doubled from 1.0 to 2.0. There was evidence that the higher concentrations reduced performance, particularly at low current densities; the presence of methanol cross-over is clearly seen. By comparison of the two carbon paper diffusion layers, it was concluded that thicker diffusion layers are capable of sustaining performance at larger $c_M$ before methanol cross-over and/or carbon dioxide generation begins to negatively affect DMFC performance.

The experimental observations of Figure 4.7 indicated that the use of $c_M > 1.0$ mol L$^{-1}$ could lead to improved performance, both in the peak power density and $i_{lim}$. However, for a particular diffusion layer, $c_M$ can become large enough to eliminate the mass transfer limitations of the DMFC at high current densities: notice the “fall-off” of the voltage-current density curve which is characteristic of mass transport limitations disappears when $c_M$ is 4.0 mol L$^{-1}$ for all three diffusion layers. Thus, oscillatory flow will not be beneficial at a $c_M$ of 4.0 mol L$^{-1}$, as Figure 4.8 shows. The fluid oscillations do enhance mass transport, but the DMFC is never limited by this mechanism. Instead, the additional mass transport provided by the oscillatory flow served only to increase the methanol cross-over. Subsequently, the performance suffers as $\omega$ increases.

The tenuous balance between methanol cross-over and mass transport enhanced by oscillatory convection is quite noticeable when the effect of fluid os-
Figure 4.7. Effect of methanol feed concentration $c_M$ on steady flow performance of the DMFC for three different diffusion layers: (a) ELAT carbon cloth, (b) carbon paper TGP-H-060, and (c) carbon paper TGP-H-120. The cell temperature was $70 \, ^\circ\text{C}$, $Q_{an} = 12 \, \text{cm}^3 \, \text{min}^{-1}$, and $Q_c = 500 \, \text{cm}^3 \, \text{min}^{-1}$. 
Figure 4.8. DMFC polarization curves observed at 70 °C for $c_M = 4.0$ mol L$^{-1}$. The diffusion layer was ELAT carbon cloth, $Q_{an} = 12$ cm$^3$ min$^{-1}$, $Q_c = 500$ cm$^3$ min$^{-1}$, and $\Delta V = 0.44$ cm$^3$. 
cillations at different $c_M$ with the diffusion layer TGP-H-120 are examined. The results are presented in Figure 4.9. At 1.0 mol L$^{-1}$, the mass transfer resistance of the layer is extreme; however, fluid oscillations significantly enhance performance. The steady flow performance of the DMFC is much improved at 2.0 mol L$^{-1}$, but the fluid oscillations still have a positive effect on performance despite the additional cross-over at low current density. When $c_M = 4.0$ mol L$^{-1}$, the benefit of fluid oscillations is lost; instead there was a negative effect on performance, just as was observed in Figure 4.8. In fact, there is no benefit when $c_M$ is increased from 2.0 to 4.0: the peak power density of the DMFC is 15% greater when $c_M = 2.0$ and in the presence of fluid oscillations the values of $i_{lim}$ differ by only 6%.

Based on these experimental observations, improved performance with fluid oscillations is possible with $c_M > 1.0$ mol L$^{-1}$, but the optimum concentration will depend strongly on the choice of the diffusion layer. It was clear that for the experimental DMFC of this chapter, a $c_M \gtrsim 2.0$ is not desirable for a diffusion layer of reasonable thickness. The proper choice of the system parameters, in particular coupling a feed concentration of approximately 2.0 mol L$^{-1}$ and a thicker diffusion layer, should provide improvements in performance over lower $c_M$ or a thinner diffusion layer. This effect is demonstrated in Section 4.3.4.

4.3.3 Anode Feed Rate

The effect of the anode steady feed rate $Q_{an}$ upon which the oscillatory flow is superimposed was investigated using the same $c_M$ that were used in Section 4.3.2. Examples of typical DMFC behavior at $Q_{an}$ of 1, 4, and 12 cm$^3$ min$^{-1}$ for an ELAT carbon cloth diffusion layer are shown in Figure 4.10. Compared to the effect that $c_M$ has on DMFC performance, $Q_{an}$ has a very minor effect. It has already been
Figure 4.9. The effect of fluid oscillations on performance of the DMFC at various methanol feed concentrations for a carbon cloth TGP-H-120 diffusion layer. The cell temperature was 70 °C, $Q_{an} = 12$ cm$^3$ min$^{-1}$, and $Q_c = 500$ cm$^3$ min$^{-1}$. The solid symbols and lines refer to steady flow experiments, whereas the open symbols and dashed lines refer to experiments where an oscillatory flow with $\Delta V = 0.44$ cm$^3$ and $\omega = 25.1$ rad s$^{-1}$ was superimposed on $Q_{an}$. 
shown that in order to significantly enhance mass transport, $Q_{an}$ needed to be increased a couple orders of magnitude (see Figure 3.14). In a DMFC which is not operating with a pre-heated feed, an increase in $Q_{an}$ of that magnitude has the negative consequence of facilitating a higher rate of heat transfer, removing heat from the cell and lowering the cell’s average temperature.

For the MEA/diffusion layer combination of Figure 4.10, mass transfer limitations were either minimal (Figure 4.10(a)) or not present in any appreciable amount (Figures 4.10(b) and 4.10(c)). The effect of oscillatory flow on the experiments, therefore, is small. The performance of the DMFC does change as $Q_{an}$ is decreased. This is simply the reverse of the effect of higher $Q_{an}$, as the fluid is removing less heat from the DMFC, keeping the cell’s average temperature higher. The oscillatory flow data is provided to demonstrate that the effect of large fluid oscillations on the heat transfer of the cell is negligible compared to the effect of $Q_{an}$. The effect of the anode feed rate depends heavily on other operating conditions, and experiments were also performed that exhibited no dependence on $Q_{an}$. This was particularly true of the experiments of Chapter 3, as is shown below in Figure 4.11.

Notice at all three feed concentrations that the performance of the DMFC becomes unstable when $Q_{an} = 1 \text{ cm}^3 \text{ min}^{-1}$. The instabilities are indicative of carbon dioxide bubbles interfering with the ability of the catalyst to react with methanol and water and produce sufficient amounts of electrons. Carbon dioxide bubble generation is a function of increasing current density, and as current increases bubbles begin to accumulate in the anode flow field. At a low feed rate, the fluid is unable to drive the bubbles through the flow channels and into the outlet stream. If enough bubbles accumulate, one or more of the three parallel channels
Figure 4.10. Polarization curves observed in the DMFC at 70 °C for various $Q_{an}$ at three different $c_M$: (a) 1.0, (b) 2.0, and (c) 4.0 mol L$^{-1}$ solutions of methanol/water. The diffusion layer was an ELAT carbon cloth and the cathode feed was pure O$_2$ at 500 cm$^3$ min$^{-1}$. The solid symbols and lines refer to experiments where the flow was steady; the open symbols and dashed lines refer to experiments where an oscillatory flow with $\Delta V = 0.44$ cm$^3$ and $\omega = 25.1$ rad s$^{-1}$ was superimposed on $Q_{an}$. 
Figure 4.11. Absence of steady flow rate dependence for the DMFC used in Chapter 3. The cell temperature was 70 °C, $Q_c$ was 500 cm$^3$ min$^{-1}$, and the diffusion layer was carbon paper TGP-H-060.
may be blocked completely. This will reduce the area available for diffusion and reaction to take place, and the performance will drop. Eventually, the flow may overcome the bubbles and force them out, but when the current density resumes its increase more bubbles will form and the same problem is encountered.

Interestingly, for all three feed concentrations oscillatory flow was able to alleviate this problem to a certain degree. The onset of the instability was delayed by the fluid oscillations. Since the instability does not disappear entirely it is not probable that the oscillations are forcing the bubbles out of the cell; there also did not appear to be an additional amount of carbon dioxide bubbles in the outlet stream. It is more likely that the oscillatory flow, which increases the fluid velocity in the flow channel, is increasing the thickness of the methanol/water film which is in contact with the diffusion layer. This provides greater amounts of methanol access to the catalyst surface and will refresh the film each period by sweeping away small CO$_2$ bubbles and shearing them into the bulk where they will coalesce with the larger CO$_2$ slugs. The effect of oscillatory flow on bubbles is revisited in section 5.5.1.2.

4.3.4 Diffusion Layer

The type of diffusion layer chosen for use in the DMFC anode will play a major role in determining the mass transfer resistance of the system. In many respects it is the primary optimization parameter, since for a given anode flow field it determines what feed concentrations are beneficial to the performance and how much energy will be required to generate fluid oscillations that give rise to mass transport enhancement. For example, Figure 4.12 presents the performance results of the DMFC using a thick diffusion layer at a low methanol concentration.
Figure 4.12. Performance of the DMFC for a carbon cloth TGP-H-120 diffusion layer for \(c_M = 1.0 \text{ mol L}^{-1}\). The cell temperature was 70 °C, \(Q_{an} = 12 \text{ cm}^3 \text{ min}^{-1}\), \(Q_c = 500 \text{ cm}^3 \text{ min}^{-1}\), and \(\Delta V = 0.44 \text{ cm}^3\).

Oscillatory flow does enhance the performance, even with a diffusion layer which has large mass transfer resistance, but it requires very large \(\omega\). At minimum, using the calculation of Equation 3.23, the gain in peak power density at 50.3 rad s\(^{-1}\) (+24.3 mW cm\(^{-2}\)) requires 1360 mW cm\(^{-2}\) to achieve, an efficiency (i.e. the ratio of the gain in peak power density in an oscillatory flow experiment versus the minimum amount of power required to obtain it: \((\Psi_{osc} - \Psi_o)/\Psi_{min}\)) of less than 2%.

A search for higher efficiencies and larger improvements in performance was conducted, using several thick carbon paper diffusion layers with \(c_M\) ranging from 1.0 to 4.0 mol L\(^{-1}\). Several examples were found where a thicker diffusion layer
would outperform a thinner diffusion layer at the same feed concentration using oscillatory flow. A typical result is presented in Figure 4.13. In this case, the ratio of the thicknesses is 2.4. The TGP-H-120 diffusion layer severely underperformed compared to the ELAT diffusion layer when only steady flow is present. When an oscillatory flow ($\Delta V = 0.44 \text{ cm}^3$, $\omega = 25.1 \text{ rad s}^{-1}$) is induced, experiments with the TGP-H-120 diffusion layer matched $i_{lim}$ and improved the peak power density by $\sim 15\%$ over the ELAT carbon cloth. A higher frequency increased the peak power density an additional 5%. The oscillatory flow results for the ELAT carbon cloth are provided to show that the enhancement in performance is not as significant as in the thicker diffusion layer.

Unfortunately, the optimization is not without cost. Despite improvements of nearly 35-40% over the steady flow case, the efficiency is still a meager 3-4% for these systems. The thicker diffusion layers require an extraordinary amount of power to generate oscillations which are of sufficient magnitude to enhance the performance. As was suggested in Chapter 3, this may be avoided by taking advantage of the relationship between the Peclet number and the fiber radius $a$ given in Equation 3.27. This hypothesis was tested by using a 316 stainless steel wire mesh as the diffusion layer, with a fiber radius almost 10 times that of the carbon paper diffusion layers. The results of these experiments are given in Figure 4.14.

Clearly, the stainless steel mesh was not optimal. It suffered from immense amounts of methanol cross-over, which was due to the much larger pore size (a factor of 4 larger than carbon paper) and ease of access to the catalyst surface (the tortuosity was essentially unity). It was more rigid than the other diffusion layers, which probably changed the morphology of the MEA as the cell was assembled and
Figure 4.13. Polarization curves demonstrating optimization of oscillatory flow in the DMFC at 70 °C. A 2.0 mol L⁻¹ solution of methanol/water was fed at 12 cm³ min⁻¹ and the cathode feed was pure O₂ fed at 500 cm³ min⁻¹. Fluid oscillations were generated using a stroke volume of 0.44 cm³. The solid circles and lines are for experiments where the diffusion layer is carbon paper TGP-H-120, whereas the open squares and dashed lines are for a diffusion layer of ELAT carbon cloth.
Figure 4.14. DMFC polarization curves obtained at 70 °C using a 316 stainless steel wire cloth as the diffusion layer. The anode steady feed rate was 5 cm$^3$ min$^{-1}$ and the cathode feed was pure O$_2$ at 100 cm$^3$ min$^{-1}$. The solid symbols and lines refer to experiments where the flow was steady; the open symbols and dashed lines refer to experiments where an oscillatory flow with $\Delta V = 0.44$ cm$^3$ and $\omega = 25.1$ rad s$^{-1}$ was superimposed on $Q_{\text{an}}$. 
blocked reaction sites. Furthermore, the combination of numerous sharp corners for bubbles to nucleate from and large pore size meant that the stainless steel mesh could have had any number of bubbles in its interior; this would explain the instabilities observed at high current densities which are similar to the performance observations when $Q_{an}$ was low in Section 4.3.3.

4.3.5 Other Considerations

The effect of the cathode feed rate $Q_c$ on performance was studied in a few experiments. A typical results is shown in Figure 4.15. Since the amount of oxygen present in the cathode fuel stream is still in excess compared to the amount of methanol required for the reaction at lower current densities, the improvement mechanisms at a lower $Q_c$ is identical to the low $Q_{an}$ case. The reduction in flow rate helps the DMFC maintain an higher average cell temperature and thus the kinetics improve. At high current densities, minor mass transfer limitations due to the cathode are observed when $Q_c = 100 \text{ cm}^3 \text{ min}^{-1}$. These limitations vanish when $c_M > 1.0 \text{ mol L}^{-1}$.

A few tests were also performed where a back pressure was placed on the cathode fuel stream. One such test is displayed in Figure 4.16. Since the DMFC was neither significantly mass transfer limited nor was the cathode fuel the limiting reagent, the primary effect of applying a back pressure on the cathode is obvious: it reduces the magnitude of the methanol cross-over occurring in the system. This is why there was a systematic increase in the cell voltage for the entire range of current densities in Figure 4.16. The pressure gradient across the cell forces some of the methanol to remain on the anode side of the membrane.
Figure 4.15. The effect of $Q_c$ on DMFC performance at 70 °C. The diffusion layer was ELAT carbon cloth, $Q_an = 12$ cm$^3$ min$^{-1}$, and $c_M = 1.0$ mol L$^{-1}$. 
Figure 4.16. The effect on DMFC performances of applying a back pressure on the DMFC cathode. The experiments were performed at 70 °C with a methanol concentration of 1.0 mol L\(^{-1}\) fed at 5 cm\(^3\) min\(^{-1}\). The diffusion layer was carbon paper TGP-H-060 and the cathode feed was pure O\(_2\) fed at 100 cm\(^3\) min\(^{-1}\).
4.4 Discussion

The optimization study presented in Section 4.3 focused on the effect of three variables: the feed concentration, the anode feed rate, and the anode diffusion layer. Several consistent trends were observed throughout experimentation that guided the effort to locate the operational parameters at which the use of oscillatory flow would be most beneficial to DMFC performance. The trends of greatest importance with respect to mass transfer limitations, and thus, the fluid oscillations, are:

1. The reduction of mass transfer limitations as $c_M$ increases;

2. The increase in mass transfer limitations as the diffusion layer thickness increases and/or permeability decreases;

3. The instability of DMFC performance at low $Q_{an}$.

The first two trends are opposed to one another and must be carefully balanced. As $c_M$ increases, the methanol cross-over will also increase and affect performance at low current densities. Decreased performance at low current densities will limit the peak power density that can be achieved in the fuel cell. Increased thickness (or alternatively, decreased permeability for a constant thickness) of the diffusion layer will balance this effect but requires an oscillatory flow of a greater magnitude to enhance the mass transport of methanol to the catalyst surface. The third trend is important in the sense that a steady flow of a sufficient feed rate should be selected to remove the possibility of carbon dioxide bubbles generation interfering with the effect of the oscillatory flow. Maximum kinetic performance for a cell without anode fuel pre-heating will be achieved when $Q_{an}$ is as small as possible while still preventing CO$_2$ from rendering the performance unstable.
The attempt to optimize the DMFC’s performance with oscillatory flow was successful insofar as these trends were identified and exploited, as Figure 4.13 shows. Improvements in the peak power density were achieved in this study which represented improvements beyond those which were obtained in the experiments of Chapter 3. However, they came at significant energy costs. Large improvements in $i_{\text{lim}}$, though interesting and a confirmation of the conclusions of Chapter 3, are not as useful in practice since DMFCs are rarely operated near the limiting current density.

The model of Equation 3.9 or 3.10 was shown in previous experiments to be a good predictor of $i_{\text{lim}}$ in the presence of oscillatory flow. Application of the model to the current study was much more difficult for two reasons. First, the model depends on the proportionality between $i_{\text{lim}}$ and $k_{\text{tot}}$ to predict performance as a function of $Pe$. Solving the diffusion equation for methanol transport in the DMFC yields

$$i_{\text{lim}} = nF c_M k_{\text{tot}} ,$$

a result which is valid provided $c_M \lesssim 1.0$ mol L$^{-1}$. This condition was true for the conditions of Chapter 3, but at values of $c_M > 1.0$ mol L$^{-1}$, $c_M$ is not necessarily zero at the catalyst surface. The limiting current density will also depend on the surface coverage of methanol, and obeys a relationship of the form

$$i_{\text{lim}} = k_{\text{lim}} c_M^\beta ,$$

where $k_{\text{lim}}$ is a constant and $\beta \sim 0.5$ (see, for example, Sgroi et al. [126] for more details). Whereas Equation 4.1 facilitated a simple mass transfer resistance model, Equation 4.2 does not and experiments where $c_M > 1.0$ mol L$^{-1}$ could not
be treated with the same type of analysis.

Second, the model of Equation 3.9 depends on two empirically determined constants. These constants are, in general, a function of all the operational parameters of the system and the diffusion layer that was used. The number of experiments required to specify these constants for all conditions was beyond the scope of the study and would have proved difficult due to concerns about the reproducibility and consistency of the DMFC’s performance.

Reproducibility of performance in the DMFC in this study was difficult to obtain. Experiments performed with a particular MEA are subject to the well-known phenomenon of performance decay over time (also called performance “fading”) \[66, 71, 116\]. However, experiments were also found to be sensitive to assembly conditions and the operating history of the DMFC, an observation which has recently been made by Casalegno et al. \[17\]. In particular, a well-functioning and kinetically active MEA would often suffer moderate to severe performance deterioration when a diffusion layer was removed and then the DMFC was reassembled with a new diffusion layer. Thus, whenever it was possible in this study, experiments were only compared to other experiments performed under the same assembly and operating conditions to establish a degree of consistency. In some cases, this could not be avoided and these comparisons have a level of quantitative uncertainty. The lack of reproducible and consistent results across the experimental study was the primary reason more quantitative analysis could not be performed and only qualitative trends are discussed in this chapter.

The most encouraging result from this study was the observation that oscillatory flow had a positive effect on DMFC performance when $Q_{an}$ was small. The instability at low $Q_{an}$ was caused by an impediment to mass transfer that arises
from bubbles physically blocking access to the catalyst surface instead of a catalytic reaction which is diffusion limited. Management of carbon dioxide bubbles is an important issue, especially as the development of micro-scale DMFC technology picks up speed. The oscillatory flow, by providing a much larger fluid velocity in the anode channel, increases the liquid film thickness at the channel-diffusion layer interface, thereby wetting the diffusion layer more effectively. The approach was investigated further in combination with the study of bubble mobility in oscillatory flow (see chapter 5).

4.5 Conclusions

In this chapter, an optimization study which was an extension of the work presented in Chapter 3 was conducted. The DMFC parameter space was explored, with a focus on variables controlling the mass transfer resistance of the anode. The complexity of the DMFC system and the sheer size of the parameter space did not permit testing over the entire range of possible conditions, but even in a limited survey performance was optimized in the DMFC with oscillatory flow.

The optimization effort was centered around striking a balance between restricting the access of the fuel to the anode catalyst at low current densities and driving enhanced amounts of fuel to the catalyst at high current densities. This approach was intended to minimize the negative effect of methanol cross-over and maximize the effect of superimposing fluid oscillations on the steady feed rate. The results show that the anode diffusion layer was the most important factor in the DMFC that controls that balance; to a lesser extent the feed concentration is also important.

Despite the realization of a DMFC which was more properly suited to take
advantage of oscillatory flow in the anode feed, the practicality of the approach is in question. Though it was demonstrated that optimization was possible, oscillatory flow has not proved itself to be an efficient performance enhancement strategy. The oscillatory flow technique has room for improvement, specifically by continuing to search for a diffusion layer better suited to permit mass transport enhancement at lower power requirements \( i.e. \) a diffusion layer with large \( a \) and low \( \kappa \). Ultimately, as the fuel cell community moves toward the miniaturization of the DMFC, the oscillatory flow technique would need to be re-configured to accommodate smaller systems.

Therefore, in its current iteration, the best use of oscillatory flow may be as a diagnostic tool for other fuel cell researchers. The oscillatory flow could be used to reduce/remove mass transport limitations to study other aspects of DMFC behavior, such as anode kinetics or membrane transport properties, at high current densities. An intriguing alternative use of oscillatory flow, which is studied in more detail in the next chapter, relates to the instabilities in DMFC performance at low \( Q_{an} \). The oscillatory flow was shown to alleviate a portion of the instability due to the accumulation of carbon dioxide bubbles in the flow field. This occurred at much lower \( \Delta V \) and \( \omega \) then was required to significantly enhance mass transport, and thus will have a much lower power requirement. In addition to the results presented herein, an asymmetric oscillatory flow pumping strategy which builds on the fundamental work of chapter 5 was later conceived which displaced bubbles out of the fuel cell and further improved the stability of performance at low feed rates (see section 5.5.1.2).
CHAPTER 5
INERTIAL MIGRATION OF PARTICLES AND BUBBLES IN
OSCILLATORY TUBE FLOW

5.1 Introduction

The motion of a single particle or bubble in a bounded shear flow is of interest for many practical applications. The concentration distribution of particles or bubbles in a fluid affects physical constants such as viscosity or diffusivity, in turn altering processing requirements for the fluid. Techniques such as field-flow fractionation or membrane filtration exploit differences in the hydrodynamic behavior of different particles to perform separations. Multiphase flow in microfluidic devices is a field attracting a great deal of attention, as the presence of particles, drops, or bubbles has a great effect on the processes occurring in microfluidic devices [129, 135]. In this chapter the behavior of particles and bubbles in a tube when the flow is purely oscillatory was investigated. The objective of the work discussed in this chapter was to study conditions at which the mobility $\Delta x_p/\Delta x$ of non-neutrally buoyant particles is governed by a balance between inertial and gravitational forces. At conditions where this force balance is valid, it was anticipated that zero-mean asymmetric oscillatory flow could be used to extract particles or bubbles from a tube or channel.

It is well known that a particle, in the presence of a shear flow, will experience a lateral or transverse migration due to an inertial lift force. This phenomenon was
first observed in the pioneering work of Segré and Silberberg [123, 124]. They measured the trajectories of neutrally buoyant rigid spherical particles when steady flow was generated through a tube of radius $R$ and found that the particles tended to an equilibrium radial position of approximately $0.6 r/R$. This “tubular pinch” effect, as it came to be known, occurred regardless of the particle’s initial position entering the tube. From the results of their experiments, Segré and Silberberg provided an empirical formula to predict the transverse velocity $v_L$ of a particle:

$$v_L = 0.205 U Re \left( \frac{a}{R} \right)^{2.83} \frac{r}{R} \left( 1 - \frac{r}{r^\dagger} \right)$$ \hspace{1cm} (5.1)

where $Re$ is the tube Reynolds number based on the mean velocity $U$ and tube diameter $2R$, $a$ is the particle radius, $r$ is the radial position of the particle ($r = 0$ is the centerline of the tube), and $r^\dagger$ is the equilibrium radial position. The numerical coefficients in Equation 5.1 were calculated directly from the data given by Segré and Silberberg.

The migration mechanism is due to fluid inertia, as solutions of the linearized Navier-Stokes equations (e.g. Simha [130], Saffman [112], and Bretherton [13]) have shown that when the flow is in the creeping regime no radially directed particle motion exists. This was experimentally verified by Goldsmith and Mason [42], who found no migration occurred at very small relative particle Reynolds numbers $(U a^3/\nu R^2) < 10^{-6}$, even for particles close to a wall. Obtaining a more complete understanding of the inertial lift force on either a single particle or a suspension of particles has been the subject of numerous studies in the past four decades (many of these studies are summarized in reviews by Cox and Mason [26] and Leal [81], as well as a more recent work by Matas et al. [94]). These studies will be discussed in more detail in the following section.
At the time of this writing, an experimental study similar to those of Segré and Silberberg has never been undertaken for bubbles. Studies on inertial lift for bubbles in a bounded, horizontal geometry of any kind, whether experimental or theoretical, are scarce. Many of the theoretical or empirical expressions for the lift force have been developed by analogy to the solid particle case; a historical summary of lift force expressions was recently compiled by Hibiki and Ishii. Provided that the bubble is small and remains spherical, it will behave like a solid particle; however, a second migration mechanism can occur if this is not strictly true: deformation-induced drift.

Nearly all of the studies performed to date have been for steady flow. Oscillatory flow was studied in a series of papers on the flow of suspensions in tubes, but the primary result of the study is an empirical formula which requires knowledge of the particle's equilibrium position. It is important to note that the empirical formula is similar to Equation with the exception that is raised to first power and is replaced by a root-mean squared velocity. A study using oscillatory flow to separate particles via inertial lift in cross-flow membrane filtration also describes a transverse velocity which scales in a similar manner as Equation and depends on system-specific empirical constants. From this it can be concluded, as has been mentioned elsewhere, that transverse velocities of particles in oscillatory flow will be similar (in a time-averaged sense) to those of steady flow. The validity of this conclusion will be considered later in the chapter.

In the following section, a dimensional analysis of the problem is conducted and various limits of interest are discussed. This analysis will depend on bubbles behaving analogously to particles, except where deviations are specifically considered. The third section outlines the experimental apparatus and procedure used.
to observe particle and bubble motion in a capillary tube. In the fourth section, the data will be presented along with a discussion of the implications of the experimental observations. The results are compared against available steady flow models in the appropriate limits. Finally, the major conclusions of this work will be summarized.

5.2 Theoretical Considerations

5.2.1 Horizontal Tube Flow

Consider a non-neutrally buoyant spherical particle of radius $a$ which is initially at rest in a tube of radius $R$ which is in the presence of an oscillatory flow as shown in Figure 5.1, where the appropriate gravity vector is shown in case (i). The oscillatory flow is generated by displacing a stroke volume $\Delta V$ at an angular frequency $\omega$ in a Newtonian fluid of viscosity $\mu$ and density $\rho$. The solution to the velocity profile in a tube was originally solved by Womersley [149] and shown to depend on a dimensionless frequency $\alpha = R(\omega/\nu)^{1/2}$, where $\nu = \mu/\rho$. The unidirectional velocity $u$ can be calculated for all values of $\alpha$ in terms of Bessel functions of complex arguments:

$$u = \mathcal{R} \left[ \frac{A}{i\rho \omega} \left\{ 1 - \frac{J_0 \left( \frac{\alpha r}{R} i^{3/2} \right)}{J_0 \left( \alpha i^{3/2} \right)} \right\} e^{i\omega t} \right], \quad (5.2)$$

where $A$ is the amplitude of the pressure gradient, $J_0$ is the Bessel function of order zero, $t$ is time, and $i^2 = -1$.

At low values of the Womersley number $\alpha \lesssim 5$ this profile is well approximated
Figure 5.1. Diagram of the problem of a non-neutrally buoyant particle/bubble in an oscillatory tube flow for two cases: (i) gravity perpendicular to the flow (horizontal tube orientation) and (ii) gravity parallel to the flow (vertical tube orientation). The velocity profile given by Equation (5.3) is shown at the two discrete times where the velocity is at its maximum.

by the simple sinusoidal parabolic velocity profile:

$$u = 2U_o \left(1 - \left(\frac{r}{R}\right)^2\right) \sin(\omega t),$$

(5.3)

where $U_o$ is the characteristic velocity $\Delta x \omega / 2$. The quantity $\Delta x$ is the displacement in the flow direction occurring with each stroke; for these experiments, it is defined as $\Delta x = \Delta V / \pi R^2$. $U_o$ is thus the amplitude of the velocity which occurs in each half-cycle, averaged across the cross-section.

An infinitesimally small particle located at some equilibrium radial position will simply oscillate back and forth with the same displacement as the fluid streamline. This equilibrium position will determine the mobility of the particle $\Delta x_p$. In general,

$$\Delta x_p = f^n(\Delta x, \omega, a, R, \rho, \Delta \rho, g, \mu, \epsilon_s, a, \mu_f, \sigma);$$

(5.4)

where $\Delta \rho$ is the density difference between the fluid and particle, $g$ is the acceleration due to gravity, $\epsilon_s$ is the dimensionless surface roughness of the sphere, $\mu_f$ is the coefficient of friction, and $\sigma$ is the surface tension. Even this list given in Equation (5.4) is not complete, as the motion depends separately on the component
of gravity in the axial and radial directions, for example. By the Buckingham II theorem, nine dimensionless quantities are necessary for a complete model of this system given twelve physical parameters. One set of dimensionless quantities can be re-arranged from the quantities in Equation 5.4 as follows:

$$\frac{\Delta x_p}{\Delta x} = f^n \left( \frac{Re_p^2}{Re_s}, Re, \alpha^2, \frac{a}{R}, \frac{\Delta \rho}{\rho} \alpha^2, \epsilon_s, \mu_f, Ca \right).$$  (5.5)

The dimensionless frequency $\alpha$ is identical to that of Womersley’s analysis. The density difference $\Delta \rho$ is defined as $\rho_p - \rho$, where $\rho_p$ is the particle density. The dimensionless surface roughness $\epsilon_s$ is scaled by the particle radius. The Reynolds number $Re$ is defined in this chapter as $U_o R/\nu$. The other three dimensionless quantities in Equation 5.5 are the particle Reynolds number $Re_p$, the sedimentation Reynolds number $Re_s$, and the Capillary number $Ca$, defined as

$$Re_p = \frac{\dot{\gamma}_w a^2}{\nu}, \quad Re_s = \frac{U_s a}{\nu} \quad \text{and} \quad Ca = \frac{\mu \dot{\gamma}_w a}{\sigma},$$

where $\dot{\gamma}_w$ is the characteristic wall shear rate $4U_o/R$ and $U_s$ is the Stokes sedimentation velocity for a sphere $2 |\Delta \rho| g a^2/9 \mu$. Note that $U_s$ will have the same definition for bubbles in order to allow direct comparison between the mobilities of particles and bubbles.

The physical significance of each term in Equation 5.5 is as follows. The main contributor to inertial lift in this problem and thus the most influential parameter in determining $\Delta x_p/\Delta x$ is $Re_p^2/Re_s$. It is a measure of the competition between the gravitational force, which drives the particle toward a tube wall, and the inertial force, which lifts the particle toward the tube’s interior. The tube Reynolds number is a measure of whether inertial or viscous effects dominate.
the disturbance flow. The Womersley number governs the distortion of the purely viscous velocity profile. As it increases the profile deviates from the parabolic form given by Equation 5.3. The ratio \( a/R \) primarily affects the mobility by limiting how close the particle center can get to the wall which changes the equilibrium position of the particle from what is expected from an infinitesimally small particle.

The quantity \( (\Delta \rho/\rho) \alpha^2 \) is a comparison of two slip velocities: \( \Delta \rho \omega^2 \Delta x a^2/\mu \), which is the slip the particle experiences during fluid acceleration because \( \rho \neq \rho_p \), and \( (a^2/R^2) \omega \Delta x \), a slip velocity which is due to the presence of the tube wall (i.e. a Faxén’s law correction). The dimensionless surface roughness \( \epsilon_s \) limits how close the surface of a particle can come into contact with the tube wall. The coefficient of friction \( \mu_f \) governs the resistance of the particle to flow when it is at the tube wall (at a separation distance \( \epsilon_s a \)). The Capillary number only applies to bubbles but is an indicator of the bubble’s ability to remain spherical in the presence of a shear flow.

There are several asymptotic limits to Equation 5.5 which have either been previously studied or are accessible with carefully planned experiments. The particles in these experiments began at rest against the tube wall. If \( Re_p^2/Re_s \ll 1 \), the inertial lift is insufficient to lift the particle off the tube surface. Provided \( \alpha^2 \ll 1 \), Equation 5.5 becomes

\[
\frac{\Delta x_p}{\Delta x} = f^n \left( \frac{a}{R}, \epsilon_s, \frac{Re_p}{Re_s} \right).
\]  

This limit has been examined for a plane wall in a steady shear flow [72, 76]. The surface roughness will govern the separation distance between the particle and the wall at zero shear. At very low shear rates, a sphere rolls along the surface with a mobility of 1.6 \( a/R \) for \( \epsilon_s \sim O(10^{-2}) \). For larger shear rates the sphere
slips along the surface with an increased mobility \(2.4 \, a/R\), again for \(\epsilon_s \sim O(10^{-2})\). The transition between these regimes occurs at \(0.1 \leq Re_p/Re_s \leq 1\). A further transition will occur between the roll-slip translation of the particle and inertial lift as \(Re_p^2/Re_s \sim 1\). In the experimental work of King and Leighton [72], a sphere was observed to begin to lift off when \(Re_p^2/Re_s \sim 4\). Lift expressions obtained by Cox and Hsu [25] and Cherukat and McLaughlin [22] indicate that the sphere will be lifted away from the plane completely when \(Re_p^2/Re_s > 10\).

If the particle is infinitesimally small \((a/R \to 0)\), has detached from the tube wall \((Re_p^2/Re_s \gg 1)\), and the flow is Stokesian with a parabolic velocity profile \((\alpha^2, Re \ll 1)\), the dimensionless mobility obeys the simple relationship

\[
\frac{\Delta x_p}{\Delta x} = f_n \left( \frac{Re_p^2}{Re_s} \right) .
\] (5.7)

Equation (5.7) requires the wall to be in the viscous sub-domain of the flow so that regular perturbation expansions are applicable. This limit is difficult to access experimentally because particles must have some finite size in order to be detected. In general, it is expected the \(a/R\) will play a role in a bounded geometry, as was first reported in the experiments of Karnis, Goldsmith and Mason [69].

The limit described by Equation (5.7) has been treated in very little detail by the fluid mechanics community. The related problem, that of a neutrally buoyant particle in a tube flow \((Re_p^2/Re_s \to \infty)\), has also not been studied in any theoretical detail. Theoretical studies for a neutrally buoyant sphere in steady fluid flow, either unbounded or bounded in a non-tube geometry, are numerous, however. To model the behavior of a particle in an oscillatory tube flow, the approach in this chapter when considering the limit of Equation (5.7) was to equate selected lift force expressions from the steady flow literature to the buoyancy force,
a procedure which is described in more detail in a later section.

The steady flow studies are briefly summarized here as they provide the framework for understanding lateral migration of a particle in these experiments. The first calculations of a steady flow lift force when $Re \ll 1$ (from which a particle mobility can be determined) were performed by Saffman in an unbounded simple shear flow [115]. The analysis was later extended by McLaughlin for a less restrictive set of conditions [96] and Legrendre and Magnaudet for a bubble [82]. Bounded geometries were considered separately by Ho and Leal [57] and Vasseur and Cox [141], who studied both two-dimensional Couette and Poiseuille flow. The results of both calculations were consistent with experimental observations in Couette flow [52] and the results of Segré and Silberberg [124]. Theoretical work performed for bubbles is limited and to this point has only been performed for unbounded geometries (for example, see Legrendre and Magnaudet [83] or Magnaudet [91, 92]).

A nice description of the various mechanisms that determine the equilibrium particle position is given by Feng et al. [39] amidst their numerical work on particle motion in two-dimensional Couette and Poiseuille flows. The behavior of particles in a tube should be similar. If the sphere was neutrally buoyant, the equilibrium position would be determined from the competition between the wall repulsing the sphere and the curvature of the flow field pushing the sphere toward the wall. The particle migrates toward the wall because of a gradient in the shear rate and not the presence of the shear rate. The spheres considered in this work are not neutrally buoyant and thus there is an additional force (gravity) which pushes the particle further toward the wall. This has been shown in the theoretical studies which have considered gravity in two-dimensional Poiseuille flows e.g. Hogg [58].
and Joseph and Ocando [68].

More recently, the case where $Re$ is not small has been considered. In this limit, Equation 5.5 becomes

$$\frac{\Delta x_p}{\Delta x} = f^n \left( \frac{Re_p^2}{Re_s}, Re, \frac{a}{R} \right).$$  \hspace{1cm} (5.8)

Equation 5.8 incorporates both non-linear effects due to the flow field and the influence of particle size (wall effects). Studies for finite $Re$ are, by necessity, numerical in nature and have been focused on neutrally buoyant spheres. Schonberg and Hinch [117] considered channel Reynolds numbers up to 150, finding that the equilibrium position of the particle moves toward the wall as the Reynolds number increases. This was confirmed by Asmolov [11] up to channel Reynolds numbers of 3000. Similar work was performed for dilute suspensions of particles in a tube at Reynolds numbers up to 2400 by Matas et al. [93]. The predictions of Matas et al. were in agreement with their experimental observations and the observations of Karnis et al. [69]. The existence of a second equilibrium position closer to the center of the tubes at higher Reynolds numbers was also observed. Calculations for inertial migration in a tube were recently performed by Yang et al. [158] at finite Reynolds number which provides a series of correlations for the lift force. The numerical work of Yang et al. is closest to the experimental conditions geometrically but has a narrow range of validity.

Experimental work has been performed for oscillatory tube flow in which radial velocities and equilibrium positions of neutrally buoyant particles (or dilute suspensions) have been measured [35, 128, 137]. These studies agree that if $\alpha < 5$, a purely oscillatory flow exhibits similar behavior to a laminar steady flow; that is, a tubular pinch effect (based on a time-averaged flow) was observed. When
α > 5, the existence of a second equilibrium position was observed closer to the tube’s axis. This effect is consistent with expectations, as oscillatory flow is no longer approximately parabolic at Womersley numbers above five. To this point, no effort has been made to model the lift force or radial migration velocity for oscillatory flow other than empirical correlations.

Practically, if the parameter $Re_p^2/Re_s$ is to be varied over a few orders of magnitude in these experiments, the particles still have finite size and the inertial slip limit will be important if $Re_p^2/Re_s \leq 1$. Provided $Re_p/Re_s \gg 1$, a combination of Equation 5.6 and 5.7 can be considered:

$$\frac{\Delta x_p}{\Delta x} = f_n \left( \frac{Re_p^2}{Re_s^2}, \frac{a}{R}, \epsilon_s \right).$$

(5.9)

At low values of $Re_p^2/Re_s$ the particle will translate along the tube wall with a constant mobility. As the shear rate increases, it will lift off and the mobility will be solely a function of $Re_p^2/Re_s$ and $a/R$. Besides the work of King and Leighton [72] which was described previously, studies in field-flow fractionation have also demonstrated the existence of a near-wall lift and a transition to inertial lift [147, 148]. Note that Equation 5.9 assumes that the wall remains in the viscous sub-domain of the flow. This was violated in many of the experiments described in the next section, but was found to describe particle behavior well regardless.

Most of the limits described thus far are focused on approximating the flow as quasi-steady ($\alpha^2 \ll 1$) where the dimensionless mobility will be a time-averaged quantity. For experiments where this is not the case, the full behavior given in Equation 5.5 will be valid and the problem becomes considerably more complex. In order to avoid this complexity, one objective of this work was to isolate the limits described in Equations 5.7, 5.8 and 5.9 and compare oscillatory flow mobilities.
with those from available steady flow studies. A second objective was to compare the lateral migration of particles to bubbles, especially in the limit that $Ca \ll 1$. In that limit, the framework which was described above for particles should also hold for bubbles if $a/R$ is reasonably small. Third, the mobility should be an increasing function of $\omega$ over a range of $Re_p^2/Re_s$; this relationship was exploited to demonstrate a particle/bubble extraction technique using asymmetric oscillations.

5.2.2 Vertical Tube Flow

Returning to Figure 5.1, consider the gravity vector to be oriented along the tube axis i.e. case (ii) instead of case (i). The simple re-alignment of the flow field with gravity represents a very different lateral migration problem that occurs when a non-neutrally buoyant particle is in the presence of a vertical tube flow. If the particle is neutrally buoyant, the problem is identical to the horizontal tube case and the various asymptotes described in section 5.2.1 will be applicable. In fact, it was found that the best way to observe the behavior in the limit described by Equation 5.8 was to use an almost neutrally buoyant particle in the vertical tube, as the effect of gravity on lateral motion became negligible.

Whereas in a horizontal tube flow, a particle or bubble follows fluid streamlines (approximately, since particles lag behind the fluid slightly due to their finite size), the same is not necessarily true for vertical flow. In order to understand particle behavior in vertical flow, a slip velocity is defined

$$U_{slip} = U_p - U_f,$$  \hfill (5.10)
case of a non-neutrally buoyant sphere in a vertical tube, \( U_{\text{slip}} \sim U_s \), as the settling velocity of the particle is the main contributor to the difference in velocities. When \( U_{\text{slip}} \) is negative, the particle lags the fluid. It will migrate toward the tube center, driven there by a lateral pressure gradient due to the fluid the particle is displacing. For the opposite case, the particle leads the fluid and migrates toward the walls of the tube. This phenomenon has been demonstrated experimentally [30, 65, 69] and is described in several studies that have considered 2-dimensional steady Poiseuille flow of non-neutrally buoyant particles [57, 58, 68, 141]. A numerical study for the tube geometry has also been recently performed for heavier-than-fluid spheres which describes the same effects [162].

Oscillatory flow is even more complex, because the fluid will spend half a cycle traveling with gravity and half a cycle opposing it. A negatively buoyant sphere will lead the fluid for a half cycle, during which the fluid is also moving with gravity, and migrate toward the tube wall. After the fluid reverses direction, the sphere will lag the fluid and migrate toward the tube axis. Conceivably, a particle or bubble could be stabilized or even be made to travel in a direction opposite its sedimentation velocity with the proper oscillatory parameters. This would require a stroke length large enough so the particle has time to migrate all the way to the wall with the downstroke, where it will be located in a region of lower velocity and \( U_s \) will be reduced by the presence of the wall. By the same token, the stroke must be large enough so that the particle migrates to the center and experiences larger velocities with the upstroke. The same would apply for bubbles, except a bubble goes to the wall with an upstroke and the center with a downstroke.

The expected behavior in these experiments can be thought of as a combination of two asymptotic limits. The first asymptote is in the limit of small sedimentation
times with respect to the period of oscillation (large $U_{slip}$). The particle will alternate between leading and lagging the flow during each half cycle, and will move rapidly from the tube center to the tube wall. This assures that the particle spends approximately half its time traveling with the centerline velocity (minus $U_s$) and half its time rolling along the wall with slip (plus $U_s$). The second asymptote is the opposite case, where the period is shorter than the sedimentation time (small $U_{slip}$). In this case, the particle does not have sufficient time to complete the wall to center motion despite the fact that it still alternates between leading and lagging the flow. Instead it only has time to fluctuate around an equilibrium radial position which it would obtain if the particle was neutrally buoyant. The fluctuation does result in different particle velocities for the forward and reverse strokes, but the difference will be much smaller in magnitude.

The two asymptotes can only be observed if the system is at pseudo steady-state. Each asymptote will have a different criteria which must be met; otherwise, the oscillations in radial position will be out of phase with the convective velocity, diminishing the migration mechanism. How these various conditions are described in terms of the experimental parameters will be discussed further in section 5.5.2.

The objective of the vertical tube experiments was to observe net particle and bubble velocities in oscillatory flow and classify the oscillatory flow conditions where different behaviors i.e. stabilization of particles or bubbles, etc. occurred. Based on the experimental observations, criteria for trapping particles or separating particular particles from a mixture will be postulated. Use of oscillatory flow as a separation technique in vertical tube flow was investigated briefly in proof-of-concept experiments using dilute suspensions of particles.
5.3 Experimental Method

5.3.1 Equipment

A series of experiments were designed to observe the behavior of both solid particles and air bubbles in the presence of either a horizontal or a vertical oscillatory tube flow at ambient temperature (\(\sim 23.5 \, ^\circ\text{C}\)). A diagram of the experimental apparatus is shown in Figure 5.2. Glass capillary tubes with interior diameters of 0.2 and 0.485 cm, respectively, and a length of approximately 100 cm were mounted over a light table. At one end a tee junction connected the glass tube to the oscillatory syringe pump (either symmetric or asymmetric) and an inlet port with a valve. At the other end another tee junction interfaced the glass tube with a large bore syringe needle and an outlet port. Both the inlet and outlet ports accepted 30 mL syringes; they provided manually actuated steady flows of sufficient magnitude to remove unwanted bubbles from the system and assist with proper placement of the particle/bubble of interest before the experiment began. An i-Speed Olympus video camera with a maximum shutter speed of 1/100,000 of a second and a maximum frame rate of 10,000 frames per second was mounted above the glass tube for the purpose of recording the instantaneous motion of the particles and bubbles.

The particles used in these experiments were solid poly-methyl methacrylate (PMMA) or glass spheres which were dyed black for easy visibility. Particle diameters were determined externally using a micrometer. The particles were confirmed to be spherical under magnification (for an example image, see Figure 5.3). Values of the particle diameter were used to validate the image analysis method which was used to determine bubble diameters. Bubbles were introduced by threading a small capillary tube through the large bore needle and applying a constant pres-
sure from a 30 mL syringe filled with air until the bubble had grown to the desired size. Bubble diameters were calculated via images taken from the high speed camera when flow was not present, using a set of references scales which were placed in the same plane as the bubble. A simple test of the bubble’s sphericity could be achieved in the same manner by measuring the bubble diameter on more than one axis. The specific particle radii and the range of bubble sizes used in these experiments are presented in Table 5.1.

5.3.2 Horizontal Orientation: Materials and Procedure

The carrier fluids used in the horizontal experiments are given in Table 5.2. The various carrier fluid-particle systems represent a range of particle settling velocities, and thus a wide range of $Re$, $\alpha$, $Re_p^2/Re_s$, etc., could be studied. Air bubbles were only studied in two fluids: water and ethylene glycol. The oscillatory syringe pump generated either a symmetric (purely sinusoidal) or an asymmetric
Figure 5.3. Magnified image of Particle A (see Table 5.1). The particle diameter was measured along 4 different particle axes and found to differ by less than 1.0% i.e. 440 ± 4 microns.

<table>
<thead>
<tr>
<th>Label</th>
<th>Type</th>
<th>$a$ (cm)</th>
<th>$\rho_p$ (g cm$^{-3}$)</th>
<th>$a/R_1^*$</th>
<th>$a/R_2^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle A</td>
<td>PMMA</td>
<td>0.022</td>
<td>1.18</td>
<td>0.22</td>
<td>0.091</td>
</tr>
<tr>
<td>Particle B</td>
<td>PMMA</td>
<td>0.038</td>
<td>1.18</td>
<td>0.38</td>
<td>0.157</td>
</tr>
<tr>
<td>Particle C</td>
<td>Glass</td>
<td>0.019</td>
<td>2.42</td>
<td>0.19</td>
<td>0.078</td>
</tr>
<tr>
<td>Bubbles</td>
<td>Air</td>
<td>0.017-0.10</td>
<td>$1.19\times10^{-3}$</td>
<td>0.20-1.00</td>
<td>0.17-0.55</td>
</tr>
</tbody>
</table>

$^*$ $R_1$ and $R_2$ refer to the radii of the two tubes used in the experiments, having diameters of 0.2 and 0.485 cm, respectively.
TABLE 5.2
HORIZONTAL ORIENTATION: FLUID-PARTICLE SYSTEMS

<table>
<thead>
<tr>
<th>Fluid†(Label)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\mu$ (p)</th>
<th>Particle</th>
<th>$U_s$ (cm s$^{-1}$)‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>0.997</td>
<td>0.009</td>
<td>A</td>
<td>-2.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>-6.23</td>
</tr>
<tr>
<td>24% Salt/76% Water (SW)</td>
<td>1.169</td>
<td>0.017</td>
<td>A</td>
<td>-0.07</td>
</tr>
<tr>
<td>Ethylene Glycol (EG)</td>
<td>1.109</td>
<td>0.188</td>
<td>A</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>-0.13</td>
</tr>
<tr>
<td>70% Glycerin/30% Water (GW1)</td>
<td>1.165</td>
<td>0.201</td>
<td>A</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>-0.03</td>
</tr>
<tr>
<td>80% Glycerin/20% Water (GW2)</td>
<td>1.201</td>
<td>0.654</td>
<td>A</td>
<td>0.003</td>
</tr>
</tbody>
</table>

† The given fluid compositions are in percent by weight.
‡ A negative $U_s$ indicates a particle is settling in the same direction as gravity.

(combination of two sinusoids) flow. Both the stroke volume and the oscillation frequency were adjustable; in this work four stroke volumes (0.08, 0.17, 0.44, and 0.79 cm$^3$) and a range of frequencies (0.42 to 3.15 s$^{-1}$) were considered. The flow profile was captured by taking images of the pump syringes and calculating its position as a function of time. The flow profiles were used to verify the symmetry/asymmetry of the flow, validate known values of the stroke volume and determine the period of the oscillations. The calibrated period was checked against the period of the particle trajectory measured in each experiment.

A single particle or bubble was hydrodynamically forced into the center of the tube once all other inhomogeneities had been removed. After the particle/bubble had come to rest, the oscillatory flow was commenced for a minimum of 20 periods.
The particle/bubble motion was recorded with the high speed camera, exported as a series of images, and analyzed using custom scripts written for the computational software MATLAB. The particle or bubble mobility was measured from peak to peak of the oscillatory trajectory, and averaged over several periods.

5.3.3 Vertical Orientation: Materials and Procedure

The carrier fluids used in the vertical experiments are given in Table 5.3. Only symmetric oscillations were used in the vertical orientation. The calibration developed for the horizontal orientation remained applicable for the vertical orientation. The period of the particle trajectory was checked against the calibrated period with each experiment.

A single particle or bubble was simply loaded into the vertical tube from the top (or bottom, depending on the sign of $U_s$) and allowed to fall/rise by gravity into the camera’s viewing area. Once in the viewing area, the fluid oscillations were commenced until the particle trajectory was no longer completely contained in the frame. The particle/bubble motion was analyzed using custom scripts very similar to those used in section 5.3.2. In some experiments, the mobility was obtained as before. In others, the net drift velocity of the particle or bubble $\langle U_p \rangle$ was calculated using the rate of change of the peak values (i.e. the slope) over time.

Not described in Table 5.3 is a three particle system which was used to test the practicality of using oscillatory flow as a particle trapping technique. The experiments were performed in water using a dilute suspension of the three spherical PMMA particles, injected from both the top and the bottom of the tube. The particles were three different sizes (radii of 138, 286, and 374 microns) and each
TABLE 5.3
VERTICAL ORIENTATION: FLUID-PARTICLE SYSTEMS

<table>
<thead>
<tr>
<th>Fluid (Label)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\mu$ (p)</th>
<th>Particle</th>
<th>$U_s$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (W)</td>
<td>0.997</td>
<td>0.009</td>
<td>A</td>
<td>-1.24</td>
</tr>
<tr>
<td>18% Salt/82% Water (SW2)</td>
<td>1.134</td>
<td>0.013</td>
<td>A</td>
<td>-0.302</td>
</tr>
<tr>
<td>25% Salt/75% Water (SW3)</td>
<td>1.173</td>
<td>0.018</td>
<td>A</td>
<td>-0.016</td>
</tr>
<tr>
<td>Ethylene Glycol (EG)</td>
<td>1.109</td>
<td>0.188</td>
<td>A</td>
<td>-0.079</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>-0.555</td>
</tr>
<tr>
<td>80% Glycerin/20% Water (GW2)</td>
<td>1.201</td>
<td>0.654</td>
<td>A</td>
<td>0.003</td>
</tr>
</tbody>
</table>

† The given fluid compositions are in percent by weight.
‡ A negative $U_s$ indicates a particle is settling in the same direction as gravity.

size was dyed a different color. A dilute suspension of glass spheres with radii of 50 microns was also used in a proof-of-concept experiment.

5.4 Results

5.4.1 Horizontal Tube Flow

The summary of the entire body of experiments for particles is shown in Figure 5.4. The experiments were performed over a range of $Re_p^2/Re_s$ spanning more than seven orders of magnitude. From Figure 5.4, three clearly defined regions of particle behavior are evident. In the first region ($Re_p^2/Re_s < 10^1$), the particle has not yet lifted away from the tube wall. This is the asymptotic limit described by Equation 5.6. In the second region, defined by $10^1 < Re_p^2/Re_s < 10^3$, the particle lifts off from the tube wall and obtains a mobility which increases rapidly.
Figure 5.4. Particle mobility as a function of the parameter $Re_p^2/Re_s$.
The legend indicates the experimental conditions in the following order: particle/tube/fluid. See Tables 5.1 and 5.2 for definitions of the labels.

with $Re_p^2/Re_s$; this is the limit of Equation 5.7. In the third region at $Re_p^2/Re_s > 10^3$, the mobility of most experiments approaches a constant value; a handful of experiments diverge from this asymptote.

The first region of particle migration behavior is shown in Figure 5.5 plotted against the ratio $Re_p/Re_s$. If $Re_p^2/Re_s \sim 10$, the particle should be lifted completely away from the tube wall. The values of $Re_p/Re_s$ where $Re_p^2/Re_s = 10$ (shown in Figure 5.5) agrees very well with the experimental observations; the mobility of the particles increased rapidly once this value was reached. When $Re_p/Re_s$ is less than this critical value, the particle mobility has a constant value which is only a function of the effective particle size. This value is in agreement with the results of King and Leighton [72]. This agreement was expected since
Figure 5.5. Particle mobility as a function of the parameter $Re_p/Re_s$ for low values of $Re_p^2/Re_s$. The legend indicates the following experimental conditions: particle, fluid, and tube. The dashed lines are the constant translational velocity of a particle rolling along a plane with slip predicted by King and Leighton [72]. The dotted lines are the values of $Re_p/Re_s$ where $Re_p^2/Re_s = 10$ and the particle lifts completely away from the wall.

these experiments were performed in the quasi-steady limits $\alpha \ll 1$ and $Re_p \ll 1$. It should be noted that King and Leighton observed a transition between rolling and rolling with slip when $Re_p/Re_s \sim 1$, but the transition did not occur until $Re_p/Re_s \sim 10$ in these experiments. The discrepancy is unsurprising considering the difference in the two geometries. The tube offered additional points of near-contact between the particle and the wall and thus a larger resistance to particle motion (a lubrication effect).

The second region demonstrated the existence of a parameter range where Equation 5.7 was valid. The particle mobility increases rapidly as a function of
Figure 5.6. Particle mobility as a function of the parameter $Re_p^2 / Re_s$. The legend indicates the experimental conditions in the following order: particle/tube/fluid. The solid line has a slope of $3/4$ calculated from the region where the mobility increases rapidly with $Re_p^2 / Re_s$ ($30 < Re_p^2 / Re_s < 200$).

only $Re_p^2 / Re_s$, as Figure 5.6 clearly shows. The collapse of $\Delta x_p / \Delta x$ with the sole parameter $Re_p^2 / Re_s$ rendered the choice of particle, fluid, or tube negligible with respect to the particle’s inertial migration. The particle was not in contact with the wall, as expected, and quickly obtained an equilibrium radial position based on the ratio of the inertial to viscous forces. This behavior was observed despite the fact that one of the limits was violated: the tube Reynolds number was not small in some experiments, becoming as large as $O(10^2)$.

In the third region, the experimental mobilities approached an asymptotic value. The behavior for different fluids and particles is presented in Figure 5.7. The lack of data points for more viscous fluids was due to an experimental error.
introduced by the presence of bubbles. Provided that

\[ 4\pi (\mu \omega L_t) / (RP_{atm}) \leq 10^{-2}, \tag{5.11} \]

where \( L_t \) is the length of the tube and \( P_{atm} \) is the atmospheric pressure, the error was found to be negligible. This is explained in more detail in Appendix D. Closer examination of Figure 5.7 reveals two effects are taking place:

1. As \( Re_p^2/Re_s \) becomes large, a large number of experimental observations of particle mobility approach a constant. This constant value more or less agreed with the experimentally determined value of Segré and Silberberg.

2. The particle mobility in less viscous fluids (water or salt/water solutions) departed from the asymptotic value. Mobilities greater than the Segré and Silberberg value were observed.

The first effect was expected. At large values of \( Re_p^2/Re_s \), the inertial force dominated the buoyancy force and thus the particle was approximately neutrally buoyant.

The larger mobilities observed in less viscous fluids were due to the onset of turbulence. Turbulence will introduce instabilities such as local eddies which increase the inertial lift, forcing the particle closer to the tube centerline (on average). The experiments were checked for turbulence using the same criterion used in chapter 3. All the horizontal oscillatory flow experiments are compared with the laminar-turbulent transition criterion in Figure 5.8. It is clear that the turbulent regime was approached only in experiments where water or a salt-water solution was used. For a handful of conditions, the flow was fully turbulent. These correspond exactly with the mobilities in Figure 5.7 which were much greater than
Figure 5.7. Particle mobility as a function of the parameter $Re_p^2/Re_s$. The legend indicates the experimental conditions in the following order: particle/tube/fluid. The solid line is the Segré-Silberberg mobility for a neutrally buoyant particle, $\Delta x_p/\Delta x = 1.2062$. 
the asymptote of Segré and Silberberg. Particle trajectories were also observed to be more chaotic in turbulent or near-turbulent experiments; this was further confirmation of the anomalous behavior in this flow regime.

If the turbulent experiments are removed from consideration, the asymptotic behavior of the particle mobility as $Re_p^2/Re_s \to \infty$ approached the neutrally buoyant case as expected. In this parameter range, $Re$ is also becoming significant and the equilibrium radial position should begin shifting toward the tube wall. Whether or not the $Re$ effect was emerging in the horizontal experiments is difficult to determine, but it may explain why the majority of observed $\Delta x_p/\Delta x$ are 5–10% less than the asymptotic value. The effect of $Re$ was more clearly demonstrated in vertical tube experiments.
Experiments in the horizontal tube with bubbles were also examined. It was suggested that very small bubbles should behave like solid particles provided they remain spherical in the presence of shear. The experiments performed in water presented in Figure 5.9 indicated that this assumption was qualitatively true but bubble behavior is ultimately more complicated. Bubbles experienced an increase in mobility as $Re_p^2/Re_s$ increased, just as particles did. However, the mobility did not collapse with $Re_p^2/Re_s$, and the rate of change of $\Delta x_p/\Delta x$ with $Re_p^2/Re_s$ was less pronounced. Bubbles were also incapable of rolling along the surface of the tube wall; instead they remain “attached” to the wall until the oscillatory flow was sufficient to mobilize them. This is what accounts for the near-zero mobilities for smaller bubbles at lower $\omega$.

In a more viscous fluid, such as ethylene glycol, the bubbles were more easily mobilized (see Figure 5.10). Again, the mobility is an increasing function of $Re_p^2/Re_s$, but the mobility began increasing at lower values of $Re_p^2/Re_s$ than they did in water. This was especially true of a bubble with larger $a/R$, which indicated the bubble was moving toward the center at lower inertial forces than was possible in water (or with particles, for that matter). Most likely this was due to deformation induced drift providing an additive effect to the inertial lift. The relative magnitude of the two drifts can be estimated by comparing their scalings. For example, using Ho and Leal [57] and Chan and Leal [19]:

$$\frac{\text{Inertial Lift}}{\text{Deformation-Induced Lift}} \sim \frac{Re_p^2 \left( \frac{a}{R} \right)}{Re_p Ca \left( \frac{a}{R} \right)} \sim \frac{a \sigma \rho}{\mu^2}. \quad (5.12)$$

The actual ratio of the two lifts will also depend on the bubble’s position in the flow field, but the dimensionless number given by Equation 5.12 is a good measure of the relative strength of the lift mechanisms. For water, $1.4 \times 10^4 \leq \sigma \rho / \mu^2 \leq 146$. 

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Figure 5.9. Bubble mobilities as a function of $Re_p^2/Re_s$ for experiments performed in water with a tube radius of 0.1 cm. The solid symbols correspond to $\Delta x = 2.39$ cm and the open symbols correspond to $\Delta x = 6.05$ cm.
Figure 5.10. Bubble mobilities as a function of $Re_p^2/Re_s$ for experiments performed in ethylene glycol. The first two sets of bubble experiments (from the top of the legend) were performed in tube R1 with the stroke lengths 2.39 and 6.05 cm. The last two sets were performed in tube R2 with the stroke lengths 0.41, 1.03, 2.38, and 4.28 cm.

$a\sigma\rho/\mu^2 \leq 7.0 \times 10^4$, so the inertial lift was dominant. However, for ethylene glycol, $26.9 \leq a\sigma\rho/\mu^2 \leq 74.2$. The inertial lift was still larger but the deformation-induced lift should not be ignored completely, especially considering that the position functions may alter that ratio further. The additional lift provided by the deformation of the bubble contributed to the increase in mobility at lower values of $Re_p^2/Re_s$.

It was difficult to extract any quantitative information about the behavior of bubbles. Experiments in higher viscosity fluids were not performed as they would be subject to even larger deformation-induced lifts. Density matching with a liquid
fluid is impossible, rendering the study of a neutrally buoyant bubble unattainable. It was observed that small bubbles did approach the mobilities measured for particles at similar $Re_p^2/Re_s$, but did not exhibit the same asymptotic behaviors. For the purposes of applying the asymmetric removal technique described in section 5.3.1 the mobility did increase rapidly with $Re_p^2/Re_s$ over a significant enough range that the technique is applicable.

5.4.2 Vertical Tube Flow

It was found that the best way to observe the effect of increasing $Re$ on particle mobility was to use an almost neutrally buoyant particle in the vertical tube. Since the particle was nearly neutrally buoyant, its settling velocity was negligible and it will not lead or lag the flow in a significant way. The vertical orientation assured that $Re_p^2/Re_s \sim \infty$. The experiments were performed in a salt/water solution which was a near density match for the particle. The results are shown in Figure 5.11. Experiments were also attempted with a glycerin/water solution but they suffered from the cavitation problem described in Appendix D.

The experimental data demonstrated the effect of finite $Re$ up to Reynolds numbers of around 200. At finite $Re$, the equilibrium position is shifted closer to the tube wall. This decreases the mobility because the particle is on a streamline of a lower velocity. The shift occurs because $r^*$ (for a neutrally buoyant particle) is determined by a balance between the inertial interaction with the walls and the curvature of the unperturbed parabolic velocity profile. As $Re$ becomes larger, the distance at which the inertial interaction is significant becomes smaller; by analogy with the two-dimensional case, it scales as $R Re^{-1/2}$. The lift force, therefore, is smaller in magnitude at $r^*$ greater than $1 - Re^{-1/2}$ but the curvature
Figure 5.11. Particle mobility (a/R = 0.22) of an almost neutrally buoyant sphere in a vertical tube flow as a function of Re. The fluid was SW3 (Table 5.3); the particle had a sedimentation velocity of 0.016 cm s$^{-1}$.

effect remains the same; this adjustment to the force balance shifts the particle’s equilibrium position closer to the wall. Studies of neutrally buoyant spheres in steady flows have determined that $r^*$ begins to shift toward the wall when $Re > 30$ \[117, 124\].

The mobility rose again sharply and became greater than the neutrally buoyant asymptotic mobility ($\Delta x_p/\Delta x = 1.2062$) for $Re \gtrsim 200$. This departure corresponds exactly with the oscillatory flow becoming turbulent, a phenomenon which was observed in the horizontal tube experiments as well.

Of more interest was the behavior of non-neutrally buoyant particles in the vertical tube. The net particle velocities (over one cycle) for various combinations of particles and fluids are shown in Figure 5.12. For three of the systems studied in
these experiments, a set of oscillatory flow conditions existed at which the particle was made to travel in a direction opposite its settling velocity. In order to observe this effect, a critical stroke length needed to be achieved. However, due to the limitations of the oscillatory syringe pump, the critical value could not be precisely determined. For a given stroke length above the critical value, the particles could also be stabilized at critical frequencies, meaning no net velocity of the particle was observed.

The results of Figure 5.12 are consistent with intuition. A drift velocity occurs because the particle has a slip velocity which arises from its density difference with respect to the fluid. Therefore, larger drift velocities were achieved in system with larger $U_s$ (Figure 5.12(a)). If $U_s$ is not large, the particle cannot be forced to reverse direction (Figure 5.12(c)) because the lift forces are very small; the particle will oscillate back and forth with a net velocity which is approximately equal to $U_s$. Intermediate values of $U_s$ (Figures 5.12(b) and 5.12(c)) fall somewhere between these two extrema.

The same experiments were repeated for bubbles, but they could not be stabilized or forced to reverse direction at similar values of $\Delta x \omega$. The magnitude of $U_s$ is much larger for bubbles than for solid particles, so the fluid oscillations only reduced the rise velocity of bubbles. Potentially, bubbles could be stabilized if the stroke is very large, but that was beyond the range of these experiments.

5.5 Discussion

5.5.1 Horizontal Tube Flow

The mobility of a particle or bubble can be predicted using existing lift expressions calculated for a neutrally buoyant particle. Numerous calculations (e.g.
Figure 5.12. Net particle velocities versus $\Delta x \omega$, the maximum oscillatory velocity. A positive velocity indicates the particle is moving in the direction opposite of gravity. Refer to Table 5.3 for the specific conditions of these experiments.
Ho and Leal [57], Vassuer and Cox [141], Schonberg and Hinch [117], etc.) have shown that a freely rotating and translating particle will experience a lift force in a quadratic shear flow. This lift force is a function of the dimensionless radial position $r^*$ and is proportional to

$$F_L \sim 6\pi \mu a^2 \dot{\gamma}_w \left( \frac{\dot{\gamma}_w a^2}{\nu} \right)$$  \hspace{1cm} (5.13)$$

in the limit that $a/R \to 0$ and $Re \to 0$, such that the wall is in the viscous subdomain of the flow.

If the lift force of Equation 5.13 is equated with the buoyant force of a non-neutrally buoyant particle, the steady-state radial position may be determined from

$$c_s \frac{Re_p^2}{Re_s} P(r^*) - 1 = 0$$  \hspace{1cm} (5.14)$$

where $P(r^*)$, by analogy with the two-dimensional quadratic shear flow studied by Schonberg and Hinch, is approximately given by a parabola with constant coefficients (see the detailed derivation in Appendix C). The constant $c_s$ is an adjustment to the dimensionless quantities of steady flow theories to match the dimensionless quantities used in this work. The majority of theories have been developed in geometries other than a tube, so $P(r^*)$ should be considered approximate.

If $P(r^*)$ could be approximated by a simple function, Equation 5.14 was used to solve for $r^*$. The value of $r^*$ is the equilibrium position for a particular value of $Re_p^2/Re_s$. If the Faxén law correction (which affects even a neutrally buoyant
particle if it has finite size) is ignored, the particle mobility is simply

$$\frac{\Delta x_p}{\Delta x} = 2 \left(1 - r^*^2\right), \quad (5.15)$$

as the particle will follow the fluid streamline corresponding to its equilibrium radial position.

The mobility given in Equation 5.15 assumes the flow is steady with average velocity $U_o$. In these experiments, however, the velocity is oscillatory and thus the radial position will be a function of time. Two asymptotic limits may be considered. If the frequency is low, the particle may come to its equilibrium position at each instant of the oscillation (pseudo steady-state). In this limit the equilibrium position must be integrated over the period. In the limit of high frequencies the particle has insufficient time to reach equilibrium within an oscillation, and thus simply experiences the root mean squared average lift force. Thus, Equation 5.15 is modified in the following ways:

$$c_s \frac{R_e p^2}{R_e s} \sin^2 (t^*) P (r^*) - 1 = 0; \quad (5.16)$$

which is the low frequency asymptote, or

$$\frac{c_s}{2} \frac{R_e p^2}{R_e s} P (r^*) - 1 = 0; \quad (5.17)$$

the high frequency asymptote. The three mobility models given in Equations 5.14, 5.17, and 5.16 are directly compared in Figure 5.13 using the model of Schonberg and Hinch [117]. The differences between the two asymptotic oscillatory models (Equations 5.17 and 5.16) are minimal. For simplicity’s sake, the version given by Equation 5.16 will be used when comparisons are being made with experimental
Figure 5.13. Particle mobility as a function of $Re_p^2/Re_s$ calculated using three different model expressions. The solid line is the mobility calculated from Equation 5.14, the dashed line from Equation 5.17, and the dash-dotted line from Equation 5.16. The asymptotic value as $Re_p^2/Re_s \to 0$ is 0.264 ($a/R = 0.22$).

data.

The comparison of steady flow theory with oscillatory flow experiment depends on assuming that a pseudo steady state applies to the oscillatory flow. This will be valid if the flow is quadratic (so the mobility can be estimated using Equation 5.15 or equivalent) and the particle has enough time to migrate laterally with each oscillation. The first condition can be checked by solving the differential equation describing the system and comparing the fluid displacement as a function of $\alpha$ with a steady flow parabolic displacement. From that calculation (see Appendix B), it was expected that for $\alpha < 3$, the flow was parabolic. Significant deviation does not occur until $\alpha \gtrsim 5$.
The second condition will be valid if the time for the particle to settle a tube radius is much smaller than the period of oscillation \( i.e. \frac{U_s}{\omega R} \gg 1 \). Although this condition was not satisfied for all the oscillatory flow experiments, it was found that if \( \frac{U_s}{\omega R} \leq 1 \), a pseudo steady state can still be achieved. For experiments where \( \frac{U_s}{\omega R} \gg 1 \), the particle obtained a steady state amplitude within one stroke (see Figure 5.14(a)). If \( \frac{U_s}{\omega R} \leq 1 \), a finite amount of time was required before a pseudo steady state was achieved (see Figure 5.14(b)). The mobility was recorded after the steady state was reached; the study of the transient behavior was left to future investigation.

Shown in Figure 5.15 is the comparison of oscillatory flow experiments with various adapted steady flow models. The methodology used to adapt the steady flow models is presented in detail in Appendix C, along with the fitting parameters used to approximate the lift calculations. The agreement is quite good for some of the models, especially at intermediate \( Re_p^2/Re_s \). Note that the models have been truncated at the limit of their validity as \( Re_p^2/Re_s \to 0 \). This truncation is due to a physical limit: the particle cannot pass through a wall and thus acquires a translational velocity which scales as \( 2.4 \frac{a}{R} \) (the asymptote described in Figure 5.5). The agreement with theory is somewhat fortuitous since many of the experimental conditions fall outside the limit of validity for the theoretical expressions. Specifically, the conditions \( \frac{a}{R} \ll 1 \) and \( Re \) or \( Re_p \ll 1 \) were often violated. It appears from this work that the steady flow theories remain good predictors of oscillatory flow particle mobility even if these restriction are relaxed, provided \( \alpha \lesssim 3 \) and a pseudo steady state has been reached.
Figure 5.14. Comparison between the displacement profiles for experiments in: (a) water with $U_s/\omega R = 2.20$ and (b) 70%/30% glycerin/water solution with $U_s/\omega R = 0.01$. The angular frequency in both experiments was 6.39 rad s$^{-1}$. 
Figure 5.15. Particle mobility predicted by several adapted steady flow theories for a particle with $a/R = 0.2$ compared to the experiment data of this work ($a/R = 0.22$ and 0.38). The model labels refer to the following (see also Table C.1): A. Schonberg and Hinch [117]; B. Asmolov [11]; C. Williams et al. [148]; D. Segré and Silberberg [124], and E. Yang et al. [158].
5.5.1.1 Asymmetric Oscillatory Flow: Particles

A promising extension of the oscillatory flow experiments in a horizontal tube was based on disrupting the symmetry of the flow. Applying an asymmetric oscillatory flow has the potential to be an effective particle removal technique. By taking advantage of the relationship between mobility and \( \frac{Re_p^2}{Re_s} \) at intermediate values (Figure 5.6), a particle can be given a net displacement upon the completion of one cycle. The displacement can be estimated by calculating \( \Delta x_p/\Delta x \) for the forward and reverse strokes, which will have the same \( \Delta x \) but different periods. Thus, if the particle obtains an equilibrium radial position quickly (the pseudo steady-state limit), it will “sit” on different streamlines for the forward and reverse strokes.

For example, if \( \omega_f = 1.25 \omega_r \), then \( \left( \frac{Re_p^2}{Re_s} \right)_f = 16/25 \left( \frac{Re_p^2}{Re_s} \right)_r \). The displacement in the forward direction will be greater than in the reverse direction, as the inertial lift will be larger. Using the amplitude measured from symmetric oscillation motion (Figure 5.6), the magnitude of this effect may be estimated. In the range \( 30 \leq \frac{Re_p^2}{Re_s} \leq 200 \), \( \Delta x_p/\Delta x \sim 0.75 \log \frac{Re_p^2}{Re_s} \). Therefore, an empirical estimate of the net displacement is

\[
\frac{\Delta x_f - \Delta x_r}{\Delta x} = 0.75 \left( \log \frac{Re_p^2}{Re_s} - \log \frac{16}{25} \frac{Re_p^2}{Re_s} \right).
\] (5.18)

The efficacy of the technique depends on operating in the range where \( \Delta x_p/\Delta x \) changes rapidly with \( \frac{Re_p^2}{Re_s} \). If \( Re_p^2/Re_s \) is outside these limits, the mobility will not change enough with \( \omega \) to impart a net motion on the particle. For a typical value inside these limits (say \( Re_p^2/Re_s = 10^2 \)), the net dimensionless displacement is predicted by Equation 5.18 to be 0.145. The particle would be expected to have a net displacement which was approximately 15% of the stroke length during each
period.

5.5.1.2 Asymmetric Oscillatory Flow: Bubbles

Asymmetric oscillatory flow should have a similar effect on bubbles as it does on particles. The utility of the technique was demonstrated using a pump with dual phase-locked syringes of different stroke volumes, which were used to generate an asymmetric oscillatory displacement of the form

$$\Delta x_{\text{asym}} \sim -\frac{\Delta x}{2} \sin(\omega t) + \frac{\Delta x}{8} \sin(2\omega t) \ .$$  

Equation 5.19

The displacement produced by this wave approximates a sawtooth wave in which the forward stroke has a period half that of the reverse stroke. The amplitude of the displacement is $0.55\Delta x$, close to that of the pure sinusoid, while the average velocities in the forward and reverse direction differ by a factor of about 1.6. The wave form of Equation 5.19 and corresponding velocity is depicted in Figure 5.16. The periods of the forward and reverse stroke can be switched by reversing the motor’s direction of rotation.

Using the smaller of the glass capillary tubes (R1), bubbles were introduced into the tube and the net displacement was tracked when an asymmetric oscillatory flow was present. The dimensionless net displacement of the bubble $\langle \Delta x_p / \Delta x \rangle$ is plotted against $Re_p^2 / Re_s$ in Figure 5.17. Unsurprisingly, smaller bubbles achieved larger net displacements than larger bubbles, as the mechanism depends on the ability of a bubble to rapidly migrate and move with the velocity of different streamlines for the forward and reverse stroke. As was observed in the symmetric oscillatory experiments, a critical shear rate must be reached before any net motion was observed.

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Figure 5.16. Displacement (solid line) and velocity (dashed line) produced by the asymmetric wave described in Equation 5.19.
Figure 5.17. Net dimensionless mobility of bubbles in water in the presence of an asymmetric oscillatory flow. The volume displacements used were 0.123 (●), 0.248 (□, ○, △), and 0.369 (◀, ▶, ⋆) cm$^3$, respectively.
For smaller bubbles \( a/R < 0.5 \), the net displacement also comes to a maximum at approximately \( 100 \leq Re_p^2/Re_s \leq 200 \), which is consistent with the range of \( Re_p^2/Re_s \) where the mobility increased at the greatest rate in symmetric oscillatory flow. This is consistent with a drift mechanism that is inertial and when \( 100 \leq Re_p^2/Re_s \leq 200 \), the bubble removal will be most effective. Even larger bubbles \( a/R > 0.5 \) were also given a net drift of a smaller magnitude; however, as the bubble size becomes larger the drift mechanism is less clear. The drift may be due to inertia, deformation, or a combination of both. Regardless, the results indicate that asymmetric oscillatory pumping would be an effective bubble removal technique, in particular for microfluidic geometries where bubbles often interfere with other transport processes.

The direct methanol fuel cell is one such microfluidic application that will benefit from improved bubble management, as previous work (see section 4.3.3) has already demonstrated. In the experiments of section 4.3.3, symmetric oscillations were used to stabilize the performance of the DMFC at low \( Q_{an} \). Generating net bubble drifts with an asymmetric oscillatory flow lends itself well to the DMFC, as it is desirable to remove the bubbles without affecting the feed rate of the liquid fuel. If bubbles are displaced, the performance of the DMFC at low \( Q_{an} \) would be further stabilized by the asymmetric flow.

A DMFC with a single serpentine flow field \((\text{width}/\text{height}/\text{length} = 0.1/0.1/32 \, \text{cm}, \, \delta = 0.64)\) was used to test this hypothesis. With the exception of the flow field, the DMFC was identical to the one used in the experiments of chapters 3 and 4. No additional diffusion layer was added; the MEA consisted of the Nafion membrane, catalyst layers, and ELAT carbon cloth diffusion layers. The asymmetric syringe pump was interfaced with a steady flow gear pump via a tee junction just before
the fuel entered the flow field of the DMFC. The cell temperature was 70 °C, with a cathode feed rate of 150 cm³ min⁻¹ (preheated to 70 °C), and the anode fuel was 1.0 mol L⁻¹ solution of methanol in water preheated to ~ 65 °C.

The minimum \( Q_{an} \) required to generate a certain current density \( i \) can be calculated using the expression

\[
Q_{an,min} = \frac{iA_e}{6F\Delta c},
\]

where \( \Delta c \) is the quantity of methanol that must be consumed. For \( i = 0.6 \) A cm⁻² (a value near the system’s \( i_{lim} \)), \( Q_{an,min} = 0.2 \) cm³ min⁻¹. However, operating the DMFC at such low feed rates has adverse effects on performance due to the presence of carbon dioxide bubbles (see Figure 5.18). For the DMFC studied, \( Q_{an} > 4 \) cm³ min⁻¹ to avoid the instabilities which are present when large quantities of bubbles are being generated. This represents not just a poor utilization of fuel, but also a significant amount of energy is being wasted in order to preheat an unnecessary amount of fuel to the cell temperature. The power density required to heat the feed is estimated by

\[
\Psi_{ph} = \frac{mC_p\Delta T}{A_e} = \frac{\rho Q_{an}C_p\Delta T}{60A_e},
\]

where \( C_p \) is the specific heat capacity of water and \( \Delta T \) is the difference in temperature between the fuel at ambient conditions (say 25 °C) and in the DMFC (70 °C). At a feed rate of 5 cm³ min⁻¹, for example, the energy required for preheating is forty times the peak power output of the cell. While efficient heat management/exchange can reduce losses, this preheating requirement still represents a significant limitation to DMFC implementation. Reducing the feed rate
Figure 5.18. Polarization curves obtained in the DMFC at $Q_{an} = 5 \text{ cm}^3 \text{ min}^{-1}$, where the performance is stable, and $Q_{an} = 1 \text{ cm}^3 \text{ min}^{-1}$, where the performance is unstable. The cell temperature was 70 °C, $Q_c = 150 \text{ cm}^3 \text{ min}^{-1}$, and $c_M = 1.0 \text{ mol L}^{-1}$.

by a factor of twenty will reduce the energy required to heat the fuel by the same amount.

The DMFC was exposed to three different oscillatory waves at the unstable $Q_{an}$ of 1 cm$^3$ min$^{-1}$: a symmetric sine wave with a $\Delta x = 9.5 \text{ cm}$ ($\Delta V = 0.095 \text{ cm}^3$), and both a forward and reverse asymmetric wave described by Equation 5.19 with $\Delta x = 9.5 \text{ cm}$ ($\Delta V = 0.095 \text{ cm}^3$). The ratio between the displacements was not precisely 0.25, as the second syringe had a $\Delta x = 2.1 \text{ cm}$ ($\Delta V = 0.021 \text{ cm}^3$), making the ratio closer to 0.22. Three different frequencies were used: 2.65, 8.38, and 14.5 rad s$^{-1}$. The results of each set of experiments are shown in Figure 5.19.

As had been observed in section 4.3.3, symmetric oscillations had a stabilizing
Figure 5.19. Polarization curves obtained in the DMFC at $Q_{an} = 1 \text{ cm}^3 \text{ min}^{-1}$ with different oscillatory displacements. The cell temperature was 70 °C, $Q_c = 150 \text{ cm}^3 \text{ min}^{-1}$, and $c_M = 1.0 \text{ mol L}^{-1}$. 
effect (Figure 5.19(a)). This is likely due to an increase in liquid film thickness which accompanies the higher velocities and the refreshing of the film with each oscillation. However, additional stabilization is possible through the use of the asymmetric forward oscillations (Figure 5.19(b)), which produced a smoother response at the highest frequency. The asymmetric reverse oscillations (Figure 5.19(c)) demonstrate that the direction of the asymmetry is important, as the oscillations negatively impact the performance compared to both asymmetric forward and symmetric oscillations. The differences in performance are most clearly seen when experiments at the highest frequency at compared directly, as is shown in Figure 5.20. The symmetric oscillations stabilize the DMFC’s performance, but the performance stability is amplified by the forward asymmetric oscillations and damped by the reverse asymmetric oscillations. This is evidence that in addition to refreshing the liquid film, as was the case with symmetric oscillations, the asymmetry of the flow is imparting a net displacement on the carbon dioxide bubbles: in the forward case, the bubbles are moved out of the cell, and in the reverse case, the bubbles are retained.

Quantitative comparison with individual bubble experiments is difficult because at high current densities (say 0.6 A cm$^{-2}$) the carbon dioxide bubble void fraction approaches 90%. For large bubbles, however, the net velocity is on the order of $0.08(\Delta x\omega/2\pi)$. For $\omega = 14.52$ rad s$^{-1}$ this corresponds to a net bubble phase velocity of about 1.8 cm s$^{-1}$. This is close to the liquid feed velocity of 1.7 cm s$^{-1}$, suggesting that substantial depletion of the bubble void fraction may be achieved under these conditions.
Figure 5.20. Direct comparison of polarization curves obtained in the DMFC for three different oscillations at a frequency of 14.52 rad s$^{-1}$. 
5.5.2 Vertical Tube Flow

An asymptotic theory describing the behavior of a particle in a vertical oscillatory tube flow was developed by considering two limits to the particle’s mobility. These limits were described briefly in section 5.2.2. The theory depends on assuming that a pseudo steady-state was achieved during each oscillation; if this was not the case, the model will not be valid. With this in mind, the two limits will be described below and then the criteria for pseudo steady-state will be discussed.

When the slip velocity is large (or \(U_s\) is large), the interaction of the parabolic velocity profile and \(U_{\text{slip}}\) produces a large migration velocity in the radial direction. If the migration time is such that the radial motion is fast with respect to the period of oscillation, the particle can, at maximum, spend exactly one half-cycle at the wall and one half-cycle in the tube center. This would give a maximum displacement of

\[
\Delta x_{\text{max}} = \left[ 2\Delta x + \frac{U_s \pi}{\omega} \right] - \left[ 2.4 \frac{a}{R} \Delta x - \frac{U_s \pi}{\omega} \right],
\]

and an average maximum particle velocity of

\[
\langle U_p \rangle_{\text{max}} = \frac{\omega}{2\pi} \Delta x_{\text{max}} = 2\omega \Delta x - 2.4 \frac{a}{R} \omega \Delta x + U_s
\]

over a full period. The dimensionless drift velocity is defined as

\[
\langle U_p \rangle^* = \frac{\langle U_p \rangle - U_s}{\Delta x \omega},
\]

where \(U_s\) can be positive or negative depending on the buoyancy of the particle. For a particle with an \(a/R = 0.22\), Equation 5.23 predicts that \(\langle U_p \rangle_{\text{max}}^* = 0.234\).
Equation 5.23 represents the maximum particle velocity which can be obtained at a given dimensionless particle size.

If the slip velocity is not large enough to produce a migration time which is short enough to sample the distance $R$, then the net particle velocity will be less than $\langle U_p \rangle_{max}$. For small $U_{slip}$, the particle will not migrate an appreciable amount during each stroke. In this limit, the particle’s radial position will be determined by competition between two lift mechanisms: the inertial lift of a neutrally buoyant particle which is identical to the horizontal case, and the “slip” lift a particle experiences because it leads or lags the flow field. The inertial lift has an equilibrium radial position associated with it, whereas the slip lift will drive the particle toward either the wall (if leading the flow) or the center (if lagging the flow) of the tube.

When $U_{slip}$ is small, however, the “slip” lift will be small. Thus, the particle can only migrate small distances away from the equilibrium position it would otherwise obtain if it was neutrally buoyant i.e. $U_{slip} = 0$. This fluctuation in position can be expressed as

$$r^* \cong r^\dagger \pm \Delta r^* \sin t^*, \quad (5.24)$$

where $\Delta r^* = \Delta r/R$ (the dimensionless fluctuation in radial position i.e. $\Delta r = r - r^\dagger$) and $t^* = \omega t$. The dimensionless net particle velocity, assuming that the particle will trace the streamline it sits upon, will be

$$\langle U_p \rangle^* = \langle (1 - r^{*2}) \sin t^* \rangle, \quad (5.25)$$

where $\langle \bullet \rangle$ denotes the time average over a half period. Substituting Equation
(using only the positive expression for simplicity) into Equation 5.25 and expanding yields

$$
\langle U_p \rangle^* = \int_0^\pi 2r^* \Delta r^* \sin^2 t^* dt^* = r^* \Delta r^* .
$$

(5.26)

All the other terms, when integrated, are zero. Based on the result of Equation 5.26 it was expected that the net particle velocity will be proportional to the fluctuation in the radial position from the equilibrium radial position when \( U_{slip} \) is small.

The fluctuation in radial position can be estimated by considering a comparison between the migration velocity of Schonberg and Hinch [117] with the migration velocity of Vasseur and Cox [141]. From those two studies, both of which were developed for \( Re \ll 1 \), the following scalings were extracted:

$$
W_p^* \sim \lambda_{SH} \Delta r^* \left( \frac{\Delta x \omega}{a} \right)^2 \frac{a^3}{4\nu R^2} ,
$$

(5.27)

where the maximum velocity has been written as \( \Delta x \omega \) for the oscillatory experiments, and

$$
u t \sim \lambda_{VC} \Delta x \omega \frac{U_s a}{\nu} .
$$

(5.28)

The constants \( \lambda_{SH} \) and \( \lambda_{VC} \) can be approximated from the appropriate figures of Schonberg and Hinch (Figure 2) and Vasseur and Cox (Figure 8) since it was assumed that the particle is being perturbed about an equilibrium position. With that in mind, \( \lambda_{SH} \sim 2.385 \) and \( \lambda_{VC} \sim 0.056 \). Using Equations 5.27 and 5.28 the radial fluctuation can be estimated as

$$
\frac{\Delta r}{R} \sim \frac{u_t}{W_p^*} \sim \frac{4\lambda_{VC} U_s R^2}{\lambda_{SH} \Delta x \omega a^2} .
$$

(5.29)
Again, if a pseudo steady-state approximation is valid, then the magnitude of \( \langle U_p \rangle^* \) will be proportional to \( \Delta r^* \) for small \( U_{\text{slip}} \):

\[
\langle U_p \rangle^* \sim 0.094 \frac{U_s R^2}{\Delta x \omega a^2}.
\] (5.30)

A pseudo steady-state will be reached if the radial fluctuations occur over a shorter time than a half period of oscillation. Thus,

\[
\frac{\Delta r}{u_t} \ll \frac{\pi}{\omega};
\] (5.31)

and using Equations 5.29 and 5.28, the condition for pseudo steady-state can be expressed as

\[
\frac{4}{\pi \lambda_{SH}} \left( \frac{\nu R^3}{\Delta x^2 \omega a^3} \right) \ll 1.
\] (5.32)

There is a similar condition for the large \( U_{\text{slip}} \) limit, except that \( \Delta r \) is replaced by \( R \) in Equation 5.31 resulting in the criterion

\[
\frac{\nu R}{\lambda_{VC} U_s a \Delta x \omega} \ll \frac{\pi}{\omega} \Rightarrow \frac{5.7 \nu R}{U_s \Delta x a} \ll 1.
\] (5.33)

The large \( U_{\text{slip}} \) limit was only valid for the experiments performed in water. For the other fluid/particle combinations, the condition in Equation 5.33 was not strictly satisfied. However, with a few exceptions, the pseudo steady-state criterion for the small \( U_{\text{slip}} \) limit was valid for the other experimental conditions.

The minimum and maximum values for the vertical tube experiments presented in Figure 5.21 are shown in Table 5.4.

A predictive model for \( \langle U_p \rangle^* \) was constructed from the two asymptotes (Equations 5.23 and 5.30). The model is a linear combination of the two asymptotes,
TABLE 5.4
MAXIMUM AND MINIMUM VALUES OF PSEUDO STEADY-STATE CRITERIA

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Particle</th>
<th>Equation 5.33 (min - max)</th>
<th>Equation 5.32 (min - max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>A</td>
<td>0.02 - 0.11</td>
<td>0.015 - 0.105</td>
</tr>
<tr>
<td>SW2</td>
<td>A</td>
<td>0.12 - 0.43</td>
<td>0.002 - 0.136</td>
</tr>
<tr>
<td>EG</td>
<td>A</td>
<td>9.28 - 23.5</td>
<td>0.044 - 1.940</td>
</tr>
<tr>
<td>EG</td>
<td>C</td>
<td>1.07 - 3.87</td>
<td>0.038 - 3.012</td>
</tr>
</tbody>
</table>

which was inverted to give the proper behavior:

\[
\langle U_p \rangle^* = \frac{1}{\langle U_p \rangle^*_{max} - 1 + (0.094 \frac{U_s R^2}{\Delta x \omega a^2})^{-1}}. \quad (5.34)
\]

The observed dimensionless drift velocities are plotted in comparison with the model of Equation 5.34 in Figure 5.21. The model, which has no adjustable parameters, is in good agreement with the experiments which were performed in water. In general, the experiments in the salt/water solution and ethylene glycol agree as well, but the large values of \(\Delta x \omega\) relative to \(\langle U_p \rangle - U_s\) may be smoothing out the variations. Evidence of turbulence at large \(\omega\) was also observed. Some of the data falls well below the model as \(\frac{U_s R^2}{(\Delta x \omega a^2)} \to 0\). These points are all experiments where the criterion of Equation 5.33 or Equation 5.32 are O(1) or larger and thus the pseudo steady-state approximation is violated.

The criterion in Equation 5.33 offers a guideline for performing particle separations when \(U_{\text{slip}}\) is large, where larger \(\langle U_p \rangle^*\) will be obtained. The expression
Figure 5.21. Experimental dimensionless drift velocities compared to the predictions of the asymptotic model (solid line) given in Equation 5.34. Refer to Table 5.3 for the experimental conditions indicated by the legend (fluid/tube/particle). The data points enclosed by circles are in violation of Equation 5.33, the points which have an ‘X’ through them are in violation of Equation 5.32.
can be rearranged to solve for $a$ using the Stokes settling velocity for $U_s$:

$$a \gg 2.95 \left( \frac{\mu \nu R}{\Delta \rho g \Delta x} \right)^{1/3}.$$  (5.35)

Equation 5.35 demonstrates the larger particles can be stabilized or reversed for a given fluid system as $\Delta x$ increases. A stroke length could be chosen such that larger particles travel against gravity but smaller ones still settle.

To test this hypothesis, a dilute suspension in water composed of three particles of different sizes ($a/R = 0.14$, 0.28, and 0.37) was injected into the vertical tube and subjected to an oscillatory flow of varying magnitude, but non-negligible multiple particle interactions in the finite size tube made separation difficult. A suspension of glass spheres (diameter = 100 microns) was observed to travel against gravity when oscillations were present, so it is likely the best application of the technique would be for dilute suspensions where the particles have $a/R \ll 1$.

5.6 Conclusions

In this chapter, inertial migration phenomena of particles and bubbles were studied in the presence of an oscillatory tube flow. Both the horizontal and vertical tube orientations were investigated. Though they differ only in their orientation with respect to gravity, the inertial lift in each case has very different effects.

In the horizontal tube orientation, the inertial lift is balanced by the buoyant force. The force balance scales as $Re_p^2/Re_s$ and governs the equilibrium position the particle obtains during each stroke. Particle mobilities were observed to transition from three distinct regions depending on the value of $Re_p^2/Re_s$. When $Re_p^2/Re_s < 30$, the particle is in contact with the wall and translates with a constant mobility which is a function of the particle size. At intermediate values
of $Re_p^2/Re_s$, the mobility increases rapidly. When $Re_p^2/Re_s \gtrsim 10^3$, the mobility approaches the neutrally buoyant asymptote of Segré and Silberberg. Some experiments deviated from the asymptotic value; if the fluid was viscous, cavitation decreased the applied fluid displacement, resulting in a smaller particle displacement, and if the fluid was less viscous, a handful of the experiments were performed where the flow was turbulent. The mobilities were predicted reasonably well by incorporating gravitational forces into existing steady flow models and assuming pseudo steady-state behavior. Bubble mobilities did increase with increasing $Re_p^2/Re_s$ but did not exhibit either the low or high asymptotic behavior of particles. In more viscous fluids, deformation-induced migration was present; this shifts the equilibrium position toward the tube center at lower values of $Re_p^2/Re_s$. Smaller bubbles behaved similarly to particles at intermediate $Re_p^2/Re_s$.

In the vertical tube orientation, the inertial lift is complicated by the presence of slip between the particle and the fluid. The particle’s equilibrium position is dictated by the direction of the oscillatory stroke: if the stroke is in the direction of the particle’s settling velocity, the particle is driven to the tube wall; otherwise, it is driven to the tube centerline. This effect was used to impart a net drift velocity on the fluid in the direction opposite its settling velocity. A properly tuned oscillatory flow was also demonstrated to stabilize the particle so that no net motion occurred. Bubbles could not be affected in the same way for the conditions of this study. A model which has the proper asymptotic behavior was developed using scaling arguments. Provided that the pseudo steady-state conditions were satisfied for a given fluid-particle system, the model fit the data quite well. Additional experiments using an almost neutrally buoyant particle
showed that the mobility as $Re_p^2/Re_s \to \infty$ decreased with increasing $Re$, which is in agreement with previous theoretical work for steady flows.

Based on experimental observations, potential particle/bubble manipulation techniques were investigated. In the horizontal orientation, an asymmetric oscillatory flow was generated to give particles and bubbles a net drift by taking advantage of the change in mobility with oscillation frequency. Asymmetric oscillatory flow could be used to removal unwanted particles, drops, or bubbles from tubes or channels. Adaptation of asymmetric oscillatory flow to separation techniques is also possible. In the vertical orientation, using symmetric oscillatory flow as a particle separation technique was also examined. Bubbles are likely too buoyant to be controlled, but separations in very dilute suspensions of solid particles may be possible, particularly if the particles are very small.
CONCLUSIONS AND FUTURE WORK

The primary goal of this dissertation was to study the application of oscillatory flow to enhance the performance of direct methanol fuel cells. Oscillations were shown to both reduce or eliminate mass transfer resistance and to aide in the control of instabilities resulting from gas generation. In addition to the specific application motivating this study, the phenomena resulting from fluid oscillations identified here have other possible uses. Some of these potential applications are discussed below.

6.1 Mass Transport in Porous Media

In chapter 2, oscillatory flow in a porous medium was used to enhance $D_T$. It was found that oscillatory flow transport enhancement could be predicted by available steady flow models provided $U_{rms}/\omega a \gg 1$. In general, this should only be true if $\alpha$ and $Re \ll 1$ as well; however, the steady flow predictions agreed with the experimental data even when operating conditions were well outside these limits. It is likely that if the flow remains laminar that the steady flow models will continue to hold, since $D_T$ is controlled by purely mechanical dispersion, depending only on the interaction of the flow field with the randomly ordered packing.
In many processes where mass transport enhancement may be useful, however, more information is required about the predicted behavior of oscillatory flow as \( Re \ll 1 \). This is especially relevant to microscale porous mediums in which the throughput will be very small, leading to small fluid velocities. Further study in this limit would be useful. Unfortunately, this will require the development of a different methodology, as the current detection limit would not permit study with any accuracy. Though of less importance, it would also be beneficial to observe the mass transport behavior in a medium which was fully three dimensional and not the pseudo-three dimensional medium which was used here.

6.2 Direct Methanol Fuel Cells

One specific benefit of oscillatory flow in a porous medium was observed in chapter 3. An oscillatory flow superimposed on the steady feed of the anode fuel stream of a mass transfer limited DMFC improved both the peak power density (up to 30%) and \( i_{lim} \) (more than twofold). An optimization study described in chapter 4 probed the DMFC’s operational parameters and discovered that the performance could be improved still further by striking a balance between methanol cross-over at low current densities and methanol diffusion at high current densities. The optimal performance came at a price, as the power required to generate the fluid oscillations was much greater than the power improvements in the DMFC. Improvements in the efficiency of the technique will be most easily gained by altering the anode geometry in one of two ways:

1. Redesign of the anode flow field \( e.g. \) changing \( w \) or \( d \);

2. Choosing or designing an alternative diffusion layer with larger \( a \).
The effect of either of these changes on power requirements is obvious from Equations 3.23 and 3.27:

\[ \Psi \sim \frac{w}{d^3} \quad \text{and} \quad \Psi \sim a^{-9/2}. \]

How these changes would affect actual DMFC performance is not well understood. Simply choosing a diffusion layer which meets the criteria will not suffice, as this work demonstrated when a stainless steel wire mesh was used. Additional design considerations would also be necessary if the oscillatory flow was to be generated inside the flow field, such as is required for a miniature DMFC suitable for small commercial electronic devices.

The most promising application of oscillatory flow in a DMFC was investigated in chapter 4. At values of \( \Delta x \) and \( \omega \) which were much smaller than the range of \( \Delta x \) and \( \omega \) where mass transfer enhancement had significant effect, oscillatory flow stabilized DMFC performance at small \( Q_{an} \). When \( Q_{an} \) is low, a large amount of \( \text{CO}_2 \) is generated (especially at higher current densities) and coalesces into bubbles or slugs of non-negligible size which the flow is unable to force out of the flow plate. The methanol/water solution is restricted to a thin film and the fuel cell, lacking enough fuel to generate the required number of electrons, experiences a drop in power output. The performance response is unstable, because the gas may collect in a flow channel, be driven out by the flow, and then collect again. It was hypothesized that the oscillatory flow, which creates a larger fluid velocity in the anode channel, refreshed the liquid film of the fuel solution at the diffusion layer/channel interface and kept the film thicker.

Furthermore, in chapter 5 it was demonstrated that an asymmetric oscillatory flow could be used to both refresh the liquid film and displace bubbles from the DMFC using a stroke volume of reasonable size. Asymmetric oscillatory flow
would allow the use of very small steady flow rates without performance instability, thereby better utilizing the fuel and saving heating costs. The methodology used in 5.3.1.2 to generate the asymmetric flow would need to be altered to be implemented in smaller DMFCs to reduce the number of mechanical parts. As the DMFC continues to shrink in size, bubble management will become an increasingly important problem. An optimized implementation of the asymmetric oscillatory flow, where the energy costs in the system are carefully considered, would be beneficial to the development of DMFC technology going forward.

6.3 Supported Liquid Membranes

Another possible application of oscillatory flow to a porous medium which was not studied in this dissertation involves supported liquid membranes. Mass transport enhancement has been demonstrated in the flow (through) direction in the past [20, 84], but a similar study of transverse mass transport enhancement has not been attempted. Instead of forcing fluid into and through the membrane’s pores, the oscillatory flow would remain in the membrane’s interior (see Figure 6.1). When the desired solute was adsorbed into the membrane’s carrier liquid, its mass transport would increase due to the convection supplied by the fluid oscillations. If the enhancement was significant enough, the stability of a support liquid membrane could be improved at the same time by increasing the membrane’s thickness. The oscillations would compensate for the increased mass transfer resistance of such a membrane. This convective benefit would be achieved without any net flow of carrier fluid, that is, none of the fluid in the support would be lost or wasted.
6.4 Separations of Particles and Bubbles

In chapter 5, some interesting uses of oscillatory flow for particle (a solid or gas sphere) separations were briefly discussed. These uses depend on taking advantage of a particle’s inertial migration to equilibrium positions in a tube or similar flow geometry. Based on experimental observation, both imparting a net drift velocity on particles in a horizontally orientated flow geometry or trapping particles in a vertically orientated flow geometry can be achieved via a properly tuned oscillatory flow.

In the horizontal case, the oscillatory flow was a zero-mean asymmetric flow. The asymmetry exploits the different equilibrium radial positions that a particle acquires during the forward and reverse strokes. Using this approach as a separation technique would require careful choice of both the oscillatory parameters, fluid, and tube/channel size. A more straightforward use would be to remove particles indiscriminately from a multiphase flow. Aside from the proof-of-concept type experiments performed in chapter 5, there is ample opportunity for future development. As mentioned, the best use of an asymmetric oscillatory flow may be as a bubble removal technique in continuous processes where bubbles are unde-
sirable: reaction processes, such as the DMFC, or heat exchangers. The approach will only be useful at intermediate $Re_p^2/Re_s$, where $\Delta x_p/\Delta x$ increases rapidly between $\sim 30 \leq Re_p^2/Re_s \leq 200$ (see Figure 5.6).

Developing a particle separation technique in a vertical oscillatory flow would be another interesting challenge. As was demonstrated in chapter 5, there was a parameter range wherein particles could theoretically be separated based on their size (particle diameter). In the experimental work of this dissertation, particle sizes were chosen based on their ability to be visually detected; however, this introduced other complications such as finite $a/R$ effects and particle-particle interactions. A better approach would be to investigate the possibility of particle separations using much smaller particles in suspensions. This would require a detection methodology that does not depend on visualization.

It is also important to note that only single particles (and bubbles) were considered. Confirmation of the observed behaviors for suspensions or other multiphase mixtures (bubbly flows, for instance) is vital before these techniques could be used in larger scale processing equipment. Deviations from single particle behavior would open up new avenues of research in oscillatory multiphase flow.
APPENDIX A

DETERMINATION OF THE PRESSURE GRADIENT FOR LAMINAR FLOW IN A CHANNEL

Consider a channel of dimension $2b$ subjected to a sinusoidal pressure gradient. Assuming the flow is unidirectional, the governing differential equation for the velocity $u$ becomes

$$\rho \frac{\partial u}{\partial t} = G_o \sin(\omega t) + \mu \frac{\partial^2 u}{\partial y^2}, \quad (A.1)$$

where $G_o$ is the undetermined amplitude of the pressure gradient. Substituting the following dimensionless quantities

$$t^* = \omega t; \quad u^* = \frac{u}{U_c}; \quad y^* = \frac{y}{b},$$

into Equation $A.1$ yields

$$\rho \omega U_c \frac{\partial u^*}{\partial t^*} = G_o \sin t^* + \frac{\mu U_c}{b^2} \frac{\partial^2 u^*}{\partial y^*^2}. \quad (A.2)$$

The pressure gradient term is driving the flow and therefore must be significant. Consequently, dividing through by $G_o$ allows for two possible choices for the characteristic velocity $U_c$, the viscous or inertial scaling:

$$U_{c,vis} = \frac{G_o}{\rho \omega} \quad \text{or} \quad U_{c,in} = \frac{G_o b^2}{\mu}.$$
Selecting the viscous scaling for the velocity leads to the final dimensionless equation

\[ \alpha^2 \frac{\partial u^*}{\partial t^*} = \sin t^* + \frac{\partial^2 u^*}{\partial y^*^2} \]  

(A.3)

where the dimensionless parameter \( \alpha^2 \) is, as before, the square of the Womersley number.

Equation (A.3) can be solved for all values of \( \alpha \) using a standard complex conjugate formulation for the velocity field. The velocity \( u^* \) can be written as the complex velocity \( \hat{u} \), which transforms Equation (A.3) into

\[ \alpha^2 \frac{\partial \hat{u}}{\partial t^*} = e^{it^*} + \frac{\partial^2 \hat{u}}{\partial y^*^2} \]  

(A.4)

where \( u^* = \Re [\hat{u}] \). To solve Equation (A.4), the temporal and spatial elements can be separated by defining \( \hat{u} = e^{it^*} f(y^*) \). Plugging this identity into Equation (A.4),

\[ i\alpha^2 f(y^*) = 1 + \frac{\partial^2 f}{\partial y^*^2} \]  

(A.5)

which is a differential equation that is only a function of \( y^* \). The original boundary conditions

\[ u^* = 0 \text{ at } y^* = 1 \]  

(A.6)

\[ \frac{\partial u^*}{\partial y^*} = 0 \text{ at } y^* = 0 \]  

(A.7)

can be recast as

\[ f(y^* = 1) = 0 \]  

(A.8)
\[
\frac{\partial f}{\partial y}(y^* = 0) = 0. \tag{A.9}
\]

The solution to Equation A.5 using the boundary conditions given in Equations A.8 and A.9 is

\[
f(y^*) = \frac{1}{\alpha^2} \left[ 1 - \frac{\cosh \left( \sqrt{-i\alpha y^*} \right)}{\cosh \left( \sqrt{-i\alpha} \right)} \right], \tag{A.10}
\]

and the dimensionless velocity profile becomes

\[
u^* = \Re \left[ \hat{u} \right] = \Re \left[ e^{it^*} f(y^*) \right] = \Re \left\{ \frac{e^{it^*}}{\alpha^2} \left[ 1 - \frac{\cosh \left( \sqrt{-i\alpha y^*} \right)}{\cosh \left( \sqrt{-i\alpha} \right)} \right] \right\}. \tag{A.11}
\]

A.1 Calculation of the Pressure Gradient

Recall that \( G_o \) is the characteristic magnitude of the sinusoidal pressure gradient \( G_o \sin (\omega t) \). The oscillatory flow in the fuel cell is not generated by applying the pressure gradient; instead the syringe is displacing a volume of fluid with each stroke. The pressure gradient can be related to \( \Delta V \) through the simple integral relation

\[
\Delta V = \frac{6bwU_c}{\omega} \int_0^\pi \int_0^1 u^* dy^* dt^* \tag{A.12}
\]

where \( w \) is the channel width. Note that the integration in \( t^* \) is only over a half-period \( \omega \). Substituting the viscous velocity scaling \( U_{c,\text{vis}} \) for \( U_c \) and the velocity profile of Equation A.11 into Equation A.12 and rearranging gives the following:

\[
\Delta V = \frac{6G_owb^3}{\omega \mu} \Re \left[ \int_0^1 f(y^*) dy^* \int_0^\pi e^{it^*} dt^* \right]. \tag{A.13}
\]
Integrating the exponential function is straightforward. After integration Equation [A.13] reduces to

\[ \Delta V = \frac{6 G_0 w b^3}{\omega \mu} \Re \left[ 2 \int_0^1 f(y^*) dy^* \right]; \quad (A.14) \]

only the integral of \( f(y^*) \) remains. After some algebraic manipulation and the substitution \( d = 2b \),

\[ \Delta V = \frac{3 G_0 w d^3}{2 \omega \mu} \left[ \left( \frac{2}{\alpha^2} \right) \left( 1 - \frac{\left( \sin(\sqrt{2} \alpha) + \sinh(\sqrt{2} \alpha) \right)}{\sqrt{2} \alpha \left( \cos(\sqrt{2} \alpha) + \cosh(\sqrt{2} \alpha) \right)} \right) \right]. \quad (A.15) \]

Calling the quantity in square brackets \( G^*(\alpha) \) i.e. the result of the spatial integration, Equation [A.15] can be rearranged to solve for \( G_0 \):

\[ G_0 = \frac{2 \mu \omega \Delta V}{3 w d^3} \frac{1}{G^*(\alpha)}. \quad (A.16) \]

The characteristic pressure gradient of Equation [A.16] depends on several experimental parameters. Table A.1 presents the values of \( 1/G^*(\alpha) \) for the experimental values of \( \alpha \). The value of \( G^*(\alpha) \) decreases rapidly with increasing \( \alpha \).
TABLE A.1
SELECTED VALUES OF THE FUNCTION $1/G^*(\alpha)$ FOR EXPERIMENTAL CONDITIONS OF CHAPTER

<table>
<thead>
<tr>
<th>$\omega$ (rad s$^{-1}$)</th>
<th>$\alpha$</th>
<th>$1/G^*(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.89</td>
<td>1.202</td>
<td>3.484</td>
</tr>
<tr>
<td>8.92</td>
<td>2.112</td>
<td>3.572</td>
</tr>
<tr>
<td>26.89</td>
<td>3.667</td>
<td>8.300</td>
</tr>
<tr>
<td>38.83</td>
<td>4.406</td>
<td>11.553</td>
</tr>
</tbody>
</table>
APPENDIX B

AMPLITUDE OF OSCILLATORY FLOW AS A FUNCTION OF WOMERSLEY NUMBER

B.1 Oscillatory Flow in a Tube

Consider oscillatory flow in a tube which is not induced by a pressure gradient but by the displacement of a fluid volume. The flow of a Newtonian fluid in a tube is unidirectional and a function of radial position alone:

\[ \rho \frac{\partial u}{\partial t} = G(t) + \mu \frac{\partial}{\partial r} r \frac{\partial u}{\partial r}. \]  

(B.1)

In Equation B.1 \( G(t) \) denotes the unknown time-dependent pressure gradient which results from the sinusoidal displacement of fluid volume. The scalings

\[ t^* = \omega t; \quad r^* = \frac{r}{R}; \quad u^* = \frac{u}{\omega \Delta x}; \quad G^* = \frac{G(t) R^2}{\mu \omega \Delta x} \]

are chosen to render Equation B.1 dimensionless. The resulting dimensionless equation of momentum

\[ \alpha^2 \frac{\partial u^*}{\partial t^*} = G^*(t^*) + \frac{1}{r^* \frac{\partial}{\partial r^*} r^*} \frac{\partial u^*}{\partial r^*}. \]  

(B.2)
is subject to the boundary conditions

\[ u^*|_{r^*=1} = 0 \]  \hspace{1cm} \text{(B.3)}

and

\[ \frac{\partial u^*}{\partial r^*}|_{r^*=0} = 0. \]  \hspace{1cm} \text{(B.4)}

The velocity profile cannot be specified without an additional constraint. The extra condition is required because the pressure gradient \( G^*(t^*) \) is unknown; however, the amount of fluid being displaced with each stroke must be constant regardless of the shape of the velocity profile. The dimensionless expression for the conservation law is the integral condition

\[ 2 \int_0^1 u^* r^* dr^* = \sin t^*. \]  \hspace{1cm} \text{(B.5)}

Recognizing that the velocity field is generally not in-phase with the pressure gradient, Equation \[\text{B.2}\] is recast in terms of the complementary complex velocity field \( \hat{u} \):

\[ \alpha^2 \frac{\partial \hat{u}}{\partial t^*} = \hat{G}(t^*) + \frac{1}{r^* \partial_{r^*} r^*} \partial_{r^*} \hat{u} \]  \hspace{1cm} \text{(B.6)}

where \( u^* = \Im(\hat{u}) \) and \( G^* = \Im(\hat{G}) \). Using the definitions \( \hat{u} = e^{i t^*} f(r^*) \) and \( \hat{G} = \hat{\lambda} e^{i t^*} \), Equation \[\text{B.6}\] can be rewritten as

\[ \alpha^2 i f = \hat{\lambda} + \frac{1}{r^*} (r^* f')' , \]  \hspace{1cm} \text{(B.7)}

subject to the revised boundary conditions

\[ f'|_{r^*=0} = 0, \quad f|_{r^*=1} = 0, \quad \text{and} \quad 2 \int_0^1 f r^* dr^* = 1. \]  \hspace{1cm} \text{(B.8)}
The notation \((A)^{\prime}\) indicates differentiation of \(A\) with respect to \(r^*\).

### B.2 Solution of Equations B.7 and B.8

The ordinary differential equation in Equation B.7 is solved by finding a particular solution \(f_p\) and a solution to the homogenous problem \(f_h\). The particular solution is trivial: \(f_p = \hat{\lambda}i/\alpha^2\). The homogenous problem is written as

\[
\frac{1}{r^*} (r^* f_h')' - i\alpha^2 f_h = 0 . \tag{B.9}
\]

Equation B.9 is Bessel’s equation with order zero. It is solved by a Bessel function of the first kind of order zero

\[
f_h = c J_0 \left( \sqrt{-i\alpha r^*} \right) , \tag{B.10}
\]

where \(c\) is an unknown constant. The boundary condition \(f'|_{r^*=0} = 0\) is already satisfied by Equation B.10. The other boundary condition is transformed using the particular solution:

\[
f|_{r^*=1} = (f_p + f_h)|_{r^*=1} \therefore f_h|_{r^*=1} = -\frac{\hat{\lambda}i}{\alpha^2} . \tag{B.11}
\]

Upon applying the condition given in Equation B.11 to solve for \(c\), the final expression for \(f_h\) is

\[
f_h = -\frac{\hat{\lambda}i}{\alpha^2} \frac{J_0 \left( \sqrt{-i\alpha r^*} \right)}{J_0 \left( \sqrt{-i\alpha} \right)} , \tag{B.12}
\]

and recalling that \(f = f_p + f_h\),

\[
f = \frac{\hat{\lambda}i}{\alpha^2} \left( 1 - \frac{J_0 \left( \sqrt{-i\alpha r^*} \right)}{J_0 \left( \sqrt{-i\alpha} \right)} \right) . \tag{B.13}
\]
The value of $\hat{\lambda}$ is still unspecified. The integral condition must be used in conjunction with Equation B.13 to solve for $\hat{\lambda}$:

$$2 \int_0^1 f r^* dr^* = 1 \Rightarrow \frac{\lambda i}{\alpha^2} \left( 1 - \frac{1}{J_0(\sqrt{-i\alpha})} \int_0^1 J_0(\sqrt{-i\alpha}r^*) 2r^* dr^* \right) = 1,$$

which is integrated using the Bessel function identity

$$\int_0^1 J_0(\sqrt{-i\alpha}r^*) 2r^* dr^* = \frac{2}{\sqrt{-i\alpha}} J_1 \left( \sqrt{-i\alpha} \right).$$

(B.15)

From Equations B.14 and B.14, the value of $\hat{\lambda}$ is computed to be

$$\hat{\lambda} = \frac{\alpha^2}{i} \left[ 1 - \frac{2}{\sqrt{-i\alpha}} J_0 \left( \sqrt{-i\alpha} \right) \right]^{-1};$$

(B.16)

the final expression for $f (r^*)$ is

$$f (r^*) = \frac{1 - \frac{J_0(\sqrt{-i\alpha}r^*)}{J_0(\sqrt{-i\alpha})}}{1 - \frac{2}{\sqrt{-i\alpha}} \frac{J_1(\sqrt{-i\alpha})}{J_0(\sqrt{-i\alpha})}}.$$

(B.17)

Since $u^* = \Im [\hat{u}] = e^{ir^*} f (r^*)$, the dimensionless amplitude ratio $\Delta x / \Delta x_o$ (where $\Delta x_o$ is the amplitude of a parabolic steady flow) of the oscillation at any $r^*$ is simply

$$\Delta x^* = \left( f (r^*) \overline{f (r^*)} \right)^{1/2}.$$

(B.18)

The expression in Equation B.18 can be used to calculate $\Delta x^*$ for any value of $\alpha$. Amplitudes resulting from the calculation for $1 \leq \alpha \leq 100$ are shown in Figure B.1.
Figure B.1. Dimensionless amplitude of oscillatory flow in a tube for different values of $\alpha$. 
APPENDIX C

EXAMPLE DERIVATION OF A MOBILITY MODEL FROM A STEADY FLOW THEORY

In this appendix, a mobility model for an oscillatory tube flow will be derived from an inertial migration study performed by Schonberg and Hinch [117]. The system used in Schonberg and Hinch was a solid particle in a channel having the following characteristic dimensions: width \( l' \), particle center to plane distance \( d' \), and radius ratio \( \alpha^* = a/l' \). They considered a Poiseuille flow with the form

\[
 u = U_m \left( \alpha^* \gamma^* \frac{\dot{z}}{a} - 4 \alpha^* \frac{\dot{z}^2}{a} \right) \tag{C.1}
\]

where \( U_m \) is the centerline velocity, \( \gamma^* = \dot{\gamma} l'/U_m \), and \( z \) is the coordinate in the lateral direction. The particle and channel Reynolds numbers are defined as:

\[
 R_p = \frac{U_m a^2}{\nu l'} \quad \text{and} \quad R_c = \frac{U_m l'}{\nu}.
\]

The particle Reynolds number \( R_{ep} \) used in chapter 5 is four times \( R_p \).

The dimensional migration velocity was calculated as

\[
 W_p^* = U_m \alpha^* R_p F \left( \frac{d'}{l'}, R_c \right) \tag{C.2}
\]

where the function \( F \) can be obtained from Figure 2 on page 522 [117]. If Stokes'
law is assumed to be valid,

\[ F_L = 6\pi \mu a W_p^* = 6\pi \mu a U_m \alpha^* R_p F \left( \frac{d'}{\nu}, R_c \right), \quad (C.3) \]

and Equation C.3 can be set equal to the buoyant force when the particle is at equilibrium to yield

\[ 6\pi \mu a U_m \alpha^* R_p F \left( \frac{d'}{\nu}, R_c \right) = \frac{4}{3} \pi a^3 \Delta \rho g. \quad (C.4) \]

Rearranging Equation C.4 results in the expression

\[ \frac{R_p^2}{2\Delta \rho g a} F \left( \frac{d'}{\nu}, R_c \right) = 1, \quad (C.5) \]

which can be recast as

\[ \frac{1}{16} \frac{Re_p^2}{Re_s} F \left( \frac{d'}{\nu}, R_c \right) - 1 = 0, \quad (C.6) \]

in terms of the variables of chapter 5. Note the similarity of Equation C.6 to the form given in Equation 5.14 with \( c_s = 1/16 \).

The particle mobility when a psuedo steady state approximation is valid (low Womersley number) will be the velocity of the fluid streamline at the particle’s equilibrium position. For a channel, this is

\[ \frac{U_p}{U_o} = 6 \frac{d'}{\nu} \left( 1 - \frac{d'}{\nu} \right), \quad (C.7) \]

where \( U_p \) is the velocity of the particle. The calculation of Schonberg and Hinch
for $R_c < 15$ can be fit quite well using a parabola with constant coefficients:

$$F \left( \frac{d'}{l'} \right) = p_1 + p_2 \frac{d'}{l'} + p_3 \left( \frac{d'}{l'} \right)^2; \quad (C.8)$$

this expression assumes (as Schonberg and Hinch discovered) that below $R_c \sim 15$, $F$ is only a function of position. The coefficients were found to be $p_1 = 1.5058$, $p_2 = -12.133$, and $p_3 = 20.93$. The maximum value of $F$ determines the minimum $Re_p^2/Re_s$ for which the model will be valid. In this case, $(Re_p^2/Re_s)_{\text{min}} = 16/p_1 \sim 10$.

The equilibrium lateral position will be the root of Equation [C.8] which is near the channel wall. Using the quadratic formula,

$$\left( \frac{d'}{l'} \right)_{eq} = \frac{-p_2 - \sqrt{p_2^2 - 4p_3 \left( p_1 - 16 \frac{Re_p^2}{Re_s} \right)}}{2p_3}, \quad (C.9)$$

where the negative root was chosen to obtain the near wall root. As $Re_p^2/Re_s \to \infty$, Equation [C.9] reduces to

$$\left( \frac{d'}{l'} \right)_{\infty} = \frac{-p_2 - \sqrt{p_2^2 - 4p_3 p_1}}{2p_3} = 0.180, \quad (C.10)$$

which is the asymptotic equilibrium position for a neutrally buoyant particle. It results in a mobility (via Equation [C.7]) of 0.886. Clearly, this is less than what is expected for a tube flow. However, $d'/l' \neq r/R$. Instead,

$$\frac{d'}{l'} = \frac{1}{2} \left( 1 - \frac{r}{R} \right), \quad (C.11)$$

so $r^* = 1 - 2d'/l'$. Thus the value of $(r^*)_{\infty}$ for the tube is 0.64, giving an equivalent
mobility of 1.181. This mobility is in agreement with the observations of Segré
and Silberberg [123, 124].

Equation C.9 was employed in one of two ways. It can be used to roughly
estimate the mobility by assuming the flow behaves like a steady flow of average
velocity $U_o$. In that case, Equation 5.15 can be used to estimate the particle
mobility:

$$\frac{\Delta x_p}{\Delta x} = 2 \left( 1 - \left[ 1 - 2 \left( \frac{-p_2 - \sqrt{p_2^2 - 4p_3 \left( p_1 - 16 \frac{Re_p^2}{Re_s} \right)}}{2p_3} \right) \right]^2 \right). \quad (C.12)$$

For a more precise calculation, the mobility can be integrated over a half-period
$\pi/\omega$ to consider the full sine wave. To simplify the presentation, Equations C.9
and C.11 will be combined into the function $P^\dagger$ which determines the particle’s
equilibrium position:

$$(r^*)_{eq} = 1 - 2 \left( \frac{d'}{b'} \right)_{eq} = P^\dagger \left( \frac{Re_p^2}{Re_s} \sin^2 (\omega t) \right).$$

Then we have the time-averaged particle displacement

$$\Delta x_p = \int_0^{\pi/\omega} U_o \left( 1 - \left[ P^\dagger \left( \frac{Re_p^2}{Re_s} \sin^2 (\omega t) \right) \right]^2 \right) \sin (\omega t) dt, \quad (C.13)$$

and the time-averaged fluid displacement

$$\Delta x = \int_0^{\pi/\omega} U_o \sin (\omega t); \quad (C.14)$$
TABLE C.1
FITTING PARAMETERS FOR STEADY FLOW MODELS

<table>
<thead>
<tr>
<th>Model</th>
<th>Source</th>
<th>$c_s$</th>
<th>$p_1$</th>
<th>$p_2$</th>
<th>$p_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Schonberg &amp; Hinch [117]</td>
<td>$\frac{1}{16}$</td>
<td>1.506</td>
<td>-12.133</td>
<td>20.93</td>
</tr>
<tr>
<td>C</td>
<td>Williams et al. [148]</td>
<td>0.065</td>
<td>1.454</td>
<td>-10.408</td>
<td>15.45</td>
</tr>
<tr>
<td>D</td>
<td>Segré &amp; Silberberg [124]</td>
<td>1</td>
<td>15.37</td>
<td>-0.63</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>Yang et al. [158]</td>
<td>1</td>
<td>0.120</td>
<td>-0.526</td>
<td>0.552</td>
</tr>
</tbody>
</table>

therefore, in terms of dimensionless quantities:

$$\frac{\Delta x_p}{\Delta x} = \frac{1}{2} \int_0^\pi \left( 1 - \left[ P^f \left( \frac{Re_p}{Re_s} \sin^2(t^*) \right) \right]^2 \right) \sin(t^*) \, dt^*. \quad (C.15)$$

This methodology was repeated, with minor variations, for several other theoretical works (see Table C.1 for the values of the various fitting parameters). A parabolic function was fit to given migration velocity or lift force data, provided it was a faithful representation of the data. In particular, the fit needed to be a good approximation of the data near the tube wall. The lift or migration velocity data from each source is provided in the figures following the table.

What follows is a presentation of the data from each model of Table C.1 versus fitting curves which approximate the lift force for a neutrally buoyant sphere. A short explanation of any variations to the methodology which was detailed above for the work of Schonberg and Hinch is also included below.

A. The development of the model adapted from Schonberg and Hinch was al-
ready described. In Figure C.1, a plot of the dimensionless migration velocity $W_p^*$ versus the dimensionless position $d/l$ is given. The parabolic approximation (solid line) is quite good.

B. Adaptation of the model of Asmolov was similar to the procedure for Schonberg and Hinch, except the data was given as a lift force. In Figure C.2, a plot of the dimensionless lift force $F_z^*$ versus dimensionless position $d'/l'$ is presented for $R_c = 15$. Again, the parabolic approximation (solid line) is good, especially near the wall (i.e. as $d/l \to 0$).

C. Adaptation of the lift force given by Williams et al for $R_c \ll 1$. The dimensionless function was given as a fifth order polynomial which was used by Williams et al. to approximate the calculations of Cox and Brenner [24]. In Figure C.3, the dimensionless function $g(x/w)$, where $x/w = d'/l'$ is plotted against the dimensionless position. The parabolic approximation (solid line) estimates the function well.

D. The model of Segré and Silberberg is the exception of the procedure which was used here. The empirical model for the migration velocity, given in Equation 5.1 can be solved directly without a parabolic approximation because it is already a quadratic equation. Upon setting the lift force equal to the buoyant force, the following expression is obtained:

$$0.0256 \frac{Re_p}{Re_s} \left( \frac{R}{a} \right)^{0.17} r^* \left( 1 - \frac{r^*}{r} \right) = 1,$$

(C.16)

and taking an average value of $a/R$ from Segré and Silberberg’s experiments gives $(R/a)^{0.17} = 1.603$. Rearranging Equation C.16 into a quadratic equa-
tion for \( r^* \) yields

\[
r^{*2} - r^\dagger r^* + 24.39r^\dagger \frac{Re_s}{Re_p^2} = 0,
\]

from which the equilibrium \( r^* \) can be solved directly given \( r^\dagger = 0.63 \).

E. The model of Yang et al. was the only theoretical calculation which was developed for a tube geometry. Despite this, the model was based on specific ratios of \( a/R \) and the lift force was calculated at finite \( Re \), so assuming that both \( a/R \to 0 \) and \( Re \to 0 \) is not strictly correct. In Figure C.4 the dimensionless lift force \( L \) (scaled so calculations at different \( Re \) are consistent) is plotted versus dimensionless radial position \( r^* \). Provided the parabolic approximation is restricted to the near wall region, the fit is very good.
Figure C.1. Migration velocity data (solid circles) of Schonberg and Hinch versus dimensionless position. The parabolic approximation (solid line) is of the form given in Equation \[C.8\] with the coefficients presented in Table \[C.1\].
Figure C.2. Dimensionless lift force data (solid circles) of Asmolov versus dimensionless position. The parabolic approximation (solid line) is of the form given in Equation C.8 with the coefficients presented in Table C.1.
Figure C.3. Dimensionless lift force position function (solid circles) of Williams et al. versus dimensionless position. The parabolic approximation (solid line) is of the form given in Equation C.8 with the coefficients presented in Table C.1.
Figure C.4. Dimensionless lift force (circles) of Yang et al. versus dimensionless radial position. The parabolic approximation (solid line) is of the form given in Equation C.8 (substituting $r^*$ for $d'/l'$) with the coefficients presented in Table C.1.
APPENDIX D

ANALYSIS OF THE PRESENCE OF BUBBLES OR CAVITATION IN HORIZONTAL TUBE EXPERIMENTS

In some experiments, a rapid fall-off of the mobility from the large $Re_p^2/Re_s$ asymptote was observed in more viscous fluids (see Figure D.1). The fall-off was a artifact of the experimental methodology. The oscillatory flow was generated by volume displacement using a syringe, but the pressure gradient which results from the volume displacement can be "absorbed" by other elements in the system. Care was taken to minimize the number of flexible parts; the tube and pump apparatus were quite rigid. However, especially at higher frequencies where the fall-off occurred, cavitation can occur. If cavitation does occur, the loss in fluid displacement due to the presence of air bubbles can be estimated using a scaling argument. The fluid displacement can also be reduced if bubbles are present somewhere in the system.

Consider a bubble of volume $V_b$ which is somewhere between the syringe (the pressure source) and the particle that is being studied. The change in volume of the fluid when the bubble is not present is simply $\Delta V = \pi R^2 \Delta x$. The bubble will soak up a portion of the available driving force because it is compressible. For small changes in bubble volume, the difference in volume of the bubble will be

$$\Delta V_b \sim \frac{\Delta P_a}{P_{atm}} V_b ,$$  \hspace{1cm} (D.1)
Figure D.1. Particle mobility as a function of the parameter $Re_p^2/Re_s$. The legend indicates the experimental conditions in the following order: particle/tube/fluid. The solid line is the Segré-Silberberg mobility for a neutrally buoyant particle, $\Delta x_p/\Delta x = 1.2062$. 
where $P_{atm}$ is the atmospheric pressure and $\Delta P_a$ is given by

$$\Delta P_a \sim \frac{2\mu \omega \Delta x_a L_t}{R^2}, \quad (D.2)$$

where $L_t$ is the length of the tube. The quantity $\Delta x_a$ is the true stroke volume modified by the presence of the bubble (or bubbles). It can be written as

$$\Delta x_a = \Delta x \left( \frac{\Delta V - \Delta V_b}{\Delta V} \right), \quad (D.3)$$

and substituting Equations D.1 and D.2 into Equation D.3

$$\Delta x_a = \Delta x \left( 1 - \frac{4\pi \mu \omega L_t}{P_{atm} R \Delta x} \Delta x_a V_b^* \right); \quad (D.4)$$

where the dimensionless bubble volume $V_b^* = V_b / 2\pi R^3$. After some additional manipulation of Equation D.4 the expression becomes

$$\frac{\Delta x_a}{\Delta x} = \frac{1}{1 + 4\pi \frac{\mu \omega L_t}{R P_{atm}} V_b^*}. \quad (D.5)$$

Equation D.5 indicates that if a bubble of volume $V_b^*$ is present in the system, the ratio of the actual displacement to the assumed displacement will decrease as $4\pi (\mu \omega L_t) / (R P_{atm})$ increases.

If the experimental mobilities which fell off at large $Re_p^2/Re_s$ are plotted against $4\pi (\mu \omega L_t) / (R P_{atm})$, as they are in Figure D.2, the rapid decrease of $\Delta x_p/\Delta x$ when $4\pi (\mu \omega L_t) / (R P_{atm})$ becomes sufficiently large ($> 10^{-2}$) is apparent. This was an effect that occurred in viscous fluids because of the dependence on viscosity. The data in Figure D.2 suggests that in some experiments, $V_b^*$ was not small. The expected effect of cavitation or bubbles was proposed a priori;
therefore, the agreement of the observations with the model of Equation \[D.5\] was taken to be evidence that cavitation was occurring. Additional indirect evidence of the effect was also observed in the particle trajectories, which became asymmetric when cavitation was present.

A selection criterion was chosen for the experiments where cavitation was affecting the measurement of a “true” mobility. Experimental conditions where the criterion \(4\pi (\mu \omega L_t) / (RP_{atm}) \geq 10^{-2}\) was satisfied were discarded from consideration.
REFERENCES


