DECLARATIVE MODELING
OF PROTON EXCHANGE MEMBRANE FUEL CELLS
FOR SYSTEM DESIGN

A Dissertation
Presented to
The Academic Faculty

by

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LISTS OF ABBREVIATIONS

Acronyms

CFD	Computational fluid dynamics
EOS	Equation of state
GDL	Gas diffusion layer
ISO	International Standards Organization
MEA	Membrane electrode assembly
PEM	Proton exchange (or polymer electrolyte) membrane
PEMFC	Proton exchange (or polymer electrolyte) membrane fuel cell
SSSF	Steady state, steady flow (noun or adjective)

Electrochemical Components

e^-	Electrons
H^+	Protons
H_2	Diatomic hydrogen
H_2O	Water
N_2	Diatomic nitrogen
O_2	Diatomic oxygen
Pt^+	Platinum ions (charge number $+1$)
SO_3^-	Sulfonic acid

Symbols

A Area $[L^2]$

a Thermodynamic activity $[1]$ or gravitational acceleration $[LT^{-2}]$

b Correlation coefficient $[\text{misc.}]$

C Heat capacity $[N]$

c Specific heat capacity $[1]$

D Hydraulic diameter $[L]$ or self diffusivity $[L^2 T^{-1}]$

d Specific particle diameter $[LN^{-1}]$

E Electric field $[LMN^{-1} T^{-2}]$

f Force $[LMT^{-2}]$

g Specific Gibbs energy $[L^2 MN^{-1} T^{-2}]$

H Enthalpy $[L^2 MT^{-2}]$

h Specific enthalpy $[L^2 MN^{-1} T^{-2}]$ or heat transfer coefficient $[NL^{-2} T^{-1}]$

I Material current $[NT^{-1}]$

i Integer index $[–]$

J Generic flux $[\text{misc.} \times L^{-2}]$

j Integer index $[–]$

k General constant or correlation coefficient $[\text{misc.}]$

Kn Knudsen number $[1]$

L Length $[L]$

M Mass $[M]$

m Specific mass $[MN^{-1}]$ or cardinality $[–]$

$m\Phi$ Linear momentum $[LMT^{-1}]$

N Particle number $[N]$

n Integer number (e.g., stoichiometric coefficient) $[–]$

Nu Nusselt number $[1]$

P Perimeter $[L]$

p Pressure $[ML^{-1} T^{-2}]$

Pe Péclet number $[1]$

Q Heat $[L^2 MT^{-2}]$

q Single particle $[N]$

R Generalized resistance $[\text{misc.}]$ or electrical resistance $[ML^2 T^{-3}]$

r Generalized resistivity $[\text{misc.}]$

Re Reynolds number $[1]$

S Entropy $[N]$

s Specific entropy $[1]$

T Temperature $[L^2 MN^{-1} T^{-2}]$

t Time $[T]$

U Internal energy $[L^2 MT^{-2}]$

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[i]The dimensions are noted in terms of angle (A), length (L), mass (M), particle number (N), and time (T). See Section **??** for details.

[ii]Although not shown here, boldface is used to denote vector quantities and operations.

V Volume $[\mathrm{L}^3]$

v Specific volume $[\mathrm{L}^3\,\mathrm{N}^{-1}]$ or electrical potential $[\mathrm{L}^2\,\mathrm{M}\,\mathrm{N}^{-1}\,\mathrm{T}^{-2}]$

X Generic conserved quantity [misc.]

x Position along the x axis or generic axis of transport $[\mathrm{L}]$

z Position along the z axis $[\mathrm{L}]$ or charge number $[1]$

α Adjusted collision interval $[\mathrm{T}]$ or charge transfer coefficient $[1]$

β Dynamic compressibility $[\mathrm{N}\,\mathrm{T}\,\mathrm{L}^{-2}\,\mathrm{M}^{-1}]$

γ Generic driving property for exchange or transport [misc.]

ε Porosity $[1]$ or permittivity $[\mathrm{N}^2\,\mathrm{T}^2\,\mathrm{L}^{-3}\,\mathrm{M}^{-1}]$

ϵ Areic electrical capacitance $[\mathrm{N}^2\,\mathrm{T}^2\,\mathrm{L}^{-4}\,\mathrm{M}^{-1}]$

ζ Fluidity $[\mathrm{L}\,\mathrm{T}\,\mathrm{M}^{-1}]$

η Self resistivity $[\mathrm{T}\,\mathrm{L}^{-2}]$

θ Thermal resistivity $[\mathrm{L}\,\mathrm{T}\,\mathrm{N}^{-1}]$

λ Mean free path $[\mathrm{L}]$

μ Mobility $[\mathrm{N}\,\mathrm{T}\,\mathrm{M}^{-1}]$ or dynamic viscosity $[\mathrm{M}\,\mathrm{L}^{-1}\,\mathrm{T}^{-1}]$

ν Thermal independity $[1]$

ρ Volumic particle number (i.e., density) $[\mathrm{N}\,\mathrm{L}^{-3}]$

τ Time constant $[\mathrm{T}]$ or mean collision interval $[\mathrm{T}]$

Φ Product of particle number and velocity $[\mathrm{L}\,\mathrm{N}\,\mathrm{T}^{-1}]$

ϕ Linear velocity $[\mathrm{L}\,\mathrm{T}^{-1}]$

ω Flow diversion angle $[\mathrm{A}]$

Accents

$\cdot$ Flow rate of _ $[\times\mathrm{T}^{-1}]$

Superscripts

^{o} _ at reference state

$'$ Modified, effective, or characteristic _

* Dimensionless _ $[\times\text{misc.}]$

Subscripts

$1, 2, 3\text{ or }\ldots$ First, second, third or ... _

A _ of advection or advective

$a, b, c\text{ or }\ldots$ First, second, third or ... _

c _ as, of, or in the condensed phase

D _ of diffusion or diffusive

DOF _ of degrees of freedom

E _ of exchange

g _ as, of, or in gas

gen _ of generation

i _ as, of, or in ionomer

i _ of index i

IG _ of ideal gas

j _ of index j

k _ of index k

l	_ as, of, or in liquid
M	_ in the majority region
m	_ in the minority region
N	Material _
n	_ at or into the negative boundary
p	Isobaric _
phases	_ of phases
p	_ at or into the positive boundary
Q	Thermal _
sat	_ at saturation
spec	Set or _ of species in the region or in the chemical reaction
T	Isothermal _
T	_ of transport
tot	Total _
v	Isochoric _
x	_ along the x axis (through the cell)
y	_ along the y axis (down the channel)
z	_ along the z axis (across the channel)
ζ	_ for fluidity
θ	_ for thermal resistivity
Φ	Translational _
$\perp$	_ perpendicular to the axis of transport
$\parallel$	_ parallel to the axis of transport

GLOSSARY

CHAPTER 1

INTRODUCTION

CHAPTER 2

BACKGROUND

CHAPTER 3

FUNDAMENTALS OF THE MODEL

> "A sound theoretical framework should not be seen as a time-consuming diversion, rather as the bedrock of fundamental innovation and optimization in fuel-cell materials and components."
>
> M. EIKERLING, A. KORNYSHEV, AND A. KULIKOVSKY [1]

This chapter describes the key physical relations and behavioral equations upon which the fuel cell model is based. The details are presented from a perspective that parallels the model's architecture, as is shown in Chapter 4. The thermodynamic properties and exchange, transport, and conservation equations are given in a general manner that is equally applicable to ideal gases, real gases, and condensed species. The motivating principle is that the assumptions and inaccuracies should be contained in adjustable parameters, and the number and complexity of the equations should scale appropriately and automatically.

The disadvantage is that some of the equations are non-traditional. To clarify how they correspond to existing theory, various traditional equations are derived from the model under the applicable conditions and necessary assumptions (see Section 3.11). An important point is that the equations are presented for a unit system where the gas and Faraday constants are normalized to one (see **??**). Also note that the *specific* adjective is used to indicate "per unit amount of material".[i] For example, specific mass is the mass per unit number of particles. It is used in preference to molar mass because the unit system is neutral to the unit used to represent the amount of material. A variable that represents the amount of material may be displayed in moles but the variable itself is not in moles (or any other unit of material).

The model is based on the following assumptions:

1. All of the boundaries are rectangular. This implies that the cross-sectional areas are uniform and the regions are rectilinear. For simplicity, many equations in this chapter are

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[i]In contrast, massic is defined by the International Standards Organization (ISO) to mean "per mass" [2].

expressed in spatial differences instead of partial derivatives.

2. The regions have fixed size.

Further assumptions are introduced throughout the chapter.

Figure 3.1 shows the control volume used in the model. All flows are positive inward. They are noted in the form of $\dot{X}$ with a subscript from the figure. The subscript xn indicates the negative boundary along the x axis, and similar subscripts are used for the other boundaries. This control volume is the lowest level of spatial resolution, but it may contain multiple species in multiple phases. Each of these *configurations*, or species in certain phases, are treated as distinct but interacting entities.
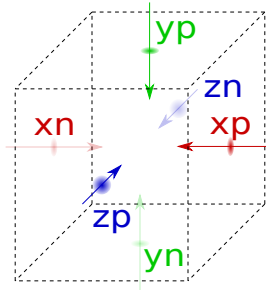
Figure 3.1: Control volume used in the model.

Figure 3.2 shows the high-level aspects that must be considered in the fuel cell model. These will each be discussed in the following sections, with the exception of geometry (see above). Many of the sections begin with a list of key features of the model that are either unusual or are new contributions. The boxed equations are the ones that are actually implemented in the model (see the next chapter for details). Other equations are presented to provide insight into the implemented equations and relate the model to established theories.

3.1 Correlated Thermodynamic Properties

Highlights:

- The correlations are necessary and sufficient to calculate basic thermodynamic properties (specific entropy, enthalpy, Gibbs energy, etc.) given temperature and pressure or specific volume.

- The correlations are polynomial and can be expanded as needed for accuracy.
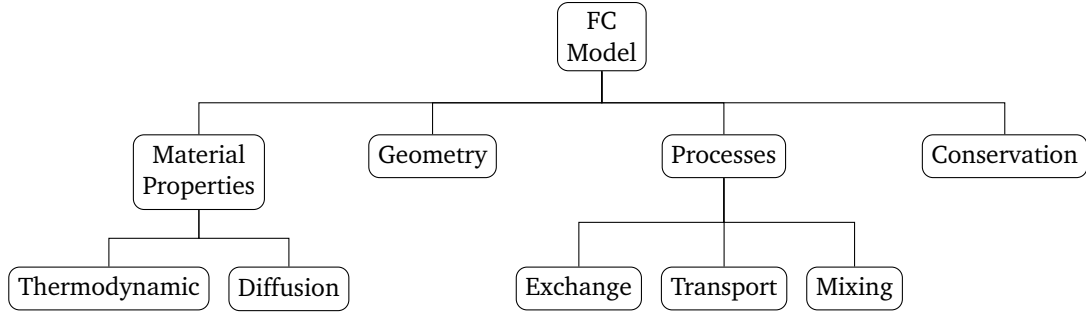
Figure 3.2: Considerations for the fuel cell model.

- The pressure-volume-temperature correlation is general enough to describe ideal gases, real gases, and incompressible species with or without thermal expansion. It is suitable to explore the effects of non-idealistic media and higher-than-ambient operating pressures. Many fuel cell models are explicitly based on ideal gases under incompressible flow [3–19].

- The specific heat capacity-temperature correlation is general enough to model media with constant specific heat or provide accurate information on the temperature dependence. This makes it possible to simplify the descriptions of inert gases (e.g., nitrogen (N_2)) and more accurately describe reacting gases (hydrogen (H_2), water (H_2O), and oxygen (O_2)) to model the temperature dependence of the cell potential.

3.1.1 Isobaric Specific Heat Capacity-Temperature Relation

Isobaric specific heat capacity is defined by

$$c_p \equiv T \left(\frac{\partial s}{\partial T} \right)_p \tag{3.1}$$

where s is specific entropy, T is temperature, and p is pressure. McBride et al. provide the isobaric specific heat capacity of many species as a correlated polynomial of temperature [20]; however, c_p is in general a function of both temperature and pressure. For condensed species, they specify the thermodynamic state by the actual temperature and a reference pressure (1 atm). The state of gases is chosen to be the ideal gas at the given temperature, since the specific heat capacity of an ideal gas is independent of pressure. The correlation for this adjusted isobaric specific heat capacity is

$$c_p^o = b_1 T^{-2} + b_2 T^{-1} + b_3 + b_4 T + b_5 T^2 + b_6 T^3 + b_7 T^4 \tag{3.2}$$

The coefficients $(b_1, b_2, \ldots)$ must be chosen for the proper temperature range but are otherwise constant. The model uses a generalized form:

$$c_p^o = \sum_{i=1}^{m} b_i T^{i+n-1}$$

(3.3)

where n is the power of the first term and the polynomial has an arbitrary number of terms (m). The order of the polynomial is $m + n - 1$. Multiple sets of coefficients may be specified; they are selected depending on the temperature range (as per McBride et al.).

3.1.2 Pressure-Volume-Temperature Relation

The model uses the virial equation of state (EOS), which was proposed by Thiesen in 1885 and validated against many gases by Kammerling-Onnes in 1901 [21, 22]. It is convenient for use with differential equations and can be expanded as needed for accuracy. The virial EOS is expressed as [23]:

$$v = b_1 \left(\frac{p}{T} \right)^{-1} + b_2 + b_3 \left(\frac{p}{T} \right)^{1} + b_4 \left(\frac{p}{T} \right)^{2} + \ldots$$

(3.4)

where the coefficients are functions of temperature only. The model uses the following generalized form:

$$v = \sum_{i=1}^{m_1} \sum_{j=1}^{m_2} b_{ij} \left(\frac{p}{T} \right)^{i+n_1-1} T^{j+n_2-1}$$

(3.5)

where n_1 and n_2 are the powers of the first term and the polynomial has an arbitrary numbers of terms in both dimensions (m_1, m_2). The p/T group is used instead of p so that (i) the matrix of coefficients (b_{ij}) is more compact for typical correlations (e.g., [23]) and (ii) the virial inverse matrix $(b'_{ij}$ below) has the same size.

The virial coefficients may be derived from the statistical mechanics of intermolecular forces [24]. For gases, the first virial coefficient (b_1) is generally the gas constant or 1. The second virial coefficient characterizes binary interactions between molecules—specifically the pair energy potential function [23]. The third coefficient is for ternary interactions, the fourth is for quaternary, and so on [25]. These effects diminish rapidly with the order of the interaction [26]. If $b_1 = 1$ and the other terms are neglected, then the virial EOS reduces to the ideal gas EOS. For gases at low pressures, only the first and possibly second virial coefficients are

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necessary. Dymond et al. correlate the second virial coefficients of many gases to polynomials in temperature [23].

Equation 3.4 is suitable for incompressible or even constant-volume species, where only the second virial coefficient (b_2) is nonzero. If the species is compressible, then the volume-explicit (or Leiden [25]) form in Equation 3.4 has an equivalent pressure-explicit (or Berlin [25]) form [23, 25]:

$$\frac{p}{T} = b'_1 v^{-1} + b'_2 v^{-2} + b'_3 v^{-3} + b'_4 v^{-4} + \dots \tag{3.6}$$

Otherwise, pressure cannot be determined from temperature and specific volume. The model uses the following generalized form:

$$v = \sum_{i=1-m_1}^{0} \sum_{j=1}^{m_2} b'_{ij} p^{i+n_1} T^{j+n_2} \tag{3.7}$$

The modified coefficients of Equation 3.6 are directly related to those of Equation 3.4 [23, 25]:

$$b'_1 = b_1 \tag{3.8a}$$

$$b'_2 = b_2 \tag{3.8b}$$

$$b'_3 = b_2^2 + b_3 \tag{3.8c}$$

$$b'_4 = b_2^3 + 3b_2 b_3 + b_4 \tag{3.8d}$$

We can determine the relations for even higher-order coefficients by setting Equations 3.4 and 3.6 equal (in terms of pv/T) and successively eliminating terms [24].

3.2 Derived Thermodynamic Properties

Highlights:

- The derivations are exact and do not involve additional assumptions besides those inherent in the correlated properties of Section 3.1.

- The properties are general and complete enough that the model does not require specialized thermodynamic correlations like the saturation pressure-temperature curve of H_2O.

3.2.1 Specific Entropy

We can write specific entropy as

$$s = \int_0^T \frac{c_p^o}{T} \, dT + \int_{p^o}^p \left(\frac{\partial s}{\partial p} \right)_T \, dp \tag{3.9}$$

where c_p^o is evaluated at reference pressure p^o. Applying the appropriate Maxwell relation, $(\partial s / \partial p)_T = -(\partial v / \partial T)_p$, this is

$$s = \int_0^T \frac{c_p^o}{T} \, dT - \int_{p^o}^p \left(\frac{\partial v}{\partial T} \right)_p \, dp \tag{3.10}$$

which can be evaluated using Equations 3.2 and 3.4. McBride et al. [20] give the integration constant of the first term for each species so that the isobaric specific heat correlation needs not be evaluated at (or even valid at) absolute zero temperature. The second integral is $\ln(p/p^o)$ for an ideal gas and typically small for condensed species. Again, the second- and higher-order virial coefficients (b_2, b_3, ...) are functions of temperature but not pressure. The coefficients of isobaric specific heat capacity (b_1, b_2, ...) may be treated as constant but must be chosen based on the temperature range.

For gases, the lower limit of the second integral of Equation 3.10 is evaluated only for the first virial coefficient. This adjustment is necessary because the reference for the c_p-T correlation is the ideal gas instead of the real gas. Formally, the modified form of Equation 3.10 for gases is

$$s = \int_0^T \frac{c_p^o}{T} \, dT - \left[\int_{p^o}^0 \left(\frac{\partial v_{\text{IG}}}{\partial T} \right)_p \, dp + \int_0^p \left(\frac{\partial v}{\partial T} \right)_p \, dp \right] \tag{3.11}$$

where the first integral in square brackets involves the specific volume of the ideal gas and the second involves the real gas. Following the approach by Rao [27, p. 271], the ideal gas contribution is integrated from the reference pressure to zero pressure and the real gas contribution is integrated from zero pressure to the actual pressure. At zero pressure, binary and higher-order molecular interactions are eliminated and a real gas behaves as an ideal gas.

Figure 3.3 depicts the integration path of the pressure terms. Assuming that the first virial coefficient (b_1) is the same for the ideal gas and the real gas (since for gases $b_1 = 1$), the contribution of the first-order virial term may be integrated directly from p^o to p. In effect,

this combines $\ln(0/p^o) + \ln(p/0)$ to give $\ln(p/p^o)$. Since the contributions of the second- and higher-order virial coefficients are zero at zero pressure, we can eliminate those integral evaluations. The net result is that the lower limit of the second integral in Equation 3.10 is evaluated for the ideal gas and the upper limit is evaluated for the real gas.
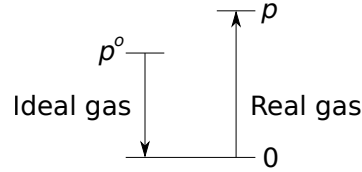
Figure 3.3: Integration path for the specific entropy of gases.

3.2.2 Specific Enthalpy

We can define specific enthalpy by the differential equation

$$dh = T ds + v dp \tag{3.12}$$

After substituting Equation 3.10 and integrating with an adjustable temperature reference, this is

$$h = \int_{T^o}^{T} c_p^o \, dT + \int_{p^o}^{p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \tag{3.13}$$

which can be evaluated using Equations 3.2 and 3.4. As for specific entropy, if the species is a gas the lower limit of the second integral is of the ideal gas and the upper limit is of the real gas. The second integral is zero for an ideal gas and typically small for condensed species. McBride et al. [20] give the sufficient integration constants and offsets to specify the enthalpy reference such that (i) the enthalpy at $0\,$K and p^o is zero, (ii) the enthalpy at $25\,°$C and p^o is zero, or (iii) the enthalpy at $25\,°$C and p^o is the enthalpy of formation at that temperature and pressure.

3.2.3 Specific Gibbs Energy

We can define Specific Gibbs energy by the following differential equation:

$$dg = v dp - s dT \tag{3.14}$$

In conjunction with Equation 3.12, this implies that

$$g = h - Ts \tag{3.15}$$

Substituting Equations 3.10 and 3.13,

$$g = \int_{p^o}^{p} v \, dp + T \int_{p^o}^{p} \left(\frac{\partial v}{\partial T} \right)_p dp - \int_{p^o}^{p} T \left(\frac{\partial v}{\partial T} \right)_p dp + \int_{T^o}^{T} c_p^o \, dT - T \int_{0}^{T} \frac{c_p^o}{T} dT \tag{3.16}$$

which can be evaluated using Equations 3.2, 3.4, and 3.6. If the species is a gas, then the lower limits of the pressure integrals are of the ideal gas and the upper limits are of the real gas (see Section 3.2.1).

3.2.4 Isobaric Specific Heat Capacity

We can express the isobaric specific heat capacity by substituting Equation 3.10 into Equation 3.1:

$$c_p = c_p^o - T \left(\frac{\partial \left[\int_{p^o}^{p} \left(\frac{\partial v}{\partial T} \right)_p dp \right]}{\partial T} \right)_p \tag{3.17}$$

which also can be evaluated using Equations 3.2 and 3.4. The second term is zero for an ideal gas and usually small for condensed species. If the species is a gas, then the lower limit of the integral is of the ideal gas and the upper limit is of the real gas (see Section 3.2.1).

3.2.5 Isochoric Specific Heat Capacity

Isochoric specific heat capacity is defined by

$$c_v \equiv T \left(\frac{\partial s}{\partial T} \right)_v \tag{3.18}$$

The isochoric and isobaric specific heat capacities are related by the following equation [28, p. 546]:

$$c_v = c_p - T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \tag{3.19}$$

Applying Equation 3.17, this is

$$c_v = c_p^o - T \left[\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial \left[\int_{p^o}^{p} \left(\frac{\partial v}{\partial T} \right)_p dp \right]}{\partial T} \right)_p \right] \tag{3.20}$$

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which can be evaluated using Equations 3.2, 3.4, and 3.6. It reduces to $c_v = c_p - 1$ for an ideal gas. If the species is a gas, then the lower limit of the integral is of the ideal gas and the upper limit is of the real gas (see Section 3.2.1).

3.3 Mixtures

Highlights:

- Dalton's and Amagat's laws are traditionally used with the ideal gas assumption, but the model does not impose that requirement.[ii]

- The volumes and pressures of mixtures can change dynamically, but the model imposes Dalton's and Amagat's laws exactly and instantaneously. There are no additional states.

3.3.1 Species within a Phase

The model combines species within a phase using Dalton's law of partial pressures, which states that the partial pressures of the components of a mixture add to the total pressure of the mixture [29]:

$$p = \sum p_i \tag{3.21}$$

Dalton's law also states that each species i exists at the total volume of the phase:

$$V_i = V \tag{3.22}$$

For example, according to this concept the atmospheric gases of N_2, O_2, etc. each occupy the total volume of the air but only contribute partially to the pressure of the air.

3.3.2 Phases within a Region

The model combines phases within a region using Amagat's law of partial volumes, which states that the partial extensive volumes of the components of a mixture sum to the total extensive volume of the mixture [29]:

$$V = \sum V_i \tag{3.23}$$

In the model, V_i is the volume of a phase and V is the volume of the region, which is fixed. Amagat's law also states that each species i exists at the total pressure of the phase:

$$\boxed{p_i = p} \tag{3.24}$$

The model only uses Amagat's law for distinct phases within a region—not for species within a phase. Amagat's law loses its physical meaning as species are mixed [30]. If species are fully mixed, then it is impossible to distinguish the particles and thus determine the partial volumes.

For example, if a system contains a solid phase and air, then the model states that the solid and the air experience the same pressure and occupy only part of the total volume (Amagat's law). Within the air, the gases mix according to Dalton's law (Section 3.3.1). The model applies Dalton's law and Amagat's law dynamically, which makes it possible to describe the formation of liquid water in the cell [31–33].

The model is classified as a Euler-Euler approach rather than a Euler-Lagrange approach [34], since all phases are tracked from a Eulerian perspective. The volume fractions are continuous functions of time and must sum to one. The Euler-Lagrange approach is limited to problems where the solid phase has a small volume in comparison to the fluid phase—10-12 % [34]. This is not appropriate for the layers of a fuel cell.

3.4 Basic Conservation Equations

Highlights:

- The model is dynamic. It includes material, momentum, and energy storage.

- Each species has its own conservation equations for material, translational momentum, and energy. However, the model's parameters can be set so that the translation tool combines certain conservation equations through index reduction. The concept of separate momentum balances for each species is unusual but not unprecedented in the literature [35–37]. Separate energy balances are used rarely (if at all).

Material, momentum, and energy are conserved throughout the model at interfaces and within regions. Each phase of each species (i.e., configuration) has individual conservation equations in every region. The conserved quantities may be stored in configurations but not at interfaces between configurations.

Below the conservation equations are introduced with minimal detail to explain the exchange and transport equations (Sections 3.5 and 3.7). The interfaces are generalized here, but they may be of two types: regional boundaries and intra-regional transitions among configurations. In general, the flow through each interface may have advective and diffusive components. In Section 3.10, detailed conservation equations will be presented.

3.4.1 Material

Material is conserved in each configuration according to

$$\underbrace{\frac{\partial N}{\partial t}}_{\text{transient}} = \underbrace{\sum \dot{N}_i}_{\text{intake}} \tag{3.25}$$

where N is the particle number or amount of material and $\dot{N}_i$ is the material current into a generalized interface. The use of a partial derivative ($\frac{\partial N}{\partial t}$) rather than a total derivative ($\frac{dN}{dt}$) serves as a reminder that the model is Eulerian. For boundaries and transitions, there is no storage and the conservation of material reduces to

$$0 = \sum \dot{N}_i \tag{3.26}$$

where the summation is now across all interacting configurations. Mass is conserved as well since the specific mass of each configuration is constant and the phase change and reaction processes are balanced in mass.

3.4.2 Rotational Momentum

The model is based on the assumption that rotational momentum is not stored. Rotational momentum is not exchanged or transported axially through regional boundaries, but it is conveyed through shear forces. It is assumed that the forces are point forces in the center of the boundaries and that the axes of rotation are centered in the region. Therefore,

$$0 = \left(\dot{m}\Phi_{\text{zny}} - \dot{m}\Phi_{\text{zpy}} \right) L_z - \left(\dot{m}\Phi_{\text{ynz}} - \dot{m}\Phi_{\text{ypz}} \right) L_y \tag{3.27a}$$

$$0 = \left(\dot{m}\Phi_{\text{xnz}} - \dot{m}\Phi_{\text{xpz}} \right) L_x - \left(\dot{m}\Phi_{\text{znx}} - \dot{m}\Phi_{\text{zpx}} \right) L_z \tag{3.27b}$$

$$0 = \left(\dot{m}\Phi_{\text{ynx}} - \dot{m}\Phi_{\text{ypx}} \right) L_y - \left(\dot{m}\Phi_{\text{xny}} - \dot{m}\Phi_{\text{xpy}} \right) L_x \tag{3.27c}$$

where $\dot{m\Phi}_{\text{zny}}$ is the force in the y-direction through the negative-z boundary, $\dot{m\Phi}_{\text{ypz}}$ is the force in the z-direction through the positive-y boundary, and so on. These equations are included in the diffusion equations for shear force around each axis (Section 3.7.2).

3.4.3 Translational Momentum

Each component of linear or translational momentum is conserved in each configuration according to

$$\underbrace{\frac{\partial (M\phi)}{\partial t}}_{\text{transient}} + \underbrace{Ma + NzE}_{\text{body}} + \underbrace{A\Delta p_i}_{\substack{\text{thermo-}\\\text{dynamic}}} = \sum \big(\underbrace{m\phi_i \dot{N}_i +}_{\text{advection}} \underbrace{\dot{m\Phi}_{\text{D}i}}_{\text{diffusion}} \big) \qquad (3.28)$$

$$\underbrace{\phantom{m\phi_i \dot{N}_i + \dot{m\Phi}_{\text{D}i}}}_{\text{intake}}$$

where ϕ is a component of velocity, z is the charge number, E is the electric field, and a represents the acceleration due to additional body forces. The advective forces in the intake group ($m\phi\dot{N}$) account for convective acceleration and the momentum transferred in reacting flows and phase change. The diffusive terms ($\dot{m\Phi}_{\text{D}}$) describe shear forces, dynamic (non-thermodynamic) normal forces, and drag among configurations. The mass M is mN, where m is the specific mass and N is the amount of material known from the state of the material conservation equation (3.25).

The difference (Δ) on the left side is across the boundaries normal to the component of translational momentum. The variable A is the area of those boundaries. The thermodynamic force term ($A\Delta p_i$) is based on the assumption that the configuration experiences pressure across the entire cross-sectional area of the region, although in reality the area is reduced if other phases are present. This is necessary to ensure that translational momentum is conserved between two adjacent regions.

The total intake (advective and diffusive) of each index is denoted without the subscript D $\dot{m\Phi}_i = m\phi_i \dot{N}_i + \dot{m\Phi}_{\text{D}i}$. For boundaries and transitions, the conservation of translational momentum reduces to

$$0 = \sum \dot{m\Phi}_i \qquad (3.29)$$

where the summation is now across all interacting configurations.

3.4.4 Energy

The following equation describes the conservation of energy in every configuration:

$$
\underbrace{\underbrace{g\frac{\partial N}{\partial t}}_{\text{material}} + \underbrace{\frac{\partial\left(M\phi^2\right)}{2\partial t}}_{\text{translational}} + \underbrace{T\frac{\partial S}{\partial t}}_{\text{thermal}}}_{\text{transient}} = \underbrace{\sum\left[\underbrace{g_i\dot{N}_i}_{\text{material}} + \underbrace{\phi_i\left(\underbrace{\frac{m\phi_i}{2}\dot{N}_i}_{\text{advection}} + \underbrace{m\dot{\Phi}_{\mathrm{D}i}}_{\text{diffusion}}\right)}_{\text{translational}} + \underbrace{T_i s_i \dot{N}_i}_{\text{advection}} + \underbrace{\dot{Q}_{\mathrm{D}i}}_{\text{diffusion}}\right]}_{\text{intake}}
$$

$$\text{(3.30)}$$

where it has been assumed that the control volume is stationary with respect to external fields (e.g., no gravitational work), although the fluid may move against those fields within the control volume. Using Equation 3.15, the material, advective translational, and advective thermal terms can be written alternatively as $\sum(h_i + \frac{1}{2}m\phi_i^2)\dot{N}_i$. Thermal diffusion is synonymous with thermal conduction.

The material and thermal transient terms $(g\frac{\partial N}{\partial t} + T\frac{\partial S}{\partial t})$ are equivalent to $\frac{\partial H}{\partial t} - V\frac{\partial p}{\partial t}$ or $\frac{\partial U}{\partial t} + p\frac{\partial V}{\partial t}$, where $p\frac{\partial V}{\partial t}$ is the boundary work done by the configuration. The boundary work can only be due to expansion of the phases in which the configuration belongs (and contraction of other phases) because the volume of the region is fixed (see Section 3.3.2). The translational transient term describes the change in macroscopic kinetic energy.

The total thermal intake (advective and diffusive) of each index is denoted without the subscript D: $\dot{Q}_i = T_i s_i \dot{N}_i + \dot{Q}_{\mathrm{D}i}$. For boundaries and transitions, the conservation of energy reduces to

$$
0 = \sum \dot{Q}_i \tag{3.31}
$$

where the summation is now across all interacting configurations.

3.5 Exchange Equations

Highlights:

- An analogy is noted between the total (advective plus diffusive) rate of exchange and the material derivative.

- The model describes phase change dynamically. It does not assume instantaneous phase equilibrium in the sense of the Gibbs phase rule [28, 29]. This avoids nonlinear systems of equations.

- Phase change is described as a diffusive process between the majority and minority sides of each phase across the boundary.

- The transfer of translational momentum and energy due to phase change and reactions is described as pure advection.

- A property called independity is defined which generalizes the concept of mobility for translational interactions to thermal interactions.

Exchange is the transfer of a conserved quantity—material, translational momentum, or energy—among different configurations of material that exist within a region. In general it is due to advection and diffusion. Advective exchange is the transfer of the quantity along with a sustained transfer of material between species (i.e., reaction) or different phases of a single species (i.e., phase change). Diffusive exchange is the transfer of the quantity due only to collisions or thermal agitation of the particles, without a sustained material transfer. In diffusion, a particle leaves one configuration (i.e., a species in a certain phase) with the specific quantity (or particle-average amount of the quantity) within the configuration and returns with the specific quantity of the other configuration. This brings certain intensive properties—explicitly density, velocity, and temperature—into equilibrium between the material configurations. Since these properties are sufficient to set the thermodynamic state, other properties (e.g., pressure) equilibrate as well.

The total rate of exchange of a quantity into a configuration j due to interaction or transition i is the sum of the advective and diffusive rates:

$$\dot{X}_{ij} = \dot{X}_{\mathrm{A}ij} + \dot{X}_{\mathrm{D}ij} \tag{3.32}$$

These rates will be evaluated separately.

The rate of advective exchange is the product of the material current and the amount of the exchanged quantity carried by the material:

$$\dot{X}_{\mathrm{A}ij} = \dot{N}_{ij} \left(\frac{\partial X}{\partial N} \right)_{ij} \tag{3.33}$$

where $\dot{N}_{ij}$ is the rate of material exchange. Both $\dot{N}_{ij}$ and $\dot{X}_{\mathrm{A}ij}$ are due to the interaction (i) and are directed into the configuration (j). The partial derivative ($\partial X/N$) is an intensive property.

For material advection it is unity (1),[iii] for translational exchange it is the product of velocity and specific mass (ϕm), and for thermal exchange it is the product of temperature and specific entropy (Ts). The material currents ($\dot{N}_{ij}$) are related by stoichiometry of the phase change or reaction: $\dot{N}_{ij} = n_{ij}\dot{N}_i$. Therefore,

$$\dot{X}_{\mathrm{A}ij} = n_{ij}\dot{N}_i \left(\frac{\partial X}{\partial N}\right)_{ij} \tag{3.34}$$

We can consider the diffusive rate of exchange to be the material derivative or the rate experienced by the particles themselves:[iv]

$$\dot{X}_{\mathrm{D}ij} = \left(\frac{\mathrm{D}X}{\mathrm{D}t}\right)_{ij} \tag{3.35}$$

where $(\mathrm{D}t)_{ij}$ is the product of the mean collision interval between particles and several correction factors: (i) a logistic function for upstream discretization (described below), (ii) two to normalize the logistic function to unity under pure diffusion, and (iii) $8/3\pi$ as a result of the Einstein relation (see Section 3.11.3.3). We will assume that the exchanged quantity is linear with respect to the driving property; therefore, $(\mathrm{D}X)_{ij} = (\gamma_i - \gamma_j)(\partial X/\partial \gamma)_j$. The following assumptions have also been implied:

1. The collision events are frequent enough for the average collision interval to be meaningful. This implies that the mean free path, or the average distance traveled between collisions, is much smaller than the length scale of the problem. It is not the case for example in effusion [26].
2. Between collisions the particles have no influence on one another.
3. The properties of a particle depend only on those of the last particle with which it collided.

It follows that

$$\frac{16\pi}{3}\tau_j \dot{X}_{\mathrm{D}ij} = \left(\frac{\partial X}{\partial \gamma}\right)_j (\gamma_i - \gamma_j)\left(1 + e^{-Pe_{ij}/2}\right) \tag{3.36}$$

where τ_j is the mean collision interval. In practice, the preceding assumptions may be relaxed by using empirical diffusion coefficients (see Section 3.6). The partial derivative $\left(\partial X/\partial \gamma\right)_j$ is

---

[iii]In this case Equation 3.33 reduces to an identity and is removed. The only source of material exchange is diffusion, as will be discussed later.

[iv]See the discussion at the end of this section.

an extensive property of the configuration. For material exchange it is volume, for translational exchange it is mass, and for thermal exchange it is heat capacity.

If two or more interacting configurations have collision intervals of zero, then their intensive driving properties (γ_j) will be equal. The transported quantity will be exchanged without loss and the number of dynamic states will be reduced.

The logistic factor $1/(1+\exp(-Pe/2))$ has been introduced to account for the change in the collision interval due to advection. The Péclet number Pe is the dimensionless rate of advection from the interaction into the configuration. The rate of advection is normalized by the rate of diffusion:

$$Pe \equiv \dot{X}_A \big/ \dot{X}_D \qquad (3.37)$$

In general, there is a continuum between purely advective flow in one direction to pure diffusion and to purely advective flow in the other direction. However, this is simplified for most of the exchange interactions.[v]

The exchange model is based on the assumption that there are separate but additive interactions which are purely advective and purely diffusive. The phase change and reaction processes are diffusive in terms of material and advective in terms of translational momentum and energy. This implies that particles from the source (e.g., reactants) carry properties through the process without intermediately mixing with particles from the sink (e.g., products). Also, there are diffusive interactions for translational momentum and energy that are independent of the phase change and reactions. These interactions may have different transition properties than those for phase change and reaction.

It follows that the Péclet numbers are zero except for the advective exchange of translational momentum and energy. The Péclet number for those interactions is infinity (∞) if the material is entering the configuration ($n_{ij}\dot{N}_i > 0$) and negative infinity ($-\infty$) if the material is exiting

---

[v]The Péclet number and the logistic factor apply in a continuous manner in transport and electrochemical reactions (Sections 3.7 and 3.9).

the configuration ($n_{ij}\dot{N}_i > 0$). For these special cases, the diffusion equation (3.36) reduces to

$$
\gamma_i - \gamma_j = \begin{cases} 0 & \text{if } Pe_{ij} = -\infty \text{ (advective source)}, \\ 8\pi\tau_j\dot{X}_{Dij}\Big/3\left(\frac{\partial X}{\partial \gamma}\right)_j & \text{if } Pe_{ij} = 0 \text{ (purely diffusive), and} \\ 16\pi\tau_j\dot{X}_{Dij}\Big/3\left(\frac{\partial X}{\partial \gamma}\right)_j & \text{if } Pe_{ij} = \infty \text{ (advective sink)} \end{cases} \tag{3.38}
$$

Therefore, the advective exchange equation (3.34) is the following under pure advection:

$$
N_j\dot{X}_{Aij} = n_{ij}\dot{N}_i\left(\frac{\partial X}{\partial \gamma}\right)_j \cdot \begin{cases} \gamma_j & \text{if } n_{ij}\dot{N}_i < 0 \text{ (source)}, \\ \gamma_i & \text{if } n_{ij}\dot{N}_i > 0 \text{ (sink)} \end{cases} \tag{3.39}
$$

This is the upwind scheme [38,39], but it is applied locally between species rather than spatially between regions. The variable γ_i represents the *conversion property* or the intensive property at which the sinks (e.g., products) are produced from the sources (e.g., reactants) during an advection.

The exchanged quantity is conserved without storage at the transition. This implies a certain value of the intensive driving property at the transition. Since advection and diffusion are independent, the sum of the advection rates ($\dot{X}_{Aij}$) over all of the interacting configurations is zero. Therefore, the sum of Equation 3.39 is:

$$
0 = \sum_{j\in\text{src}} \frac{n_{ij}}{N_j}\dot{N}_i\left(\frac{\partial X}{\partial \gamma}\right)_j \cdot \begin{cases} \gamma_j & \text{if } n_{ij}\dot{N}_i < 0 \text{ (source)}, \\ \gamma_i & \text{if } n_{ij}\dot{N}_i > 0 \text{ (sink)} \end{cases} \tag{3.40}
$$

Solving for the conversion property:

$$
\gamma_i = \frac{\sum_{j\in\text{src}} \gamma_j \left|n_{ij}\right| \left(\frac{\partial X}{\partial \gamma}\right)_j\Big/N_j}{\sum_{j\in\text{sink}} \left|n_{ij}\right| \left(\frac{\partial X}{\partial \gamma}\right)_j\Big/N_j} \tag{3.41}
$$

where the numerator is summed over the sourcing configurations and denominator is summed over the sinking configurations. The designations of source and sink depend on the direction of the phase change or reaction at a given time.

The sum of the diffusion rates is also zero over all of the interacting configurations. If we add the exchange rates of Equation 3.36 for each of the configurations,

$$
0 = \sum_j (\gamma_i - \gamma_j)\left(1 + e^{-Pe_{ij}/2}\right)\left(\frac{\partial X}{\partial \gamma}\right)_j\Big/\tau_j \tag{3.42}
$$

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and solve for the intensive property at the transition,

$$\gamma_i = \frac{\sum_j \gamma_j \left(1 + e^{-Pe_{ij}/2}\right) \left(\frac{\partial X}{\partial \gamma}\right)_j \Big/ \tau_j}{\sum_j \left(1 + e^{-Pe_{ij}/2}\right) \left(\frac{\partial X}{\partial \gamma}\right)_j \Big/ \tau_j} \tag{3.43}$$

Therefore the intensive property at the transition is a conductance-weighted average of the intensive properties of the interacting configurations. For pure advection only the sourcing configurations have any effect due to the values of the Péclet numbers.

A diffusive non-reacting exchange process that encompasses three or more interacting configurations has multiple binary transitions and at least one higher-order transition. The intensive property of the interaction (γ_i) is henceforth called the *mediation property* rather than the transition property, since it may describe the collective effect of multiple transitions.

The total rate of exchange (Equation 3.32) can be expanded with the rates of advection and diffusion from Equations 3.33 and 3.36:

$$\dot{X}_{ij} = \dot{N}_{ij} \left(\frac{\partial X}{\partial N}\right)_{ij} + \left(\frac{DX}{Dt}\right)_{ij} \tag{3.44}$$

Since the model uses a Eulerian perspective, the total exchange rate $\dot{X}_{ij}$ is actually a partial derivative in the form of $\partial X / \partial t$. Dropping the subscripts and rearranging,

$$\frac{DX}{Dt} = \frac{\partial X}{\partial t} - \dot{N}\frac{\partial X}{\partial N} \tag{3.45}$$

This is essentially the definition of a material derivative [40]. Usually the scalar property in the material derivative is intensive, i.e., the driving property for the diffusion (γ), but it is coupled to the conserved property (X) through the extensive property $\partial X / \partial \gamma$. The usual advective term $\boldsymbol{\phi} \cdot \nabla X$ is a loss. The advective source is $-\boldsymbol{\phi} \cdot \nabla X$ or $\dot{N}\partial X / \partial N$, although the material exchange current itself is purely diffusive (as mentioned previously). The concept here is that particles experience the collisions that lead to diffusive exchange, but they do not experience advection. Advection is an artifact of the Eulerian basis of the model.

There are several types of material exchange processes. The simplest is phase change, which is discussed in the following section. Electrochemical reactions are introduced later (Section 3.9) because they involve geometric dimensions and orientation like the transport equations (also to follow). Chemical reactions are outside the present scope; they are only intermediate to the electrochemical reactions in a fuel cell.

3.5.1 Phase Change

Phase change is purely diffusive.[vi] It is driven by density as formulated in the classical Hertz-Knudsen equation [41] (see Section 3.11.1.2). However, in order to avoid nonlinear systems of equations, the rate equation is written in terms of activity. This form is derived below given a plausible physical description. It is appropriate for the condensation and evaporation or absorption and desorption of an ideal gas to and from an incompressible phase.

3.5.1.1 Introduction

In each configuration or phase, a species has different thermodynamic properties. If a species exists in two or more phases within a region, then at equilibrium the specific Gibbs energy-temperature quotients (g/T) of the species are equal between or among the phases. **use Gibbs potential directly, not quotient

Even though the phases may equilibrate rapidly, we will not assume that the process is instantaneous. Doing so would require that the specific Gibbs energy-temperature quotients are equal—exactly and instantaneously. Since the Gibbs function (Equation 3.16) is only analytically invertible in certain cases, this would lead to nonlinear systems of equations and conditional index reduction. Instead the model includes the dynamics of the phase change process. In terms of Gibbs' phase rule ($n_{\mathrm{DOF}} = 2 + n_{\mathrm{spec}} - n_{\mathrm{phases}}$) [28, 29], we are not subtracting the number of phase equilibria ($n_{\mathrm{phases}} - 1$). Therefore the number of thermodynamic state variables or degrees of freedom is one plus the number of species ($n_{\mathrm{DOF}} = 1 + n_{\mathrm{spec}}$).[vii]

Water may be absorbed and desorbed between the ionomer and the gas in the catalyst layer, as shown in Figure 3.4a. The catalyst layer extends from the plane just inside the region where the solid is entirely the gas diffusion layer (GDL) material to the plane just inside the region where the solid is entirely the ionomer or proton exchange membrane (PEM) material. Figure 3.4b shows that water may also condense and evaporate between the liquid and gas in

---

[vi]Particles must collide to change configurations, and collisions are diffusive in nature. As mentioned in Footnote iii, the advective exchange equation (3.33) is not applicable to material exchange.

[vii]In fact, without certain optional assumptions enabled (see **??**) the model often has even more thermodynamic state variables. The number of thermodynamic state variables in the model is the number of species plus the number of compressible species, and there are often several compressible species in a region. In general, the total number of state variables is equal to the number of ways in which energy (not limited to thermal and compressive) may be stored.

the flow plate, the GDL, or the catalyst layer.

In any case, there is a boundary between the phases. On one side, the water is predominantly in the gas phase and on the other side it is predominantly in the condensed phase (ionomer or liquid). Around the boundary is a transition or surface layer. Water may also exist as a minority in the gas phase on the condensed side or in the condensed phase on the gaseous side.
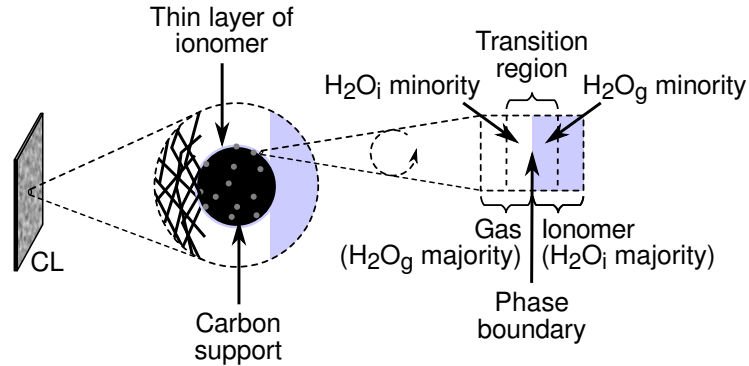
(a) Gas to ionomer.
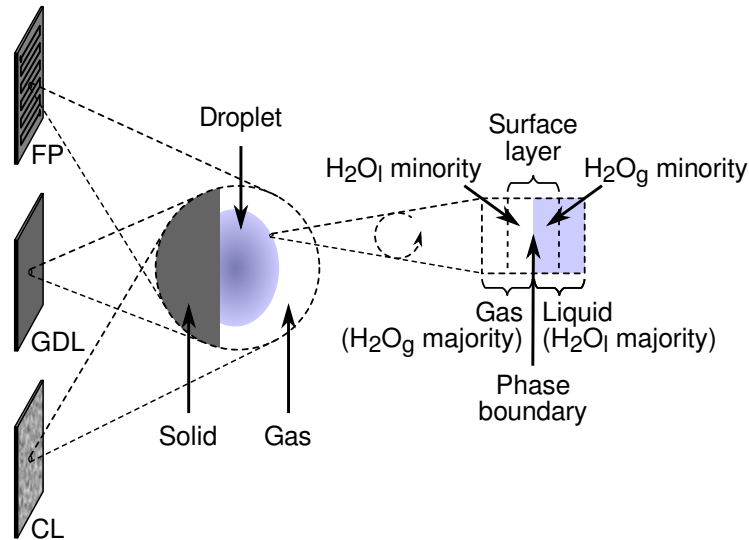
(b) Gas to liquid.

Figure 3.4: Phase change occurs between the gas and (a) the ionomer in the catalyst layers (CLs) and (b) the liquid in the flow plates (FPs), gas diffusion layers (GDLs), and CLs.

As mentioned previously, phase change is only due to diffusion (no advection) and thus is driven by density. If we assume that the condensed phase is isochoric (e.g., incompressible and isothermal) as shown in Figure 3.5a, then there is no diffusion of the condensed phase. The

density of the gas phase, however, depends on the thermodynamic state. Figure 3.5b shows that condensation and evaporation or absorption and desorption are driven by a density gradient between the gas at the interface and the edge of the transition region within the minority gas region (majority condensed), where the gas is saturated. It is assumed that the gas diffuses much more easily through the majority side than the minority side; therefore the gradient appears only in the minority side.
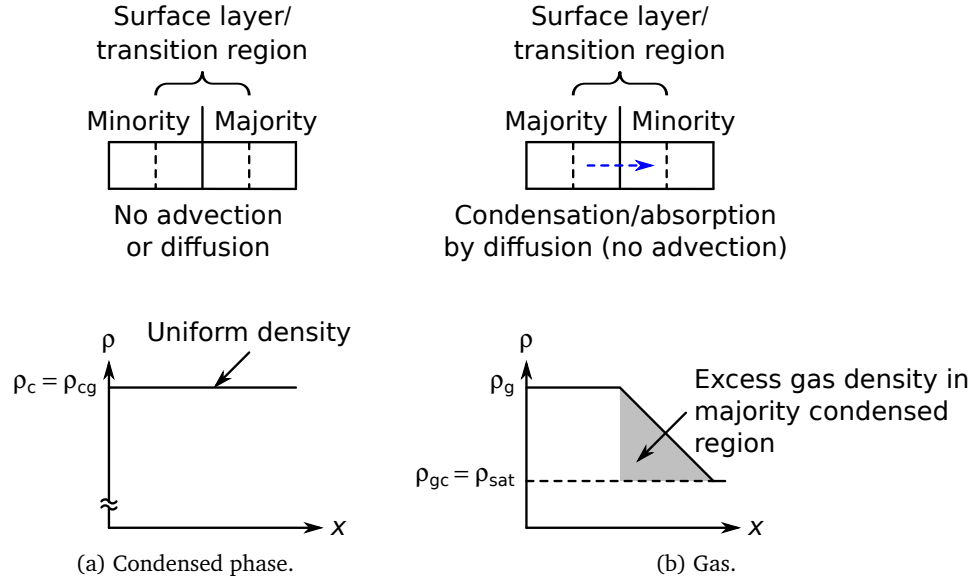
Figure 3.5: Diffusion and density (ρ) across the surface layer or transition region. The subscript g indicates the gas phase, c indicates the condensed phase, and sat is saturation.

3.5.1.2 Equations

The rate of diffusion of a phase from the phase boundary into the majority is given by the diffusive exchange equation (3.36) for material ($X = N$, $\gamma = \rho$):

$$\frac{16\pi}{3} \tau_M \dot{N}_{DiM} = Kn_M V_M (\rho_i - \rho_M) \tag{3.46}$$

where the subscript M indicates the majority side. The Knudsen number Kn_M has replaced the reciprocal of the logistic function ($1/(1 + e^{-Pe/2})$). Its reciprocal is the number of collisions that are necessary to span the majority side of the surface layer or transition region. Nominally the Knudsen number is two, which corresponds to the case of pure diffusion. Likewise for the

minority side (with subscript m),

$$\frac{16\pi}{3}\tau_{\mathrm{m}}\dot{N}_{\mathrm{D}im} = Kn_{\mathrm{m}}V_{\mathrm{m}}(\rho_i - \rho_{\mathrm{m}}) \tag{3.47}$$

Material is conserved in each phase without storage at the phase boundary ($0 = \dot{N}_{\mathrm{D}iM} + \dot{N}_{\mathrm{D}im}$). Therefore the previous two equations can be written in terms of the rate of exchange into the majority side:

$$\frac{16\pi}{3}\left(\frac{\tau_{\mathrm{M}}}{Kn_{\mathrm{M}}V_{\mathrm{M}}} + \frac{\tau_{\mathrm{m}}}{Kn_{\mathrm{m}}V_{\mathrm{m}}}\right)\dot{N}_{\mathrm{D}iM} = \rho_{\mathrm{m}} - \rho_{\mathrm{M}} \tag{3.48}$$

We will assume that the collision interval is much larger in the minority side than the majority side ($\tau_{\mathrm{m}} \gg \tau_{\mathrm{M}}$), therefore

$$\frac{16\pi}{3}\tau_{\mathrm{m}}\dot{N}_{\mathrm{D}iM} = Kn_{\mathrm{m}}V_{\mathrm{m}}(\rho_{\mathrm{m}} - \rho_{\mathrm{M}}) \tag{3.49}$$

The previous equation applies to both phases. However as mentioned previously and shown in Figure 3.5a, it is assumed that the condensed phase has the same density across the phase boundary. Therefore its rate of phase change is zero and the phase change is only due to the difference in the density of the gas. The previous equation is rewritten with notation applying it to the gas:

$$\frac{16\pi}{3}\tau_{\mathrm{gc}}\dot{N}_{\mathrm{g}} = Kn_{\mathrm{gc}}V_{\mathrm{gc}}\left(\rho_{\mathrm{gc}} - \rho_{\mathrm{g}}\right) \tag{3.50}$$

where the subscript g indicates the gas in the majority gas side and gc indicates the gas in its minority side (i.e., the majority condensed side). The variable $\dot{N}_{\mathrm{g}}$ indicates the total rate of change into the gas phase (e.g., evaporation minus condensation).

As mentioned previously, we will assume that the gas is ideal. Therefore from Equation 3.16,

$$g_{\mathrm{g}} = T_{\mathrm{g}}\ln\left(\frac{p_{\mathrm{g}}}{p_{\mathrm{g}}^o}\right) + g_{\mathrm{g}}\left(T_{\mathrm{g}}, p_{\mathrm{g}}^o\right) \tag{3.51}$$

where g_{g} is at the actual thermodynamic state of the gas in its majority region (T_{g}, p_{g}) but $g_{\mathrm{g}}\left(T_{\mathrm{g}}, p_{\mathrm{g}}^o\right)$ is evaluated at the reference pressure and only the actual temperature. Solving for the pressure of the gas:

$$p_{\mathrm{g}} = p_{\mathrm{g}}^o \exp\left(\frac{g_{\mathrm{g}} - g_{\mathrm{g}}\left(T_{\mathrm{g}}, p_{\mathrm{g}}^o\right)}{T_{\mathrm{g}}}\right) \tag{3.52}$$

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and for the density of the gas:

$$\rho_g = \frac{p_g^o}{T_g} \exp\left(\frac{g_g - g_g\left(T_g, p_g^o\right)}{T_g} \right)$$ (3.53)

The density of the gas at the edge of the transition in the majority condensed region (ρ_{gc} or ρ_{sat}) is the density of the gas given the saturation condition ($g_g/T_g = g_c/T_c$). Therefore it is:

$$\rho_{gc} = \frac{p_g^o}{T_g} \exp\left(\frac{g_c}{T_c} - \frac{g_g\left(T_g, p_g^o\right)}{T_g} \right)$$ (3.54)

where the temperature of the gas is assumed to be equal between the majority and minority sides.

Substituting the solutions for ρ_g and ρ_{gc} into Equation 3.49,

$$\frac{16\pi}{3} T_g \exp\left(\frac{g_g\left(T_g, p_g^o\right)}{T_g} \right) \tau_{gc} \dot{N}_g = Kn_{gc} V_{gc} p_g^o \left[\exp\left(\frac{g_c}{T_c} \right) - \exp\left(\frac{g_g}{T_g} \right) \right]$$ (3.55)

This shows that the rate of phase change can be written in terms of differences in activity ($a = \exp\left(g/T\right)$). However the volume of the gas in the majority condensed region (V_{gc}) is not explicitly known. We can refactor the equation to be explicit in the total amount of gas instead:

$$\boxed{\tau' \dot{N}_g = N_g\left(a_c - a_g\right)}$$ (3.56)

where the effective collision interval, or the mean time between collisions that yield phase change, is

$$\boxed{\tau' = \frac{16\pi}{3} \frac{N_g}{V_{gc}} \frac{T_g}{p_g^o} \frac{\tau_{gc}}{Kn_{gc}} \exp\left(\frac{g_g\left(T_g, p_g^o\right)}{T_g} \right)}$$ (3.57)

It is an intensive property. The reciprocal of the first variable factor, V_{gc}/N_g, is the volume of the transition region on the condensed side relative to the total amount of gas.

3.5.2 Drag and Translational Advection

The translational exchange equations follow from the generalized exchange equations (3.33 and 3.36). The exchanged quantity (X) is translational momentum ($m\Phi$). The intensive property $\partial X/\partial N$ is the product of velocity and specific mass (ϕm). Therefore,

$$\dot{m\Phi}_{Aij} = \dot{N}_{ij}\phi_{ij}m_{ij}$$ (3.58)

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Since advective exchange is independent of diffusive exchange (see Equation 3.39),

$$m\dot{\Phi}_{Aij} = m_j \dot{N}_{ij} \cdot \begin{cases} \phi_j & \text{if } \dot{N}_{ij} < 0 \text{ (source)}, \\ \phi_i & \text{if } \dot{N}_{ij} > 0 \text{ (sink)} \end{cases} \tag{3.59}$$

where the specific mass has been factored out of the conditional factor since it is constant for each species ($m_{ij} = m_j$).

For advective translational exchange, Equation 3.41 becomes the following:

$$\phi_i = \frac{\sum_{j\in\text{src}} \phi_j \left| n_{ij} \right| m_j}{\sum_{j\in\text{sink}} \left| n_{ij} \right| m_j} \tag{3.60}$$

where ϕ_i is the *conversion velocity* and n_{ij} is a stoichiometric coefficient of the phase change or reaction process. If the process is well-posed, then it must conserve mass ($\sum_{j\in\text{src}} |n_{ij}|m_j = \sum_{j\in\text{sink}} |n_{ij}|m_j$), and

$$\phi_i = \frac{\sum_{j\in\text{src}} \phi_j \left| n_{ij} \right| m_j}{\sum_{j\in\text{src}} \left| n_{ij} \right| m_j} \tag{3.61}$$

Therefore, the conversion velocity is the mass-weighted average of the velocities of the configurations consumed by the process.

The driving property (γ) for translational diffusion is velocity (ϕ). The extensive property $\partial X/\partial \gamma$ is mass (M). Under pure diffusion ($Pe = 0$), the diffusive exchange equation (3.36) is written for translational exchange as

$$\frac{8\pi}{3} \tau_j \, m\dot{\Phi}_{Dij} = M_j \left(\phi_i - \phi_j \right) \tag{3.62}$$

This can be written as

$$\mu_j \, m\dot{\Phi}_{Dij} = N_j \left(\phi_i - \phi_j \right) \tag{3.63}$$

where μ_j is the mobility:

$$\mu = \frac{8\pi\tau}{3m} \tag{3.64}$$

For purely diffusive translational exchange and with the definition of mobility, Equation 3.43 can be written as:

$$\phi_i = \frac{\sum_j \phi_j \, N_j/\mu_j}{\sum_j N_j/\mu_j} \tag{3.65}$$

where ϕ_i is the *mediation velocity*. This indicates that the mediation velocity is the conductance-weighted average velocities of the configurations interacting by diffusion.

3.5.3 Thermal Conduction and Advection

**Cite a reference thermal conductivity and thermal resistivity are reciprocals (Incropera2002?)

The thermal exchange equations follow from the generalized exchange equations (3.33 and 3.36). The exchanged quantity (X) is heat (Q). The intensive property $\partial X / \partial N$ is the product of temperature and specific entropy ($\partial Q / \partial N = T \partial S / \partial N = Ts$). The advective exchange equation (3.33) can be written as

$$\dot{Q}_{Aij} = \dot{N}_{ij} T_{ij} s_{ij} \tag{3.66}$$

Since advective exchange is independent of diffusive exchange (see Equation 3.39),

$$\boxed{\dot{Q}_{Aij} = \dot{N}_{ij} \cdot \begin{cases} T_j s_j & \text{if } \dot{N}_{ij} < 0 \text{ (source)}, \\ \\ T_i s_i & \text{if } \dot{N}_{ij} > 0 \text{ (sink)} \end{cases}} \tag{3.67}$$

where the specific entropy must remain within the conditional factor (unlike specific mass in Equation 3.59) because it is not constant. **Specific entropy is of the source, like temperature.

For advective thermal exchange, Equation 3.41 becomes the following:

$$T_i = \frac{\sum_{j \in \text{src}} T_j \left| n_{ij} \right| s_j}{\sum_{j \in \text{sink}} \left| n_{ij} \right| s_j} \tag{3.68}$$

where T_i is the *conversion temperature*. The temperature may be discontinuous at the transition because the stoichiometrically-weighted specific entropies of the sources (e.g., reactants) is not necessarily equal to that of the sinks (e.g., products).

The driving property (γ) for thermal diffusion is temperature (T). The extensive property $\partial X / \partial \gamma$ is heat capacity (C). The heat capacity is isobaric (C_p) since the pressures of the configurations are assumed to be at equilibrium (see Section 3.3.2). Under pure diffusion ($Pe = 0$), the diffusive exchange equation (3.36) is written for thermal exchange as

$$\frac{8\pi}{3} \tau_j \dot{Q}_{Dij} = C_{pj} \left(T_i - T_j \right) \tag{3.69}$$

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This can be written as

$$\nu_j \dot{Q}_{\mathrm{D}ij} = N_j \left(T_i - T_j \right)$$

(3.70)

where ν_j is called thermal *independity* here.[viii] It is:

$$\nu = \frac{8\pi\tau}{3c_p}$$

(3.71)

For purely diffusive thermal exchange and with the definition of thermal independity, Equation 3.43 can be written as:

$$T_i = \frac{\sum_j T_j \, N_j \big/ \nu_j}{\sum_j N_j \big/ \nu_j}$$

(3.72)

where T_i is the *mediation temperature*. This indicates that the mediation temperature is the conductance-weighted average temperatures of the configurations interacting by diffusion.

3.6 Exchange Properties

The base factor in the diffusive exchange properties is the collision interval or the mean time between collisions. It depends on the thermodynamic state and possibly other properties, but it can be estimated from kinetic theory under the following assumptions [26]:

1. The particles are smooth and rigid but elastic spheres with identical radii. This is the "billiard-ball" assumption. It implies that the collisions are instantaneous and conserve kinetic energy.

2. The mean free path, or the average distance a particle travels between collisions, is much larger than the diameter of a particle.

3. The speeds of the particles follow the Maxwell-Boltzmann distribution.

With these assumptions the mean free path is

$$\lambda = \frac{\nu}{\sqrt{2}\pi d^2 q}$$

(3.73)

where ν is the specific volume of the particles (reciprocal of density), d is the specific rigid-sphere or Van der Waals diameter, q is the particle number representing a single particle [26,

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[viii]This is the thermal analog of mobility, but there is no established name. It is not called resistivity. Resistivity is resistance times the quotient of area and length, whereas independity is resistance (or *independence*) times particle number.

42]. The denominator is the product of the intercept area per particle with particles of the same type ($\pi d^2 q$) and a correction due to the Maxwell-Boltzmann distribution ($\sqrt{2}$).[ix] The derivation is beyond the present scope (see [26, pp. 31–32] and [42, p. 229]). The collision interval is the mean free path divided by the mean thermal speed ($\sqrt{8T/\pi m}$):

$$\boxed{\tau = \lambda \sqrt{\frac{\pi m}{8T}}} \tag{3.74}$$

The collision interval is called the relaxation time in solid state physics [43]. For a typical species the collision interval is small. For oxygen as an ideal gas at 25[C]**fix and 21% of atmospheric pressure, the specific volume (v) is $0.12\,\mathrm{m}^3/\mathrm{mol}$. The diameter of a particle is approximately $220\,\mathrm{pm}$; therefore the mean free path is approximately $0.9\,\mu\mathrm{m}$ and the collision interval is approximately $2\,\mathrm{ns}$.

The effective collision interval, which is used for phase change, can be determined from the collision interval using Equation 3.57. Mobility and thermal independity can be determined from the collision interval using Equations 3.64 and 3.71. Due to the assumptions implicit in the diffusive exchange equation (3.36), the equations for the effective collision interval, mobility, and thermal independity are only taken to be estimates. However, they are useful if more precise data is not available.

3.7   Transport Equations

Highlights:

- The model describes the transport of every species individually, even in advective flow. However, the diffusive exchange of translational momentum (Section 3.9) tends to couple the velocities of the species and thus the rates of advective transport.

- A general transport equation is proposed to handle upstream discretization. It meets the exact solution to a mixed advection/diffusion problem [38].

- The transport equation changes continuously from neutral discretization under pure diffusion to complete upstream discretization in the limiting case of pure advection. This avoids switching events that could slow the simulation if diffusion were not included.

[ix]It is counterintuitive that the distribution of molecular speeds has an effect on the mean free path, but this is stated in the literature [26, p. 32].

- The model is expressed in resistivity instead of conductivity so that it is well-posed under all representable values.

- The model allows zero or finite dynamic compressibility. The reciprocal, bulk viscosity, is rarely studied [44] and seldom included in fluid simulations [45], let alone fuel cell simulations. The associated effect may be neglected for monoatomic ideal gases and incompressible fluids [37, 45], but following a plausible formation (see Section 3.7.1) the effect is dominant for lightweight particles such as electrons.

- The material transport equation combines the effects of self diffusivity and bulk viscosity to describe material advection and diffusion. That way, the same equations can describe the primarily advective flow down the channels of a proton exchange membrane fuel cell (PEMFC) and the primarily diffusive flow through the layers.

Transport is the transfer of a conserved quantity between adjacent regions. Like exchange (Section 3.5), it is due to advection and diffusion. In transport, however, advection and diffusion are not independent. The transport equations are based on the following assumptions:

1. Transport only occurs between like configurations (e.g., liquid water). The cross-configurational effects (e.g., between liquid water and steam) are described within a region via exchange (Section 3.5).

2. The coordinate system is aligned with the principle axes of transport. For example, if a phase is stratified within a region, the layers must be parallel to one of the planes in the rectilinear grid. This implies that a gradient which induces diffusion along an axis does not induce diffusion along axes orthogonal to it [29].

3. There is no radiative heat transfer.

The total rate of transport of a quantity into configuration j from boundary i is the sum of the advective and diffusive rates:

$$\dot{X}_{ij} = \dot{X}_{\mathrm{A}ij} + \dot{X}_{\mathrm{D}ij} \tag{3.75}$$

This is the same as for exchange (Equation 3.32) except i stands for a regional boundary rather than an intra-regional transition. The advective and diffusive terms will be evaluated separately.

The rate of advective transport is the product of the material current and the change in the transported quantity with respect to the material:

$$\dot{X}_{\mathrm{A}ij} = \dot{N}_{ij} \left(\frac{\partial X}{\partial N} \right)_{ij} \tag{3.76}$$

where $\dot{N}_{ij}$ is the total (advective plus diffusive) rate of material transport into the configuration within the region. Like $\dot{X}_{\mathrm{AT}ij}$, it is from the boundary (i) into configuration (j). The partial derivative $(\partial X/\partial N)_{ij}$ is an intensive property at the boundary.

Like for exchange (Section 3.7), we can consider the diffusive transport rate to be the material derivative or the transport rate experienced by the particles themselves:[x]

$$\dot{X}_{\mathrm{D}ij} = \left(\frac{\mathrm{D}X'}{\mathrm{D}t} \right)_{ij} \tag{3.77}$$

where $(\mathrm{D}t)_{ij}$ is the time for a particle to pass from the boundary to the center of the region. It is the product of (i) the mean collision interval (τ), (ii) a logistic function for upstream discretization ($1/(1 + \exp(\mp Pe/2))$, described below), (iii) a factor of three due to the geometry of randomly-moving particles striking a boundary [26, p. 33–35], (iv) a factor to adjust the available area to account for other phases (k), and (v) the number of collisions required to span the distance from the boundary to the center of the region. That number is the reciprocal of the Knudsen number (Kn) or the length across the region divided the mean free path ($1/Kn = L/\lambda$). The effective difference in the transported quantity $(\mathrm{D}X')_{ij}$ is the actual difference $(\mathrm{D}X)_{ij}$ divided by the number of collisions required to span the distance between the boundary and the center (again, the reciprocal of the Knudsen number). We will assume that the transported quantity is linear with respect to the driving property (γ); therefore, $(\mathrm{D}X)_{ij} = (\gamma_i - \gamma_j)(\partial X/\partial\gamma)_j$. The following assumptions have also been implied:

1. The collision events are frequent enough for the average collision interval to be meaningful. This implies that the mean free path, or the average distance traveled between collisions, is much smaller than the length scale of the problem. It is not the case for example in effusion.

2. Between collisions the particles have no influence on one another.

3. The properties carried by a particle depend only on those of the last particle with which it collided.

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[x]See the discussion at the end of this section.

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It follows that

$$3\tau_j \dot{X}_{\mathrm{D}ij} = k_{ij}Kn_{ij}^2 \left(\frac{\partial X}{\partial \gamma}\right)_j (\gamma_i - \gamma_j)\left(1 + e^{\mp Pe_{ij}/2}\right) \tag{3.78}$$

where the negative of $\mp$ is for the negative side of the region along an axis and the positive is for the positive side.[xi] This can be written as

$$R_{ij}\dot{X}_{\mathrm{D}ij} = (\gamma_i - \gamma_j)\left(1 + e^{\mp Pe_{ij}/2}\right) \tag{3.79}$$

where the generalized resistance is

$$R_{ij} = \frac{3\tau_{ij}}{k_{ij}Kn_{ij}^2} \bigg/ \left(\frac{\partial X}{\partial \gamma}\right)_j \tag{3.80}$$

The resistance can be written as

$$R_{ij} = \frac{r_j L_i}{k_{ij}A_i} \tag{3.81}$$

where the resistivity is

$$r_j = \frac{3\tau_{ij}V}{\lambda_j^2} \bigg/ \left(\frac{\partial X}{\partial \gamma}\right)_j \tag{3.82}$$

using the definition of the Knudsen number ($Kn \equiv \lambda/L$). In terms of resistivity, the diffusive transport equation is:

$$r_{ij}\dot{X}_{\mathrm{D}ij} = \frac{k_j A_i}{L_i} (\gamma_i - \gamma_j)\left(1 + e^{\mp Pe_{ij}/2}\right) \tag{3.83}$$

If two adjacent regions have zero resistivity, then their intensive driving properties (γ_j) will be equal. The transported quantity will flow between the regions without loss in order to meet that requirement and the number of dynamic states will be reduced by one.

The model uses resistance and resistivity instead of conductance and conductivity (the reciprocals) because the equations are numerically well-posed for zero resistivity and resistance but not for zero conductance and conductivity. Values of zero can be directly represented in the modeling language but infinite values cannot (see Chapter 4). Infinite values of resistivity (zero conductivity) can be represented by directly imposing zero flow rate (by a disconnected interface; see Chapter 4).

The logistic factor $1/(1+\exp(-Pe/2))$ has been introduced to account for the change in the effective length due to advection. The factor of one half appears in the exponential because by

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[xi]This convention is used throughout the chapter. Likewise, the $\pm$ operator indicates that the positive is for the negative side of the region and the negative is for the positive side.

default half of resistance is to either side of the region along the axis of transport. As mentioned in Section 3.5, the Péclet number (Pe) is the ratio between the rates of advection and diffusion (Equation 3.37). Using the rate of advection from Equation 3.76 and the rate of diffusion across a region (Equation 3.79 as in Equation 3.100) at a differential level along with the definition of resistance (Equation 3.81),

$$Pe = \frac{R\dot{N}}{\mathrm{d}\gamma} \frac{\partial X}{\partial N} \tag{3.84}$$

where the subscripts have been dropped. Taking the material current to be advective ($\dot{N} = \phi \partial N / \partial x = \phi \partial N / L$),

$$Pe = \frac{R\phi}{L} \frac{\partial X}{\partial \gamma} \tag{3.85}$$

In terms of resistivity,

$$Pe = \frac{r\phi}{kA} \frac{\partial X}{\partial \gamma} \tag{3.86}$$

where $\partial X / \partial \gamma$ is an extensive material property. The Péclet number is extensive too; its magnitude is smaller for shorter transport lengths, assuming the intensive properties are the same (and the velocity is nonzero) **reword –simply prop to transport length; **write previous equation again showing length explicity on numerator; **add footnote to state that the Peclet number here has diffusion and advection parallel whereas in traditional fluid transport advection and diffusion are perpendicular, thus characteristic length is here along the transport axis. If the problem domain is discretized into small enough regions, then the Péclet numbers will be nearly zero. Although the Péclet number is scaled by other factors, it is best seen as an alternative state of the translational momentum balance (Equation 3.28).

The Péclet numbers tend to **proper word usage? zero at the differential level of discretization or when there is no bulk velocity. Then the transport equation (3.79) reduces to a typical diffusion relationship:

$$R\dot{X}_i = 2(\gamma_i - \gamma) \tag{3.87}$$

where the flow rate is evaluated at one side rather than between the locations of the properties. The factor of two appears because the property difference ($\gamma_i - \gamma$) spans only half the length of the region. We can consider the factor of $1/(1 + e^{\mp Pe/2})$ in the general transport equation

(3.79) to be a length scaling factor which is one half in this case. With a length factor of one half, the transport equation implements the central difference scheme [39].

As the Péclet number becomes large, the length factor becomes one for the upstream side and zero for the downstream side. The property in the region is weakly coupled to the upstream boundary and strongly coupled to the downstream boundary. Equivalently, from the perspective of a boundary, the value of the property at the interface between regions is nearly the value in the upstream region. The downstream region determines the diffusion rate. The limiting cases are listed in Table 3.1. As stated by Patankar [38],

> "It is true that the one-way nature of a space coordinate is a one-way process, but diffusion (which is always present) has two-way influences. However, when the flow rate is large, convection overpowers diffusion and thus makes the space coordinate nearly one-way."

Here the term "advection" is used instead of "convection" because convection is the serial combination of diffusion and advection, at least in the thermal context.

Table 3.1: Limiting cases of the transport equation.

Péclet Number (Pe)	Negative-side Equation	Positive-side Equation
$-\infty$	$\gamma_n = \gamma$	$R\dot{X}_p = \gamma_p - \gamma_n$
0	$R\dot{X}_n = 2(\gamma_n - \gamma)$	$R\dot{X}_p = 2(\gamma_p - \gamma)$
∞	$R\dot{X}_n = \gamma_n - \gamma_p$	$\gamma_p = \gamma$

If the resistivity is infinite, then the transport equation reduces to the upwind scheme (also known as the upwind-difference scheme, upstream-difference scheme, and donor-cell method) [38]. The exponential switches immediately upon flow reversal. The property at the interface is exactly the property of the upstream region. The downstream region imposes the diffusion rate, which is zero.

As long as the resistivity is finite, the property changes continuously between the limiting cases. If we implement the transport equation (3.79) twice—once for each boundary of a region along an axis—and place the restriction that no material is stored $(0 = \dot{X}_n + \dot{X}_p)$, then

$$\frac{\gamma - \gamma_n}{\gamma_p - \gamma_n} = \frac{1}{1 + e^{-Pe/2}} \tag{3.88}$$

where the right side is the logistic function of $Pe/2$. Figure 3.6 shows the sigmoid curve which it represents. The property at the interface between two regions is

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{R_1\left(1 + e^{-Pe_2/2}\right)}{R_1\left(1 + e^{-Pe_2/2}\right) + R_2\left(1 + e^{Pe_1/2}\right)} \tag{3.89}$$

where positive Péclet numbers indicate advection directed from the first to the second region. If the regions have identical Péclet numbers and resistances ($Pe_1 = Pe_2 = Pe$ and $R_1 = R_2$), then this reduces to the same logistic function as for a single region except reflected over the $Pe = 0$ axis:

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{1}{1 + e^{Pe/2}} \tag{3.90}$$

This means that an interface's property is biased towards the source whereas a region's property is biased towards the exit. Figure 3.7 shows the relation in contrast to Figure 3.6.
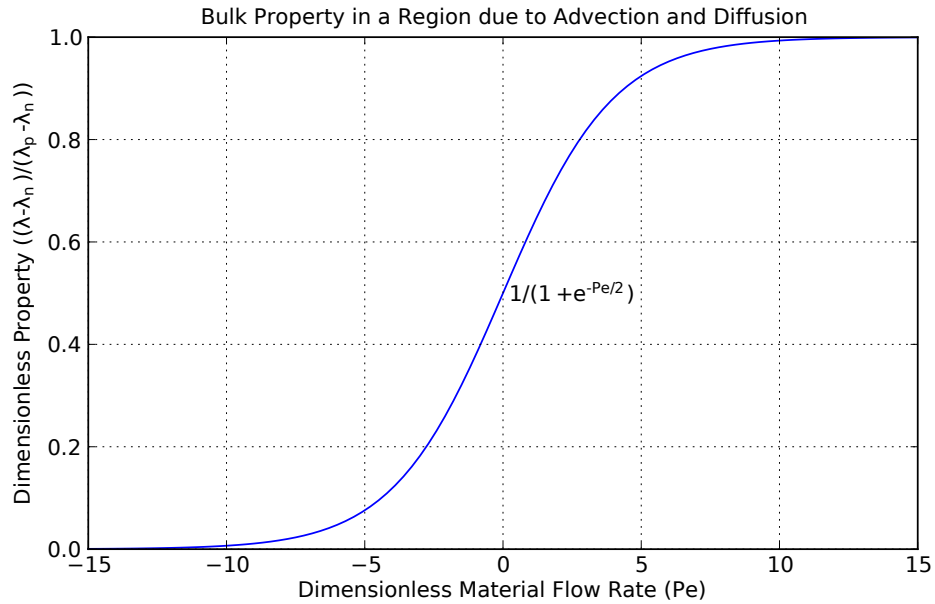

Figure 3.6: Property in the bulk of a region due to advection and diffusion.

Equation 3.89 can be used to provide the profile of the property between the centers of adjacent regions. If we assume that the resistivity and cross-sectional area are uniform, then Equation 3.80 implies that

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{L_1\left(1 + e^{-Pe_2/2}\right)}{L_1\left(1 + e^{-Pe_2/2}\right) + L_2\left(1 + e^{Pe_1/2}\right)} \tag{3.91}$$
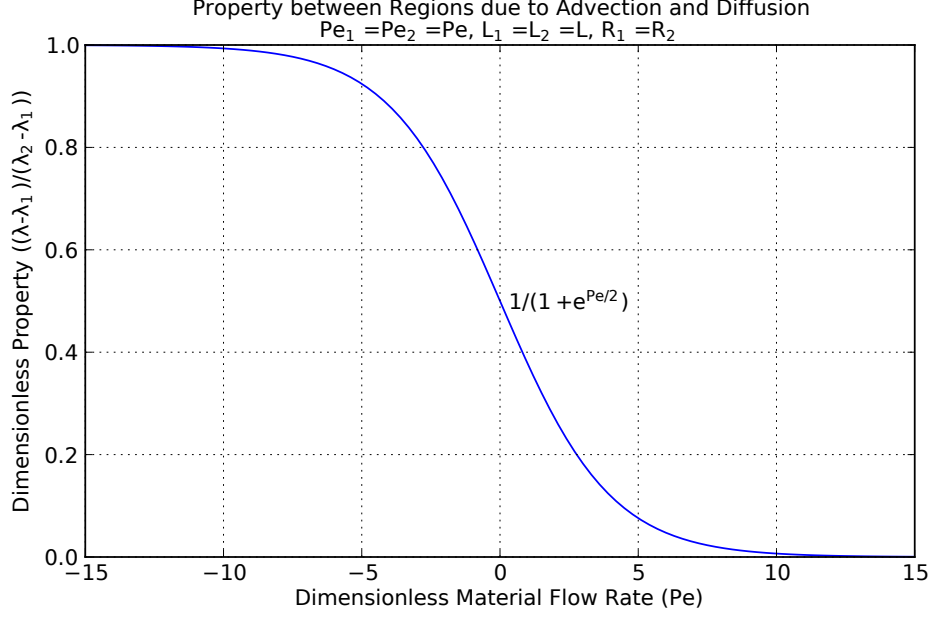
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Figure 3.7: Property at the interface between regions due to advection and diffusion.

where L_1 is the length across region 1 and L_2 is the length across region 2. If we vary the position of the interface while keeping the center-to-center distance the same (constant $L = (L_1 + L_2)/2$), then we can express the value of the property as a function of position:

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{x^\star \left(1 + e^{-Pe_2/2}\right)}{x^\star \left(1 + e^{-Pe_2/2}\right) + \left(1 - x^\star\right)\left(1 + e^{Pe_1/2}\right)} \tag{3.92}$$

where $x^\star = (x - x_1)/L$ is the dimensionless position between the first and second region as a function of x, the absolute position of the interface. Finally, if the Péclet numbers are equal then

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{1}{1 + \left(\frac{1}{x^\star} - 1\right)e^{Pe/2}} \tag{3.93}$$

Figure 3.8 shows the resulting profile for various Péclet numbers (solid lines). The profile is linear under pure diffusion ($Pe = 0$). Otherwise, the profile is biased towards the property of the source. The profile increases or decreases monotonically (or remains constant). Equation 3.93 reduces to Equation 3.90 when $x^\star = 1/2$, as shown in the figure.

For comparison, Patankar [38] provides the solution to the following general advection/diffusion equation:

$$\dot{X} = \gamma I - \frac{A}{r}\nabla\gamma \tag{3.94}$$

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under the condition of no material storage due to advection ($\mathrm{d}I/\mathrm{d}x = 0$) and no storage of the transported quantity due to combined advection and diffusion ($\mathrm{d}\dot{X}/\mathrm{d}x = 0$). The equation has been refactored here under the assumption of uniform cross-sectional area. The solution is

$$\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1} = \frac{1 - e^{Pex/L}}{1 - e^{Pe}} \tag{3.95}$$

where L is the center-to-center distance between regions and x is the position. Note that this equation contains a numerical singularity in the case of pure diffusion ($Pe = 0$). It matches Equation 3.93 when $x^\star = 1/2$, as shown by Figure 3.8. However, the model and the solution from Patankar are different at other positions. This may be due to one of the following reasons: (i) the model is based on the requirement that the flow rate of the quantity out of one region is the flow rate into the other ($\dot{X}_{1\mathrm{p}} + \dot{X}_{2\mathrm{n}} = 0$ at the interface plane) whereas Patankar's solution is based on the requirement that there is no storage in a differential space around the interface ($\mathrm{d}\dot{X}/\mathrm{d}x = 0$) or (ii) the assumption of equal Péclet numbers (used in the derivation of Equation 3.93 from Equation 3.89) is unreasonable. The Péclet number is extensive in nature (as discussed previously), so it may not be appropriate to assume that it remains equal as the adjacent regions are resized.

The previous evaluations are based on the condition that the flow rates of opposing transport equations are equal and opposite. This is true at an interface between regions because the flow rate into one region is the rate out the other. However, it is not necessarily the case across a region because the quantity may be stored within the region. If we relax the previous assumption and provide the values of the driving property in the bulk of the region and at both boundaries, then we can determine the rate of storage in a region:

$$\sum \dot{X} = \frac{\left(\gamma_{\mathrm{n}} - \gamma\right)\left(1 + e^{-Pe/2}\right) + \left(\gamma_{\mathrm{p}} - \gamma\right)\left(1 + e^{Pe/2}\right)}{R} \tag{3.96}$$

If there is no advection, then the rate of storage is proportional to the first-order approximation of the second derivative of the property over space:

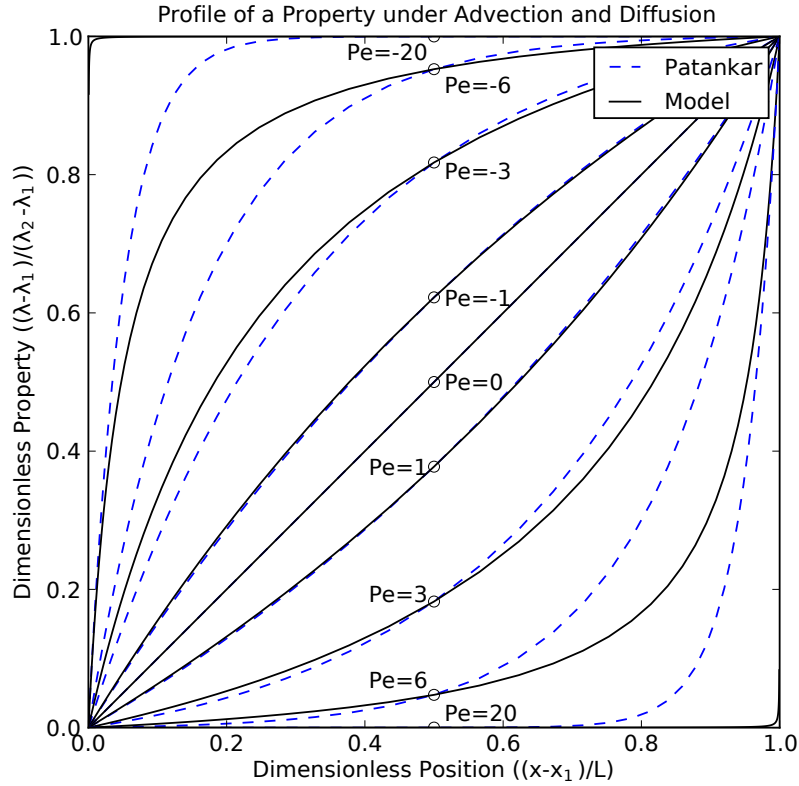$$\sum \dot{X} = \frac{2}{R}\left(\gamma_{\mathrm{n}} + \gamma_{\mathrm{p}} - 2\gamma\right) \tag{3.97}$$
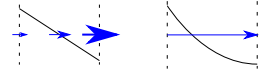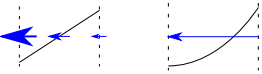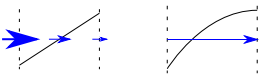
Figure 3.8: Center-to-center profile of a property between regions under advection and diffusion. The model is equivalent to the solution from Patankar [38] at the midplane ($x = L/2$).

Table 3.2 shows the implications of Equation 3.96. The third textual column and first graphic column indicate the rate of storage induced by positive or negative velocities and positive or negative property gradients under the condition of a linear property profile. The fourth textual column and second graphic column indicate the concavity of the profile under the condition of no storage. The curves are not to scale; Figure 3.8 gives the exact shape. The boundary-to-boundary profile across a region must either match the first or second graphic column (and third or fourth textual column). The center-to-center profile of a property must match the second graphic column—not the first since there is no storage at the interface between regions.

The first row of the table (3.2) indicates that if the property increases in the positive direction and the velocity is in the negative direction, then either the conserved quantity is being removed from the region or the profile is concave up, or both. If the gradient or the velocity is reversed, but not both, then the quantity is stored instead or the concavity changes sign. If both

the gradient and the velocity are reversed, then the storage regime and the concavity remain the same. If the material flow is from higher to lower property values, then the quantity is removed from the region; otherwise it is stored. The concavity is always such that the gradient is lower on the side receiving the advection.

Table 3.2: Scenarios of one-dimensional advection with diffusion.

Gradient $(\Delta\gamma)$	$\wedge$	Velocity (ϕ)	$\Leftrightarrow$	Intake $(\sum \dot{X})$	$\vee$	Inflection $(\Delta^2\gamma)$	Graphically: $\gamma_n \cdots \gamma \cdots \gamma_p$	or
< 0		< 0		> 0		< 0		
< 0		> 0		< 0		> 0		
> 0		< 0		< 0		> 0		
> 0		> 0		> 0		< 0		

The difference between the properties of adjacent regions is related to the flow rate between them by

$$\gamma_2 - \gamma_1 = \dot{X}\left(\frac{R_1}{1 + e^{Pe_1/2}} + \frac{R_2}{1 + e^{-Pe_2/2}}\right) \tag{3.98}$$

This follows from Equation 3.79 (implemented for each region) and conservation of the transported quantity at the interface. If the Péclet numbers are equal ($Pe_1 = Pe_2$) and the resistances are equal ($R_1 = R_2 = R$), then

$$R\dot{X} = \gamma_1 - \gamma_2 \tag{3.99}$$

which is typical diffusion. This is applicable even if there is bulk material flow (again, as long as $Pe_1 = Pe_2$). It confirms that the transport equation is a diffusion equation—only with upstream discretization so that advection can be properly determined. Since the local gradient is affected by advection, the rate of diffusion is generally not proportional to the local gradient at the interface (given by Equation 3.93) but rather the average gradient between the centers of the regions. Likewise, if there is no storage within a region along an axis then

$$R\dot{X} = \gamma_n - \gamma_p \tag{3.100}$$

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where $\dot{X} = \dot{X}_n = -\dot{X}_p$.

The rate of advection is the product of the material flow rate and the amount of the quantity per unit of material (i.e., specific quantity). In the case of material flow this specific quantity is unity, since the material is the quantity [26]. In the case of the translational advection the specific quantity is velocity, the gradient of which also drives property. In the case of thermal advection, the specific quantity is temperature times specific entropy. Temperature is the driving property for thermal diffusion, but specific entropy must be calculated from the temperature and pressure at the boundary.

Figure 3.9 shows the combined effects of advection and diffusion if the specific quantity is the same as the driving property for diffusion (e.g., translational advection). The advection and diffusion are evaluated at the interface of two regions with the same resistances and Péclet numbers. The property in the second region (γ_1) is arbitrarily five times the property in the first region (γ_2). The rate of diffusion is constant (in dimensionless units), as predicted by Equation 3.99. As advection is initially increased, the property at the interface is nearly the mean of the properties of the regions. The actual rate of advection is quite different from the ideal rate given by the upstream scheme. A correction must be applied because the property at the interface is not the property of the upstream region. Here, that correction is called *irreversible advection*. As the magnitude of the Péclet number becomes large, the irreversible advection becomes negligible because the interface takes on the property of the upstream region. **Give physical meaning of irreversible advection

**Add lambda1 - lambda2 = 4 both places

So far, we have evaluated the transport equations along one axis. It is possible to implement Equation 3.79 for all three dimensions simultaneously as long as the coordinate system is aligned with the principle axes of transport (Assumption 3).

Although the transport equation (3.79) contains an exponential, it is not equivalent to the exponential scheme. The exponential scheme is derived by (i) solving the advection/diffusion equation analytically for the profile of the driving property under the assumption of no storage and (ii) reintroducing the solution into the advection/diffusion equation without that original assumption [38, 39]. It results in a solution that is numerically singular unless there
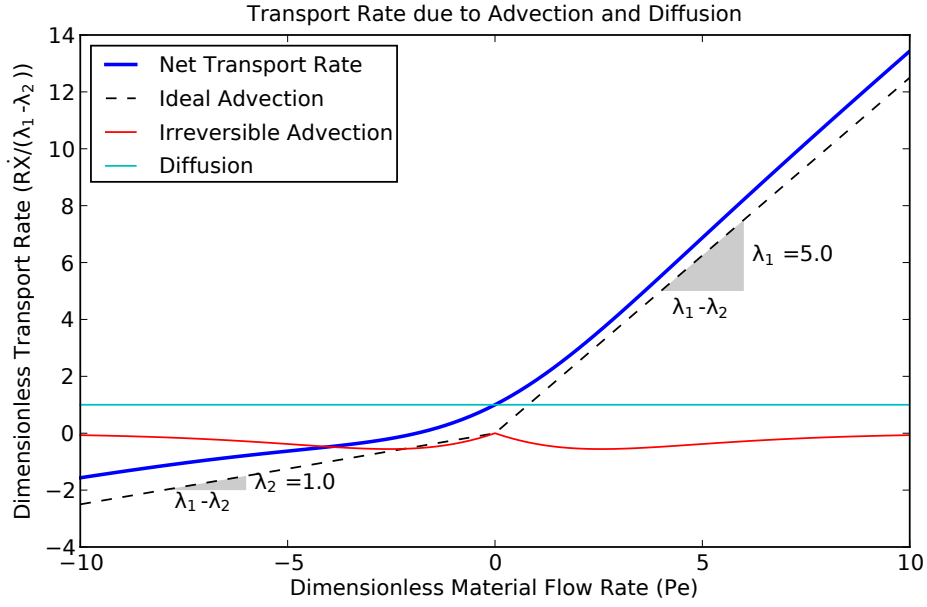
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Figure 3.9: Transport rate of a conserved quantity under mixed advection and diffusion.

is advection. The main argument against the exponential scheme—that it is computationally expensive—also applies to the proposed transport equation. However, the transport equation is used within a framework that (i) does not require a large number of regions for convergence and (ii) eliminates all nonlinear systems of equations. The argument may also be out of context now because it dates back to at least 1980 [38], when computational resources were relatively limited.

As demonstrated in Section 3.5, the traditional material derivative is the rate of diffusion. This holds for transport as well. The total rate of transport (Equation 3.75) can be expanded with the rates of advection and diffusion from Equations 3.76 and 3.78:

$$\dot{X}_{ij} = \dot{N}_{ij} \left(\frac{\partial X}{\partial N} \right)_{ij} + \left(\frac{\mathrm{D}X}{\mathrm{D}t} \right)_{ij} \tag{3.101}$$

We will take this to be the positive side of the region so that the derivatives are in the positive direction and assume that the material current is advective ($\dot{N} = -\phi A \rho = -\phi \partial N / \partial x$). Then dropping the subscripts,

$$\dot{X} = -\phi \frac{\partial X}{\partial x} + \frac{\mathrm{D}X}{\mathrm{D}t} \tag{3.102}$$

Since the model uses a Eulerian perspective, the total transport rate $\dot{X}$ is actually a partial derivative in the form of $\partial X/\partial t$. After rearranging,

$$\frac{\mathrm{D}X}{\mathrm{D}t} = \frac{\partial X}{\partial t} + \phi \frac{\partial X}{\partial x} \tag{3.103}$$

Usually the scalar property in the material derivative is intensive (e.g., γ, the driving property for diffusion). Dividing by $\partial X/\partial \gamma$,

$$\frac{\mathrm{D}\gamma}{\mathrm{D}t} = \frac{\partial \gamma}{\partial t} + \phi \frac{\partial \gamma}{\partial x} \tag{3.104}$$

and generalizing to three dimensions,

$$\frac{\mathrm{D}\gamma}{\mathrm{D}t} = \frac{\partial \gamma}{\partial t} + \boldsymbol{\phi}\boldsymbol{\nabla}\gamma \tag{3.105}$$

This is the definition of the material derivative [40].

3.7.1 Material Transport, Compression, and Normal Translational Advection

As stated by James Clerk Maxwell, "Mass transfer is due partly to the motion of translation and partly to that of agitation" [46]. The "translation" component of mass transfer is described by the normal force equation. It follows from Equations 3.83 and 3.85 with the normal component of translational momentum as the transported quantity and the normal component of velocity as the driving property. The subscript for the configuration (j) has been dropped, but this equation still only applies to a single configuration (in a single region):

$$\beta m\dot{\Phi}_{\mathrm{D}\perp i} = \frac{kA_i}{L_i}\left(\phi_{\perp i} - \phi_\perp\right)\left(1 + e^{\mp\beta M\phi_\perp/2kA_i}\right) \tag{3.106}$$

where $m\dot{\Phi}_{\perp i}$ is the non-equilibrium normal force on boundary i or rate of translational momentum into the region through the boundary due to diffusion. The variable $\phi_{\perp i}$ is the normal component of velocity at the boundary. The bulk velocity in the region in the same direction ($\phi_\perp$) may be considered known since it is a state of the momentum balance (Section 3.4.3). The variable β represents the *dynamic compressibility* which describes the extent to which a non-equilibrium normal force causes or requires transient compression. It can be estimated from the generalized definition of resistivity (Equation 3.82):

$$\beta = \frac{3\tau}{\lambda^2 \rho m} \tag{3.107}$$

**write this and other transport resistivities in terms of 3/(lambda*thermal velocity) Dynamic compressibility is the reciprocal of bulk viscosity as a dynamic (rather than kinematic) viscosity. Although bulk viscosity differs from shear viscosity [44, 47–49], the same initial estimate is used.

The "agitation" component is described by the material transport equation. It also follows from Equations 3.83 and 3.85. Material is the transported quantity and density is the driving property:

$$\eta \dot{N}_{\mathrm{D}i} = \frac{kA}{L}(\rho_i - \rho)\left(1 + e^{\mp\eta\phi_\perp L/2k}\right) \tag{3.108}$$

where $\dot{N}_i$ is the diffusive material current into the region through boundary i and ρ_i is the density or volumic particle number at the boundary. The density in the region (ρ) may be considered known, since it is a state of the material balance (Section 3.4.1). If a species is isochoric in a phase (e.g., liquid H_2O), then it will not diffuse.

The material resistivity, η, can be estimated from the generalized definition of resistivity (Equation 3.82):

$$\eta = \frac{3\tau}{\lambda^2} \tag{3.109}$$

The material resistivity is the reciprocal of self diffusivity, which is the ability of trace particles of a species to diffuse through other particles of the same species [26]. This is the essence of Equation 3.108; it describes the rate of diffusion through an advected stream of particles of the same type.

The total current into the region through boundary i is the sum of the diffusive ("agitation") and advective ("translation") currents:

$$\dot{N}_i = \dot{N}_{\mathrm{D}i} \pm \phi_{\perp i}\rho_i A_i \tag{3.110}$$

where the positive of $\pm$ is for the negative boundaries and the negative is for positive boundaries, since current is positive into the region. The generalized advection equation (Equation 3.76) is singular and not applicable for material advection.

The force on boundary i is due to the sum of the diffusive and advective forces:

$$m\dot{\Phi}_{\perp i} = m\dot{\Phi}_{\mathrm{D}\perp i} \pm m\dot{N}_i\phi_{\perp i} \tag{3.111}$$

where the advective term (second on the right) follows from Equation 3.76. Thermodynamic pressure is excluded here, but it is included in the translational momentum balance (Equation 3.28).

The material transport equation is closely related to Fick's law. If we assume that the bulk velocity (and advective current) is zero along the axis of transport and the area factor is unity, then the material transport equation (3.108) reduces to

$$\eta \dot{N}_i = 2\frac{A}{L}(\rho_i - \rho) \tag{3.112}$$

If the density gradient is uniform, then there is no material storage due to diffusion ($\dot{N}_{\mathrm{n}} = -\dot{N}_{\mathrm{p}} = AJ$). In that case, we can combine the negative- and positive-side equations as:

$$\eta J = \frac{\rho_{\mathrm{n}} - \rho_{\mathrm{p}}}{L} \tag{3.113}$$

Taking the limit as length goes to zero and generalizing to three dimensions,

$$\eta \mathbf{J} = -\nabla \rho \tag{3.114}$$

which is Fick's first law $[35, 46, 49\text{--}52]$.

Fick's law also appears in other forms in the literature. In theory, any intensive thermodynamic property could be used as long as it is sufficient to fix the thermodynamic state of the species given its temperature. The choice affects the transport rate and thus the resistivity must be set properly, but it will not affect the equilibrium. All of the intensive thermodynamic properties are uniform between two regions in thermodynamic equilibrium (aside from outside forces), and the equilibrium point is determined by the conservation equations (Sections 3.4 and 3.10).

Since the species has constant specific mass, we can write Fick's law in terms of mass density $[29, 46]$:

$$m\eta J = -\nabla(m\rho) \tag{3.115}$$

If the species exists in small amounts within an otherwise uniform mixture, then the extensive volume (in $\rho = N/V$) can be replaced by the total amount or mass of the phase. For mole fractions, this is $[39, 46, 52, 53]$

$$\frac{V\eta}{N_{\mathrm{tot}}} J \approx -\nabla\left(N/N_{\mathrm{tot}}\right) \tag{3.116}$$

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where N is the number of particles of the transported species and N_{tot} is the total number of particles in the phase. For mass fractions, we can write this as [39, 46, 52, 53]

$$\frac{mV\eta}{M_{\text{tot}}} J \approx -\nabla\left(M/M_{\text{tot}}\right) \tag{3.117}$$

We can also write Fick's law in terms of partial pressure [46]:

$$\left(\frac{\partial p}{\partial \rho}\right)_T \eta J = -\nabla p \tag{3.118}$$

For ideal gases, this is

$$T\eta J = -\nabla p \tag{3.119}$$

Since the material resistivity is roughly the base resistivity factor divided by specific volume (see Equation 3.109), we can write this as (again, assuming ideal gas)

$$\alpha J = -\nabla \ln p \tag{3.120}$$

For an isothermal ideal gas, Equation 3.14 implies that

$$T\alpha J = -\nabla g \tag{3.121}$$

Since α is only dependent on temperature and fixed properties (specific mass and particle diameter), chemical potential (here, g) may be preferred as the driving property for material diffusion. The magnitude of the diffusion rate in the previous forms of Fick's law is coupled to the density, which is affected over time by the diffusion itself (if storage is allowed). We can also express Fick's law in terms of chemical potential for species that are not ideal gases [54]:

$$\eta\left(\frac{\partial g}{\partial \rho}\right) J = -\nabla g \tag{3.122}$$

If temperature is uniform, then this is

$$\frac{\eta}{\rho}\left(\frac{\partial p}{\partial \rho}\right)_T J = -\nabla g \tag{3.123}$$

If the species is an ideal gas, then this again reduces to Equation 3.121. The model uses density as the driving property for diffusion because the boundary pressure is needed for the momentum balance (Section 3.10.2) and density is available as a dynamic property anyway. Pressure is an explicit function of density as long as the species is compressible (Equation 3.6), but pressure cannot generally be expressed as a function of specific Gibbs energy (except in special cases).

3.7.2 Friction and Transverse Translational Advection

The friction or shear force along a boundary follows the generalized diffusive transport equation (3.83) with an adjustment factor. The transported quantity is a component of translational momentum parallel to the boundary ($m\Phi_\parallel$) and the driving property is the component of velocity with the same orientation ($\phi_\parallel$):

$$\zeta \dot{m\Phi}_{\parallel i}{}' = \frac{Nu_\Phi kA}{L}\left(\phi_{\parallel i} - \phi_\parallel\right)\left(1 + e^{\mp \zeta M \phi_\perp / 2kA}\right) \tag{3.124}$$

where $\dot{m\Phi}_{\parallel i}{}'$ is the shear force. The reason for the prime superscript will be discussed below. The boundary velocity ($\phi_{\parallel i}$) is an effective velocity. Its usage does not imply that the velocity is uniform over the boundary (which would generally lead to discontinuities in the velocity at the edges of the boundary). The fluidity, ζ, can be estimated from the generalized definition of resistivity (Equation 3.82):

$$\zeta = \frac{3\tau}{\lambda^2 \rho m} \tag{3.125}$$

Fluidity is the reciprocal of shear viscosity as a dynamic (rather than kinematic) viscosity. If two adjacent regions have zero fluidity (ζ), then the parallel components of their velocities are equal and the number of states is reduced by two. Translational momentum will flow between the regions without loss.
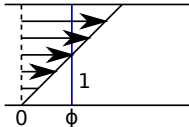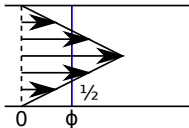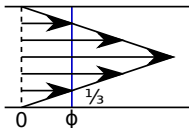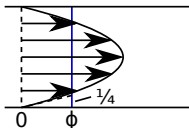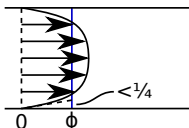
The additional variable Nu_Φ is the *translational Nusselt number*—the analog of the traditional or thermal Nusselt number for the diffusion of translational momentum. It allows the shear force equation to be used at relatively coarse levels of discretization. It is defined as the ratio of the average inward velocity gradient along the perimeter divided by the difference between the boundary velocity and the bulk velocity over the distance from the boundary to the center of the region:

$$Nu_\Phi \equiv \left(\frac{\partial \phi_\parallel}{\partial x}\right)_i \bigg/ 2\frac{\phi_{\parallel i} - \phi_\parallel}{L_{\mathrm{x}}} \tag{3.126}$$

Table 3.3 summarizes the shear shape factor given two assumptions: (i) the material density is uniform and (ii) the boundary velocities are uniform around the perimeter. The first assumption implies that the bulk, mass-average velocity is equal to the volume-average velocity. The shape factor is one in a two-dimensional case (where no force is applied the third dimension,

e.g., its length is infinite) with a linear velocity profile. The velocity changes from the boundary velocity to the bulk velocity (blue line) in half of the distance between the boundaries. The shape factor is two in a two-dimensional case with a piecewise linear velocity profile. Then, the velocity changes from the boundary velocity to the bulk velocity in one fourth the distance between the boundaries. The shape factor is three in a three-dimensional case with a piecewise linear velocity profile because the volume of a pyramid is one third the product of its base area and height. The shape factor is four if the flow is fully developed and laminar (Hagen-Poiseuille flow, discussed below). If the flow is turbulent, then the shape factor is greater than four; the velocity gradient at the wall is greater than for laminar flow.

Table 3.3: Values of the shear shape factor.

Shape Factor (Nu_Φ)	Profile	Number of Dimensions	Description
1		2	Couette flow (linear)
2		2	Piecewise linear (triangle)
3		3	Piecewise linear (pyramid)
4		3	Laminar fully developed (parabola)
> 4		3	Turbulent (higher order)

**Make the blue line lighter and more thick (or refer to solid vertical line) **use "shear shape factor"->translational Nusselt number

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Translational momentum is advected according to the generalized advective transport equation (3.76). In terms of the present variables, this is

$$\dot{m}\Phi_{Aij} = \dot{N}_{ij} m_j \dot{\phi}_{ij} \tag{3.127}$$

The model does not directly use the shear force equation (3.124) because the forces apply torques and the model is based on the assumption that rotational momentum is not stored (see Section 3.4.2). This is the reason for the prime superscript in the shear force equation (3.124). The conservation of rotational momentum (Equation 3.27a) gives one of the four equations required for the four boundaries around the perimeter of the region along the x axis. The first of the remaining three equations requires that the total force in the y direction is the force determined by the y-direction shear force equations:

$$\boxed{\dot{m}\Phi_{ynz} + \dot{m}\Phi_{ypz} = \dot{m}\Phi'_{ynz} + \dot{m}\Phi'_{ypz}} \tag{3.128}$$

Similarly in the z direction:

$$\boxed{\dot{m}\Phi_{zny} + \dot{m}\Phi_{zpy} = \dot{m}\Phi'_{zny} + \dot{m}\Phi'_{zpy}} \tag{3.129}$$

The final equation requires that the torque applied to the y-boundaries opposes the torque applied to the z-boundaries to the same extent calculated by the shear force equations:

$$\boxed{\left(\dot{m}\Phi_{zny} - \dot{m}\Phi_{zpy}\right)L_z + \left(\dot{m}\Phi_{ynz} - \dot{m}\Phi_{ypz}\right)L_y = \left(\dot{m}\Phi'_{zny} - \dot{m}\Phi'_{zpy}\right)L_z + \left(\dot{m}\Phi'_{ynz} - \dot{m}\Phi'_{ypz}\right)L_y}$$
$$\tag{3.130}$$

Similar equations apply to the perimeters around the y and z axes. The translational advection equation (3.127) is applied directly; it is assumed that it interacts with the center of the region and produces no torque.

In three dimensions, this method involves a system of twelve equations which can be solved for the twelve shear forces (two for each of six boundaries). The shear forces in the x direction

are:

$$4\dot{m}\Phi_{ynx} = 3\dot{m}\Phi'_{ynx} + \dot{m}\Phi'_{ypx} + \frac{L_x}{L_y}\left(\dot{m}\Phi'_{xny} - \dot{m}\Phi'_{xpy}\right) \tag{3.131a}$$

$$4\dot{m}\Phi_{ypx} = 3\dot{m}\Phi'_{ypx} + \dot{m}\Phi'_{ynx} + \frac{L_x}{L_y}\left(\dot{m}\Phi'_{xpy} - \dot{m}\Phi'_{xny}\right) \tag{3.131b}$$

$$4\dot{m}\Phi_{znx} = 3\dot{m}\Phi'_{znx} + \dot{m}\Phi'_{zpx} + \frac{L_x}{L_z}\left(\dot{m}\Phi'_{xnz} - \dot{m}\Phi'_{xpz}\right) \tag{3.131c}$$

$$4\dot{m}\Phi_{zpx} = 3\dot{m}\Phi'_{znx} + \dot{m}\Phi'_{znx} + \frac{L_x}{L_z}\left(\dot{m}\Phi'_{xpz} - \dot{m}\Phi'_{xnz}\right) \tag{3.131d}$$

Thus the force applied to a boundary is three fourths of the force calculated directly from Equation 3.124 plus one fourth of the calculated force on the opposing boundary minus the calculated forces on the perpendicular faces which are scaled to oppose the torques implied by Equation 3.124. This is shown graphically in Figure 3.10 for a cubic region ($L_x = L_y = L_z$). The sum of the applied forces is equal to the forces calculated directly from Equation 3.124:

$$\dot{m}\Phi_{ynx} + \dot{m}\Phi_{ypx} + \dot{m}\Phi_{znx} + \dot{m}\Phi_{zpx} = \dot{m}\Phi'_{ynx} + \dot{m}\Phi'_{ypx} + \dot{m}\Phi'_{znx} + \dot{m}\Phi'_{zpx} \tag{3.132}$$

Similar equations apply around the y and z axes.
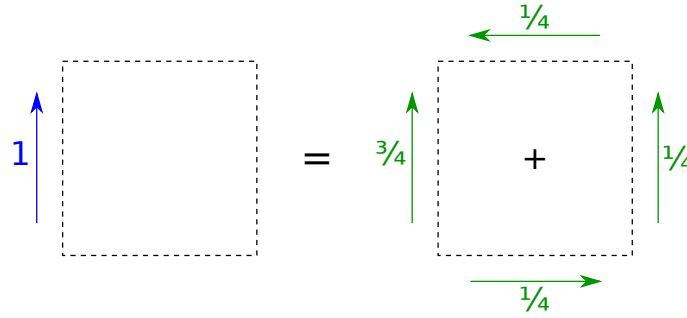
Figure 3.10: Weighting scheme to achieve zero torque. The left side is the force applied to a boundary and the right side contains the forces calculated from Equation 3.124.

This mapping of shear velocities to shear forces is different from Stokes' viscous deformation law [39]. Both methods impose zero torque (i.e., conservation of rotational momentum without storage), but a discrete implementation of Stokes' viscous deformation law would do so at every boundary. This is not necessary; the boundaries have zero thickness and thus zero moment. However there is a moment from the boundaries to the center of the control volumes. Thus the model imposes zero torque on each control volume as a whole.

The model and the Navier-Stokes equations (via Stokes' viscous deformation law) give the same result for incompressible flow, which is shown in Section 3.10.2. In order to achieve this the full, compressible Navier-Stokes equations require volumetric divergence terms ($\nabla \cdot \boldsymbol{\phi}$). The model does allow compressible flow; its effects are included in the dynamic compressibility of the normal force equation (3.106).

If the normal bulk velocity is zero, then the shear force equation reduces to

$$\dot{m}\Phi_{\|i} = \frac{2Nu_\Phi A}{\zeta L}\left(\phi_{\|i} - \phi_\|\right) \tag{3.133}$$

If the velocity gradient is uniform ($Nu_\Phi = 1$), then translational momentum is not stored due to diffusion ($\dot{m}\Phi_{\|n} = -\dot{m}\Phi_{\|p} = AJ$). In that case, we can combine the negative- and positive-side equations as:

$$J = \frac{\phi_{\|n} - \phi_{\|p}}{\zeta L} \tag{3.134}$$

This maps directly to the actual shear stress if there is no shear force from the other two boundaries along the perimeter. It is the first-order approximation to Newton's law of viscous shear, which describes Couette flow [55].

The shear force equation results in the expected pressure loss for fully-developed laminar pipe flow (i.e., Hagen-Poiseuille flow). Suppose that material is flowing in the x direction with velocity ϕ through a region with dimensions L_x, L_y, and L_z. The bulk velocities in the y- and z-directions are zero and the x-direction velocity is zero at the y- and z-boundaries (i.e., no slip). According to Equation 3.124, the total shear force on the y- and z-boundaries is

$$\dot{m}\Phi_{\text{tot}} = -\frac{4Nu_\Phi L_x \phi}{\zeta}\left(\frac{L_z}{L_y} + \frac{L_y}{L_z}\right) \tag{3.135}$$

If the flow is fully developed, steady, and laminar, then $Nu_\Phi = 4$. We may write the equation in terms of the hydraulic diameter ($D \equiv 4A/P$) [53], which is $2L_y L_z/(L_y + L_z)$ in this case. If there are no other forces the shear force must be balanced by the normal force ($L_y L_z \Delta p = \dot{m}\Phi_{\text{tot}}$; see the conservation of translational momentum in Section 3.4.3). With these assumptions and substitutions,

$$\Delta p = \frac{64 L_x \phi}{\zeta D^2}\left(\frac{2}{2 + \frac{L_y}{L_z} + \frac{L_z}{L_y}} - 1\right) \tag{3.136}$$

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If we assume that the cross section is square ($L_y = L_z$), then this reduces to

$$\Delta p = -\frac{32 L_x \phi}{\zeta D^2} \tag{3.137}$$

which is directly related to Poiseuille's law. It can be derived by integrating a differential representation of the shear force equation (3.124) with a translational Nusselt number of one under the assumption of uniform pressure and a no-slip condition around a circular pipe [56]. This implies that the model should give the same result without the shape factor (i.e., $Nu_\Phi = 1$) under a sufficiently fine level of discretization. As mentioned previously, the shape factor is introduced to allow much coarser levels of discretization, and here it is set to four.

The model cannot directly describe turbulence because it assumes that the rotational momentum is zero. This implies that eddies are not generated or are dissipated immediately upon generation. A full description would require equations for the storage, exchange, and transport of rotational momentum. Instead, correlations for turbulent flow are cast into the shape factor, which may vary with time and depend on the conditions. This approach is consistent with the statement by Patankar [38]: "From a computational viewpoint, a turbulent flow within this framework is equivalent to a laminar flow with a rather complicated prescription of viscosity." Here the adjustment (Nu_Φ) is separate from the fluidity (or reciprocal of viscosity).

If rotational momentum were included, it is plausible that at a sufficiently fine level of discretization the model could describe turbulence. In reality, shear force generates eddies that drive material towards alternating boundaries around the perimeter—normal to the direction of primary flow. This effect would decrease the advection-adjusted length between the bulk velocity and a boundary (see Equation 3.124) and increase the shear force for any velocity difference. The criteria for the effect is that a sufficient amount of translational momentum is diverted from the direction of primary flow towards a boundary (e.g., by surface roughness). It is a positive feedback mechanism; as more translational momentum is diverted towards the boundary due to shear force, more shear force is produced, until the translational momentum in the primary direction is sufficiently depleted. Suppose we let ω be the diversion angle at the onset of the positive feedback. Then the Péclet number in the applicable shear force equation

is

$$Pe = \frac{\zeta M \phi \sin \omega}{kA} \tag{3.138}$$

where ϕ is the bulk velocity in the primary direction. If we assume that the cross section is square, then the hydraulic diameter is the length of a side ($D = L = V/A$). If we also assume that the area factor is one ($k = 1$), then

$$Pe = m\rho\zeta D\phi \sin \omega \tag{3.139}$$

The factor $m\rho\zeta D\phi$ is the Reynolds number; therefore

$$Pe = Re \sin \omega \tag{3.140}$$

The discretization scheme becomes nearly saturated (as the upwind scheme) at roughly $Pe = 10$ (see Figure 3.6) whereas turbulence begins at roughly 2300 [56]. If we assume that turbulence corresponds to saturation of the discretization scheme, then $\omega \approx 0.25°$.

3.7.3 Thermal Conduction and Advection

Like friction, thermal conduction follows the form of the general transport equation (3.79) with an adjustment factor. Heat (Q) is the conserved quantity and temperature (T) is the driving property.

$$\theta\dot{Q}_i = \frac{Nu_Q kA}{L}(T_i - T)\left(1 + e^{\mp\theta N c_v \phi_\perp/2kA}\right) \tag{3.141}$$

The variable T_i is the temperature at boundary i and $\dot{Q}_i$ is the diffusive heat flow rate into the region through the boundary. The bulk temperature in the region (T) may be considered known, since it is a state of the energy balance (Section 3.4.4). The thermal resistivity, θ, can be estimated from the generalized definition of resistivity (Equation 3.82):

$$\theta = \frac{3\tau}{\lambda^2 \rho c_v} \tag{3.142}$$

where the partial derivative is taken at constant volume because the regions have fixed volume. Thermal resistivity is the reciprocal of thermal conductivity.

The additional variable Nu_Q is the traditional or thermal Nusselt number. It allows the thermal conduction equation to be used at relatively coarse levels of discretization. It is the

ratio of the average inward temperature gradient along the perimeter divided by the difference between the boundary temperature and the bulk temperature over the distance from the boundary to the center of the region:

$$Nu_Q \equiv \left(\frac{\partial T}{\partial x}\right)_i \bigg/ 2\frac{T_i - T}{L_x} \tag{3.143}$$

Here the Nusselt number is defined more generally than usual [53]; it need not be used at a solid boundary. It is the ratio of convective (advective plus diffusive) heat transfer to conductive (diffusive) heat transfer. The additional heat that is advected past the boundary must also diffuse in the normal direction through the boundary. Thus it may be clearer to describe this Nusselt number as the actual temperature gradient at the boundary divided by the temperature gradient that would exist at the boundary if it were linear. For fully developed laminar flow in a circular pipe under a uniform boundary temperature the Nusselt number is approximately 3.66 and under uniform boundary heat flux it is 48/11 or approximately 4.36 [53].

Heat is advected according to the generalized advective transport equation (3.76). In terms of the present variables, this is

$$\dot{Q}_{Aij} = \dot{N}_{ij} s_{ij} T_{ij} \tag{3.144}$$

If the bulk velocity (and current) is zero along the axis of transport and the area factor and Nusselt number are unity, then the thermal conduction equation (3.141) reduces to

$$\theta \dot{Q}_i = \frac{2A}{L}(T_i - T) \tag{3.145}$$

If the temperature gradient is uniform, then energy is not stored due to diffusion ($\dot{Q}_n = -\dot{Q}_p = AJ$). In that case, we can combine the negative- and positive-side equations as:

$$\theta J = \frac{T_n - T_p}{L} \tag{3.146}$$

which is the first-order approximation to Fourier's law or the law of heat conduction [35, 53].

The thermal Nusselt number is related to the heat transfer coefficient by

$$Nu_Q = \frac{h\theta L}{1 + e^{\mp \theta N c_v \phi_\perp / 2kA}} \tag{3.147}$$

where $L/(1 + e^{\mp \theta N c_v \phi_\perp / 2kA})$ is the characteristic length. Substituting this into the thermal conduction equation (3.141) under the assumption that the area factor is unity ($k = 1$),

$$\dot{Q}_i = hA(T_i - T) \tag{3.148}$$

which is Newton's law of cooling [53].

3.8 Transport Properties

Highlights:

- By default, the model estimates all diffusion properties based on the kinetic theory of gases, which only depends on the temperature, pressure, and the particle's mass and diameter. It includes refinements where they are available and necessary.

Due to the assumptions implicit in the diffusive transport equation (3.78), the equations for the dynamic compressibility (3.107), material resistivity (3.109), fluidity (3.125), and thermal resistivity (3.142) are only taken to be estimates. However, they are useful if more precise data is not available. Those equations require the collision interval (τ) and the mean free path (λ), which were given for the exchange properties (Section 3.6) under additional assumptions from the kinetic theory of gases.

The estimate of fluidity (Equation 3.125) predicts that fluidity is independent of pressure or specific volume, which accurately matches observations [26]. However, the fluidity generally falls more rapidly with temperature than predicted [26]. Higher accuracy can be achieved for many common gases using the correlations by Svehla, McBride, and Gordon [57, 58]. Those correlations have the following form:

$$\zeta = b_{\zeta 1} \ln T + b_{\zeta 2}/T + b_{\zeta 3}/T^2 + b_{\zeta 4}$$ (3.149)

Higher accuracy can be achieved for thermal resistivity than Equation 3.142 using the correlations from the same source [57, 58]:

$$\theta = b_{\theta 1} \ln T + b_{\theta 2}/T + b_{\theta 3}/T^2 + b_{\theta 4}$$ (3.150)

3.9 Electrochemical Reactions

**Address comments from discussion with Haynes 6/3/13.

Highlights:

- The Butler-Volmer equation is used in the model but is first derived from other model equations.

> - Thermal advection is essential to the chemical reaction; it captures the enthalpy of formation (see Section 3.10.3). Translational advection may be excluded without loss of accuracy in a typical PEMFC since the reaction occurs on stationary catalyst sites. However, it is included in the model for completeness and may be important in other devices.

The electrochemical reactions are described using the Butler-Volmer equation [51, 59, 60], but we will first derive it from the transport equations of the model (Section 3.7). This helps to provide insight into the physical meaning of the Butler-Volmer equation and also to further justify the transport equations.

3.9.0.1 Introduction

The electrochemical reactions occur near the junction of the catalyst (e.g., platinum), which has free (conductance-band) electrons (e^-), and the ionomer, which has free protons (H^+). The junction is located in the catalyst layer as shown in Figure 3.11. When the catalyst and the ionomer are joined (during the manufacture of the membrane electrode assembly), electrons begin to diffuse from the catalyst into the ionomer, where they are minority charge carriers. Likewise, protons diffuse from the ionomer into the catalyst where they are minority carriers. This forms an injection region surrounding the junction where the catalyst is positively charged and the ionomer is negatively charged.[xii]

After the catalyst and ionomer are joined, diffusion decreases as the carrier density becomes more uniform between the majority and minority regions. Meanwhile, excess charge builds on the minority side. It produces a built-in electric field which is directed from the catalyst (positive) to the ionomer (negative). The electric field causes charge carriers to drift. The drift or advection increases as the excess charge and the electric field increase. Eventually the advection cancels diffusion; then the charge difference is constant and equilibrium is achieved.

Figure 3.12 shows the case where there is a steady-state reaction. Material resistivity is

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[xii]Normally (aside from the junction) the catalyst is charge neutral because the density of e^- is equal to the density of platinum ions (Pt^+) for example. If H^+ is introduced, then the catalyst is positively charged. Likewise, the ionomer is normally charge neutral because the density of H^+ is equal to the density of sulfonic acid (SO_3^-) groups. If e^- is introduced the ionomer is negatively charged.
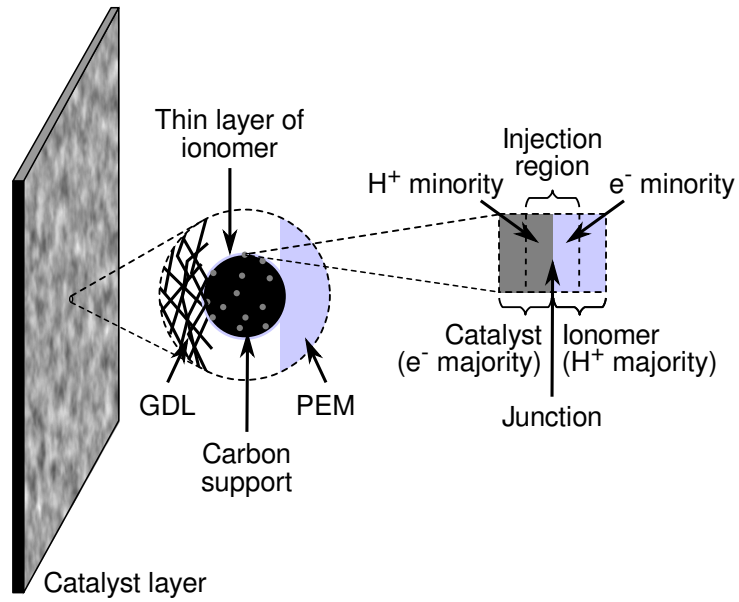
Figure 3.11: The electrochemical reaction occurs in the injection region near the catalyst/ ionomer junction (elaborated from [61, p. 74] and [62]).
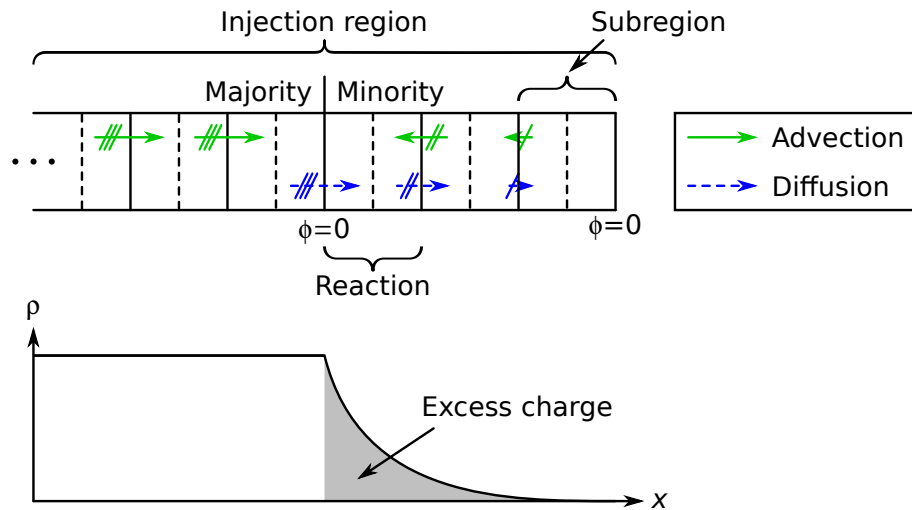

Figure 3.12: Advection, diffusion, and density of a charge carrier across the injection region. The case for the second charge carrier is a mirror image of the scenario depicted here.

essentially zero for majority carriers (this is assumed in the derivation of Ohm's law, see Section 3.11.3.2), which means that the carrier density is uniform in the majority region. All of the current through the majority region (and the conductive materials connected to it) is advective. The velocity is zero at the junction, however; carriers can only diffuse across the junction. In the bulk of the minority region, advection cancels diffusion.[xiii] Therefore at steady state the diffusion current across the junction is equal to the reaction rate. The force from an external circuit, relative to any chemical bias, affects the drift velocities and the rates of advection. It alters the rate of diffusion through the minority region as well (since advection cancels diffusion there), which builds back to the junction where the diffusion rate is the reaction rate.

3.9.0.2 Equations

Since advection cancels diffusion in the minority regions, the total *material current* or rate of material flow is zero. If the two minority subregions have the same Péclet numbers for a given charge carrier (discussed later), then the model (Equations 3.99 and 3.110) implies that

$$0 = A\phi\rho + \frac{\rho_1 - \rho_2}{R} \tag{3.151}$$

where ϕ is the velocity at the junction and ρ is the density there. The resistance (R) is $\eta L/kA$ (see Equation 3.80, where the resistivity r is the material resistivity η). Therefore,

$$0 = \eta\phi\rho + k\frac{\rho_1 - \rho_2}{L} \tag{3.152}$$

We can write this as a differential equation (taking the limit as $L \to 0$):

$$\frac{\eta\phi}{k}\rho = \frac{d\rho}{dx} \tag{3.153}$$

We will integrate the previous equation to determine the minority carrier densities in the middle of the two regions relative to the densities at the junction. Over the positive half of first region, the solution is

$$\rho_{a1} = \rho_a e^{-Pe_a/2} \tag{3.154}$$

where the Péclet number (Pe) is $\eta\phi L/k$. The subscript a indicates the first charge carrier, which is a minority carrier in the first region (subscript 1). Thus ρ_a is the density of the first charge

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[xiii]The materials (catalyst and ionomer) are insulators to the minority carriers. There can be no net flow of minority carriers at steady state (aside from cross-over current).

carrier at the junction and ρ_{a1} is the density of the first carrier in the first region (where it is a minority). Over negative half of second region,

$$\rho_{b2} = \rho_b e^{Pe_b/2} \tag{3.155}$$

These equations indicate that the minority carrier densities in the respective regions (electrons in the ionomer and protons in the catalyst) depend on the related densities at the junction (ρ_a and ρ_b) and the dimensionless material flow rates into those regions ($-Pe_a$ and Pe_b). The densities at the junction are fixed by the majority regions since the material resistivities are essentially zero there. As the flow rates increase, so do the densities in the minority regions.

Now we will apply the differential solutions (Equations 3.154 and 3.155) to the material diffusion equation (3.108) for the two half regions adjacent to the junction. For the first region this reduces to

$$\dot{N}_{a1} = \frac{\rho_a kA}{\eta_a L}\left(e^{-Pe_a/2} - e^{Pe_a/2}\right) \tag{3.156}$$

where $\dot{N}_{a1}$ is the rate of diffusion of the first carrier a into the first region (where it is a minority). For the second region and the second carrier,

$$\dot{N}_{b2} = \frac{\rho_b kA}{\eta_b L}\left(e^{Pe_b/2} - e^{-Pe_b/2}\right) \tag{3.157}$$

We can determine the Péclet numbers from steady-state momentum balances that involve the electrical and chemical potentials. We will assume that the charge carriers are consumed by the reaction or they are produced and their velocity is equal to the conversion velocity (see Section 3.5.2). We will also assume that the dynamic compressibility is zero and there are also no body forces. Then the conservation of translational momentum (Equation 3.28) of a differential region reduces to

$$A\,\mathrm{d}p_i = \sum \dot{m}\Phi_{\mathrm{D}i} + \dot{m}\Phi_{\mathrm{D}} \tag{3.158}$$

We will take the difference in pressure to be directed from the reactants to the products. If the charge carriers are consumed by the reaction, then the difference in pressure yields a force on the carriers away from the junction—in the negative direction on the negative side of the junction and in the positive direction on the positive side. Stated alternatively, the reactants are at the junction and the products are just outside it. We will assume that the only diffusive

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boundary force is the normal force at the junction, which is the electrical force $(-NzE)$. We will also assume that the exchange force is due solely to the interaction with the stationary solid (by Equation 3.63, $m\dot{\Phi}_D = -N\phi/\mu$). Therefore

$$0 = zE + \frac{\phi}{\mu} \pm \frac{A}{N}dp \tag{3.159}$$

where the positive of $\pm$ is for the region on the negative side of the junction and the negative is for the positive side. Multiplying by the length of the differential region (dx),

$$0 = \left(zE + \frac{\phi}{\mu} \right)dx \pm vdp \tag{3.160}$$

where v is the specific volume of the charge carriers within the solid phase. We will assume that the temperature, the electric field, and the specific drag force are uniform. Integrating the previous equation from the actual state of the reactants to the reference state (including enthalpy of formation) and from the reference state to the actual state of the products,

$$0 = \left(zE + \frac{\phi}{\mu} \right)L \pm \Delta g \tag{3.161}$$

where L is a characteristic length of the reaction. We will assume that the mobility is related to the material resistivity by the Einstein relation ($\mu\eta T = 1$, see Section 3.11.3.3); then

$$\phi\eta L = \frac{\mp\Delta g - zEL}{T} \tag{3.162}$$

which is the Péclet number (Pe). If the carrier carriers are consumed by the reaction and the catalyst is in the first region (H^+ is the minority carrier there, with $z = 1$), then

$$Pe_a = -\frac{\Delta g + EL}{T} \tag{3.163}$$

The ionomer is in the second region and $Pe_b = -Pe_a$, since e^- is the minority carrier there (with $z = -1$).

The total reaction rate is the sum of the diffusion rates into the minority regions:

$$\dot{N} = \dot{N}_{a1} + \dot{N}_{b2} \tag{3.164}$$

Using Equations 3.157 and letting Pe denote Pe_a (Equation 3.163) or $-Pe_b$,

$$\dot{N} = \frac{kA}{L}\left(\frac{\rho_a}{\eta_a} + \frac{\rho_b}{\eta_b} \right)\left(e^{-Pe/2} - e^{Pe/2} \right) \tag{3.165}$$

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If the catalyst is on the negative side then the total reaction rate ($\dot{N}$) is the negative of the electrical current ($-zI$). We can write this as

$$zJ = J^o \left(e^{Pe/2} - e^{-Pe/2} \right) \tag{3.166}$$

which is the Butler-Volmer equation [51, 59, 60] where zJ is the electrical current density, the Péclet number (Pe) is $-(\Delta g + EL)/T$, and the exchange current density is

$$\boxed{J^o = \frac{k}{L} \left(\frac{\rho_a}{\eta_a} + \frac{\rho_b}{\eta_b} \right)} \tag{3.167}$$

**write this in terms of tauprime (see phase change) The factor of one half has appeared in the exponential because it has been assumed that the resistance is equal to either side (see Section 3.7) and that the two regions are equal in length nominal to the junction (above in this section). These assumptions may be relaxed by introducing a charge transfer coefficient α which is by default one half [63]:

$$\boxed{zJ = J^o \left(e^{\alpha Pe} - e^{(\alpha-1)Pe} \right)} \tag{3.168}$$

It is theoretically possible to model the reaction with a series of very small subregions within the minority regions. The previous spatial integrals would be replaced by summations. However, the Butler-Volmer equation is more practical. One drawback of using the Butler-Volmer equation is that the electric field is only a function of the chemical potentials and the external forces; the advection/diffusion equilibrium is assumed to be instantaneous. This ignores the fact that the charge must accumulate in the minority regions in order to reach equilibrium.

In order to model the dynamics, we can add an electrolytic capacitor in parallel with the generalized resistance of the Butler-Volmer equation ($\partial EL/\partial zI$). In reality, it is not a separate entity but rather an artifact of the assumptions used to derive the Butler-Volmer equation. Assuming that the area is constant, the electrolytic capacitor introduces the following dynamics:

$$zJ = \frac{d(\epsilon EL)}{dt} \tag{3.169}$$

The areic electrical capacitance ϵ is ε/L, assuming the plates of the electrolytic capacitor are parallel planes. The capacitance may be a function of the operating conditions.

As in the literature (e.g., [51,59]), the Tafel equation can be derived from the Butler-Volmer equation under the assumption of large positive or negative overpotential. The Nernst equation can be derived from the Butler-Volmer equation under equilibrium condition [51].

The Butler-Volmer equation is closely related to the Shockley diode equation [43, 51, 64]. Both electrodes and diodes involve the diffusion of charge carriers from the domain where they are a majority to where they are a minority. The Shockley equation can in fact be derived as above for the Butler-Volmer equation except that (i) there is no chemical bias ($\Delta g = 0$), (ii) protons are replaced by holes, (iii) the catalyst is the n-doped region and the ionomer is the p-doped region, (iv) the orientation is typically opposite such that the electric field is from the p- to the n-doped side, and (v) the densities at the junction are considered to be dependent on the carrier densities in the middle of the minority regions (which are determined by the doping levels) rather than vice versa. It follows from the last point that the densities ρ_a and ρ_b in Equation 3.167 are the minority densities rather than the densities at the junction (which are essentially the majority densities). Also as a result, the entire electric field is applied to one exponential:

$$zJ = J^o \left(e^{Pe} - 1 \right) \tag{3.170}$$

which is the Shockley diode equation where $Pe = EL/T$.

3.10   Detailed Conservation Equations

Highlights:

- The conservation equations explicitly and exactly account for all flows into the configuration due to exchange and transport. Convergence does not depend on the mesh size as in computational fluid dynamics (CFD) methods [65] because the flow rates are shared between adjacent regions. As long as the simulation runs, then conservation is guaranteed within the simulation tolerance. This allows the discretization to be coarse; only several regions are necessary to model a PEMFC.

- The model includes all of the effects in the compressible Navier-Stokes equations—convective acceleration, unsteady acceleration, pressure gradients, shear stresses, and body force.

- The energy conservation equation includes heat generation due to all of the modeled diffusive or irreversible effects.

The basic conservation equations were given in Section 3.4. Here they are expanded with the terms developed in the exchange, transport, and reaction sections (3.5, 3.7, and 3.9).

The conservation equations result in dynamics in conjunction with the exchange and transport equations. In general, the time constants are given by

$$\tau = \left(\frac{\partial X}{\partial \gamma}\right)\left(\frac{\partial \gamma}{\partial \dot{X}}\right) \tag{3.171}$$

where X is a conserved quantity and γ is an intensive property that drives its diffusive exchange or transport.

3.10.1 Material

The intake terms of the basic material conservation equation (Equation 3.25) can be divided into exchange and transport:

$$\underbrace{\frac{\partial N}{\partial t}}_{\text{transient}} = \underbrace{\sum_{i \in E} \dot{N}_{Di}}_{\text{exchange}} + \underbrace{\sum_{i \in T} (\underbrace{\dot{N}_{Di}}_{\text{diffusion}} \pm \underbrace{\phi_{\perp i} \rho_i A_i}_{\text{advection}})}_{\text{transport}} \tag{3.172}$$

where the transport current has been expanded into advective and diffusive parts using Equation 3.110. As noted in Section 3.5, there is no advective exchange of material. The sum in the exchange group is over all phase change and reaction processes in which the configuration participates. The sum in the transport group is over the boundaries.

If the phase in which the configuration exists has constant volume, then the material conservation equation may be written as

$$V\frac{\partial \rho}{\partial t} = \sum_{i \in E} \dot{N}_{Di} + \sum_{i \in T} (\dot{N}_{Di} \pm \phi_{\perp i} \rho_i A_i) \tag{3.173}$$

The advective material currents $(\phi_{\perp i} \rho_i)$ may be written as J_i. Dividing this by volume, expanding the transport terms, and assuming that there is no diffusive transport,

$$\frac{\partial \rho}{\partial t} = \frac{\sum_{i \in E} \dot{N}_{Di}}{V} + \frac{J_{xn} - J_{xp}}{L_x} + \frac{J_{yn} - J_{yp}}{L_y} + \frac{J_{zn} - J_{zp}}{L_z} \tag{3.174}$$

which is the first-order spatial approximation of the continuity equation [34,53]. Nevertheless, this is sufficient because the model's formulation allows the temporal integrator to guarantee

convergence within a prescribed simulation tolerance. The fluxes or currents are represented by variables that are explicitly shared between adjacent regions; therefore, the mass lost by one region is exactly the mass gained by another.

Using Equation 3.171, the time constant due to material exchange is

$$\tau_{NE} = \left(\frac{\partial N}{\partial (g/T)} \right) \left(\frac{\partial (g/T)}{\partial \dot{N}} \right) \tag{3.175}$$

where the first partial derivative is an extensive material property and the second is due to the phase change or reaction equation (3.56 or 3.168). If we use Equation 3.15 assuming constant temperature and extensive volume, then the time constant for a given species due to phase change or reaction i is

$$\tau_{NE} = -\frac{NT}{v^2} \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial (g/T)}{\partial \dot{N}} \right)_i \tag{3.176}$$

The first partial derivative is a now an intensive property that can be determined from Equation 3.4 or 3.6. The second partial derivative can be evaluated from Equation 3.50 or 3.168.

Using the material transport equation (3.108), the time constant due to material transport through a boundary at constant extensive volume is

$$\tau_{NT} = \frac{\eta L^2}{k \left(1 + e^{\mp \eta \phi L / 2k} \right)} \tag{3.177}$$

where the negative of $\mp$ is for negative-side boundaries and the positive is for a positive-side boundaries. If the bulk material flow is towards a boundary, then the associated time constant is smaller because the effective resistance is smaller. The limiting cases are $\tau_N = 0$ (direct coupling) for infinite dimensionless material flow rate towards a boundary, $\tau_{NT} = \eta L^2 / 2k$ for pure diffusion, and $\tau_{NT} = \eta L^2 / k$ for infinite flow away from the boundary.

3.10.2 Translational Momentum

We can rewrite the conservation of translational momentum (Equation 3.28) in terms of an intensive derivative by expanding the transient term using the chain rule and incorporating Equation 3.25:

$$M \frac{\partial \phi}{\partial t} + M a + N z E + A \Delta p_i = \sum \left[m (\phi_i - \phi) \dot{N}_i + \dot{m} \Phi_{\mathrm{D}i} \right] \tag{3.178}$$

For each transport interaction, the material current consists of advective and diffusive parts according to Equation 3.110. For each advective exchange interaction, the material current ($\dot{N}_i$) is only the diffusive current ($\dot{N}_{\mathrm{D}i}$) since there is no advective material exchange.

The previous equation can be expanded by separating the exchange and transport terms and applying Equation 3.59 for advective exchange:

$$M\frac{\partial\phi}{\partial t} + Ma + NzE + A\Delta p_i = \sum_{i\in\mathrm{E}}\left[m\left\{\begin{array}{ll}\phi_i - \phi & \text{if } \dot{N}_{\mathrm{E}i} > 0,\\[2mm] 0 & \text{if } \dot{N}_{\mathrm{E}i} \leq 0\end{array}\right\}\dot{N}_i + m\dot{\Phi}_{\mathrm{D}i}\right]$$

$$+ \sum_{i\in\mathrm{T}}\left[m(\phi_i - \phi)\dot{N}_i + m\dot{\Phi}_{\mathrm{D}i}\right] \quad (3.179)$$

As mentioned in Section 3.5, the exchange interactions are either (i) advective, whereby the diffusion term ($m\dot{\Phi}_{\mathrm{D}i}$) is zero or (ii) diffusive, whereby the material current $\dot{N}_i$ is zero. This form of the translational momentum balance more clearly shows the conditions that cause the material to accelerate in the region from a Eulerian perspective.[xiv] Phase change and reaction have effects if the configuration is produced and the conversion velocity is different from the present velocity. The conversion velocity depends on the velocities of the configurations being consumed (see Section 3.5.2). If the configuration itself is consumed, then the phase change or reaction has no effect since the configuration is consumed at its own velocity. If material enters through a boundary ($\dot{N}_i > 0$) with a velocity greater than the velocity of the material within the region ($\phi_i > \phi$), then the material accelerates in the region. The velocity is also affected by other configurations in the same region and the same configuration in other regions through the diffusion terms ($m\dot{\Phi}_{\mathrm{D}i}$). Finally, the body forces (Ma and NzE) and the thermodynamic force ($A\Delta p_i$) affect the velocity.

The thermodynamic pressure at each boundary is a function of the local temperature and density ($p_i = p(T_i, \rho_i)$). If the configuration is incompressible, then the pressure is the reference pressure (p^o). In that case, the difference is zero and there is no thermodynamic force in

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[xiv]Acceleration from a Eulerian perspective indicates that the mean velocity of particles within the region increases. Individual particles may or may not accelerate; that would be indicated by acceleration from a Lagrangian perspective. For example, consider a case where material is advected from a region of higher density to a region with lower density. Particles must accelerate from a Lagrangian perspective, but this acceleration is at the expense of negative convective acceleration in the Eulerian specification (which may be balanced by a pressure difference). This is the advective term on the second line of Equation 3.179. As expected, it is the time-independent term in the material derivative of velocity [50].

the balance.

Equation 3.179 is closely related to the Navier-Stokes equations. If we combine the momentum balances of all the configurations in the region, then the exchange terms disappear:

$$M\frac{\partial \phi}{\partial t} + Ma + NzE + A\Delta p_i = \sum_{i \in T}\left[m(\phi_i - \phi)\dot{N}_i + \dot{m}\Phi_{Di}\right] \tag{3.180}$$

We will assume that density is uniform. This implies that there is no material diffusion and each boundary current is directly related to the bulk velocity in the normal direction (e.g., $\dot{N}_{xn}/V = -\dot{N}_{xp}/V = \rho\phi_x/L_x$). Dividing the equation by volume and applying subscripts for the x-axis,

$$m\rho\left(\frac{\partial \phi_x}{\partial t} + \frac{\phi_{xpx} - \phi_{xnx}}{L_x}\phi_x + \frac{\phi_{ypx} - \phi_{ynx}}{L_y}\phi_y + \frac{\phi_{zpx} - \phi_{znx}}{L_z}\phi_z\right) + m\rho a_x + \rho zE_x + \frac{P_{xp} - P_{xn}}{L_x}$$
$$= \frac{\dot{m}\Phi_{Dxnx} + \dot{m}\Phi_{Dxpx} + \dot{m}\Phi_{Dynx} + \dot{m}\Phi_{Dypx} + \dot{m}\Phi_{Dznx} + \dot{m}\Phi_{Dzpx}}{V} \tag{3.181}$$

where ϕ_{xnx} is the velocity at the negative-x boundary in the x direction, ϕ_{ypx}, is the velocity at the positive-y boundary in the x direction, etc. The same convention applies to the subscripts in the shear force terms. We can expand the viscous forces using Equation 3.106 for the normal axes and Equation 3.124 for the transverse axes, assuming the Péclet numbers are negligible and the area factors and translational Nusselt numbers are unity. We will also rewrite the volumic body terms ($\rho(ma + zE)$) as $-f/V$:

$$m\rho\left(\frac{\partial \phi_x}{\partial t} + \frac{\phi_{xpx} - \phi_{xnx}}{L_x}\phi_x + \frac{\phi_{ypx} - \phi_{ynx}}{L_y}\phi_y + \frac{\phi_{zpx} - \phi_{znx}}{L_z}\phi_z\right) + \frac{P_{xp} - P_{xn}}{L_x}$$
$$= \frac{f_x}{V} + 2\left(\frac{\phi_{xnx} + \phi_{xpx} - 2\phi_x}{\beta L_x^2} + \frac{\phi_{ynx} + \phi_{ypx} - 2\phi_x}{\zeta L_y^2} + \frac{\phi_{znx} + \phi_{zpx} - 2\phi_x}{\zeta L_z^2}\right) \tag{3.182}$$

If we assume that the dynamic compressibility (β) and the fluidity (ζ) are both equal to the reciprocal of dynamic viscosity (μ), then this is

$$m\rho\left(\frac{\partial \phi_x}{\partial t} + \frac{\phi_{xpx} - \phi_{xnx}}{L_x}\phi_x + \frac{\phi_{ypx} - \phi_{ynx}}{L_y}\phi_y + \frac{\phi_{zpx} - \phi_{znx}}{L_z}\phi_z\right) + \frac{P_{xp} - P_{xn}}{L_x}$$
$$= \frac{f_x}{V} + 2\mu\left(\frac{\phi_{xnx} + \phi_{xpx} - 2\phi_x}{L_x^2} + \frac{\phi_{ynx} + \phi_{ypx} - 2\phi_x}{L_y^2} + \frac{\phi_{znx} + \phi_{zpx} - 2\phi_x}{L_z^2}\right) \tag{3.183}$$

which is the first-order approximation to the x-axis Navier-Stokes equation for an incompressible, Newtonian, and homogeneous fluid [39, 60, 66]. The first of the two groups on the left

side is the material derivative of translational momentum [50]. The variable f is force rather than volumic force. Similar equations apply to the other axes.

Although the model characterizes compressible flow, it is not equivalent to the Navier-Stokes equations for compressible flow. As discussed in Section 3.7.2, the shear force equations are mapped differently than by Stokes' viscous deformation law.

For a given species, the time constant due to diffusive translational exchange is

$$\tau_{\Phi E} = m\mu \tag{3.184}$$

This time constant is directly related to the mean collision interval (τ) under the assumptions of kinetic theory (Section 3.5). By applying Equation 3.64,

$$\tau_{\Phi E} = \frac{8\pi\tau}{3} \tag{3.185}$$

which is typically small—on the order of 20 ns for oxygen in air (see Section 3.6). Thus it is appropriate to assume that the velocities of different species are equal within a phase unless they are driven by significant opposing forces. The time constant due to dynamic compression is

$$\tau_{\Phi T} = \frac{M\beta L}{kA\left(1 + e^{\mp\beta M\phi/2kA}\right)} \tag{3.186}$$

and the time constant due to shear force is

$$\tau_{\Phi T} = \frac{M\zeta L}{kA\left(1 + e^{\mp\zeta M\phi/2kA}\right)} \tag{3.187}$$

3.10.3 Energy

We can express the energy conservation equation (3.30) in terms of intensive derivatives by expanding the transient terms and incorporating the material conservation equation (3.172):

$$M\phi\frac{\partial\phi}{\partial t} + NT\frac{\partial s}{\partial t} = \sum\left[\left(h_i - h + m\frac{\phi_i^2 - \phi^2}{2}\right)\dot{N}_i + \phi_i m\dot{\Phi}_{Di} + \dot{Q}_{Di}\right] \tag{3.188}$$

where the Gibbs energy relation (Equation 3.15) has been applied. Furthermore, we can eliminate the local acceleration term (at the expense of adding other terms) using the translational

momentum balance (Equation 3.178):

$$NT\frac{\partial s}{\partial t} = \phi\left(Ma + NzE + A\Delta p_i\right)$$

$$+ \sum\left[\left(h_i - h + \frac{m}{2}(\phi_i - \phi)^2\right)\dot{N}_i + (\phi_i - \phi)\dot{m}\Phi_{Di} + \dot{Q}_{Di}\right] \quad (3.189)$$

If the configuration is a source ($\dot{N}_i \leq 0$), then the advective term $h_i - h + \frac{m}{2}(\phi_i - \phi)^2$ is $g_i - g + T(s - s_i)$ according to Equations 3.59 and 3.67.

$$NT\frac{\partial s}{\partial t} = \phi\left(Ma + NzE + A\Delta p_i\right)$$

$$+ \sum_{i\in E}\left[\begin{cases} h_i - h + \frac{m}{2}(\phi_i - \phi)^2 & \text{if } \dot{N}_i > 0, \\ g_i - g + T(s - s_i) & \text{if } \dot{N}_i \leq 0 \end{cases} \cdot \dot{N}_i + (\phi_i - \phi)\dot{m}\Phi_{Di} + \dot{Q}_{Di}\right]$$

$$+ \sum_{i\in T}\left[\left(h_i - h + \frac{m}{2}(\phi_i - \phi)^2\right)\dot{N}_i + (\phi_i - \phi)\dot{m}\Phi_{Di} + \dot{Q}_{Di}\right] \quad (3.190)$$

Based on Equation 3.10, the transient term $NT\frac{\partial s}{\partial t}$ is $Nc_p^o\frac{\partial T}{\partial t}$ if the species has no thermal expansion and $Nc_p^o\frac{\partial T}{\partial t} - V\frac{\partial p}{\partial t}$ if it is an ideal gas. Those limiting cases indicate the conditions that affect the temperature of the species. **Review here and below:

gi - g + T(s - si) gi - h + T-si

The temperature of the products or sinks will increase if the conversion specific enthalpy (h_i) is greater than the specific enthalpy of the sinks and decrease otherwise. The temperature of the sources will

If a phase change or reaction is occurring, then it is towards lower specific Gibbs energy.

or decrease depending on whether the

increases the temperatures of both the sources and the sinks due to the difference in specific Gibbs energy. That effect cannot decrease the temperature because $g_{AEi} - g$ and $n_i\dot{N}_{Ei}$ have the same sign in the phase change and reaction equations (3.56 and 3.168). However, if the species is produced by the phase change or reaction, then the heat of formation affects its temperature through the difference $T_{AEi}s_{AEi} - Ts$. That can either further increase the temperature (exothermic) or mitigate and even reverse the temperature increase (endothermic). The phase change or reaction also heats the product if the conversion velocity is different from the product's present velocity. Then, internal friction increases the product's temperature, although

the advective exchange force also acts to decrease the magnitude of the velocity difference (see Equation 3.28).

Material transport causes effects similar to those of material exchange. Differences in specific enthalpy between the species and the boundary may increase or decrease the temperature depending on whether the material is flowing with or against the difference. Differences in velocity between the species and the boundary tend to increase the temperature if material is flowing into the region and decrease it otherwise. However, in the limit of pure advection ($Pe \to \mp\infty$), the velocity difference is zero for outgoing flow and becomes zero rapidly for incoming flow due to the translational momentum balance (Equation 3.28). Therefore, in the ideal case of steady state, steady flow (SSSF) pure advection there is no heating effect except by viscous shearing (translational diffusive transport). The effects of diffusive translational exchange and transport can only cause an increase since $\phi_{DE} - \phi$ and $\dot{m}\Phi_{DE}$ have the same sign in Equation 3.63 and $\phi_{Ti} - \phi$ and $\dot{m}\Phi_{Ti}$ have the same sign in Equation 3.124.

Thermal diffusion ($\dot{Q}_{DE}$ and $\dot{Q}_T$) tends to increase the temperature of the species if it is colder than other species within the region or the same species in other regions. Equations 3.70 and 3.141 require that heat flows from hot to cold regions or species. This does not include thermal convection; it is included in the advective terms.

The energy conservation equation (3.188) is related to the heat equation. If we neglect material exchange and transport and assume pressure is constant, then the energy conservation equation reduces to

$$N\frac{\partial c_p}{\partial t} = (\phi_{DE} - \phi)\dot{m}\Phi_{DE} + \dot{Q}_{DE} + \sum(\phi_{Ti} - \phi)\dot{m}\Phi_{Ti} + \sum\dot{Q}_{Ti} - \phi(A\Delta p_{Ti} + Ma) \quad (3.191)$$

If the energy balances of all of the species are combined, then we can eliminate the thermal and translational exchange among the species.

$$N\frac{\partial c_p}{\partial t} = \sum(\phi_{Ti} - \phi)\dot{m}\Phi_{Ti} + \sum\dot{Q}_{Ti} - \phi(A\Delta p_{Ti} + Ma) \quad (3.192)$$

Grouping the viscous dissipation into a heat generation term, this is

$$N\frac{\partial c_p}{\partial t} = \sum\dot{Q}_{Ti} + \dot{Q}_{gen} \quad (3.193)$$

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We can evaluate the thermal conduction sum using Equation 3.141 under the assumption of no advection and an area factor of unity. After dividing by volume,

$$\rho \frac{\partial c_p}{\partial t} = \frac{2}{\theta} \left[\frac{T_{\mathrm{xn}} + T_{\mathrm{xp}} - 2T}{L_x^2} + \frac{T_{\mathrm{yn}} + T_{\mathrm{yp}} - 2T}{L_y^2} + \frac{T_{\mathrm{zn}} + T_{\mathrm{zp}} - 2T}{L_z^2} \right] + \frac{\dot{Q}_{\mathrm{gen}}}{V} \tag{3.194}$$

which is the first-order approximation of the heat diffusion equation using spatial differences and assuming uniform thermal resistivity [53].

The thermal time constant due to diffusive exchange is

$$\tau_{QE} = \frac{\theta N c}{2 L_i'} \tag{3.195}$$

where c may be c_p or c_v depending on the conditions. The time constant due to thermal conduction at constant specific volume is

$$\tau_{QT} = \frac{\theta N c_v L}{kA\left(1 + e^{\mp \theta c_v \Phi / 2kA}\right)} \tag{3.196}$$

****Ts advected (as advective exchange effort), not T (explain)

3.11   Related Theory

The previous sections describe how certain aspects of the model are related to existing theory. This section presents similar derivations that span multiple aspects of the model. The derivations begin from the model equations and finish with selected theories.

3.11.1   Mass Transfer and Fluid Dynamics

The following equations and topics are discussed in the related sections of the model:

- Fick's law and self diffusion: Section 3.7.1

- Newton's law of viscosity and Couette flow: Section 3.7.2

- Laminar pipe flow and Poiseuille's law: Section 3.7.2

- Reynolds number and turbulent flow: Section 3.7.2

- Continuity equation: Section 3.10.1

- Material derivative and Eulerian vs. Lagrangian specification: Section 3.5 and Footnote xiv in Section 3.10.2

- Navier-Stokes equations: Section 3.10.2

- Stokes' law of viscous deformation: Sections 3.7.2 and 3.10.2

- Hertz-Knudsen and Hertz-Knudsen-Langmuir equations: Section 3.5.1

- Stokes-Einstein relation: Section 3.5.2

- Gibbs phase rule: Section 3.5.1

This section relates the model to several other theories in mass transfer and fluid dynamics—Darcy's law, the Hertz-Knudsen equation, and the Maxwell-Stefan equations. The dusty-gas model is also related in Footnote xvi.

3.11.1.1   Darcy's Law

The model is consistent with Darcy's law, which is used to describe fluid flow through a porous medium. To relate the model to Darcy's law, we begin with the translational diffusive exchange equation (3.63) of a fluid species (rewritten here with velocity on the left):

$$\phi_{\mathrm{DE}} - \phi_i = \frac{\mu_i}{N_i} \dot{m} \Phi_{i\mathrm{DE}} \tag{3.197}$$

If the species is in contact with a stationary solid that has zero fluidity, then the mediation velocity (ϕ_{DE}) is zero. If also the discretization is coarse enough that the solid appears homogeneously distributed within the region, then we may neglect the shear force with the fluid in adjacent regions. At SSSF and without body forces or chemical reactions, the only remaining force is the thermodynamic force. The conservation of translational momentum reduces to $A\Delta p_{\mathrm{T}i} = \dot{m}\Phi_{i\mathrm{DE}}$ and thus

$$\phi_i = -\frac{\mu_i}{N_i} A\Delta p_{\mathrm{T}i} \tag{3.198}$$

As a differential equation in three dimensions (and dropping the subscripts), this is

$$\boldsymbol{\phi} = -\mu v \boldsymbol{\nabla} p \tag{3.199}$$

which is Darcy's law [33, 50]. The product of the mobility and the specific volume (μv is the permeability, where the volume is the total volume of the region. ****factor as the volume of the phase using volumetric porosity ****Dimensions wrong by factor of L.T/N... Fix equation

This derivation considers only one fluid species, but a similar result can be obtained for multicomponent transport with equal velocities of the species. The permeability of the single species would be replaced by an effective permeability of the mixture.

3.11.1.2 Hertz-Knudsen Equation

The Hertz-Knudsen equation describes the rate of phase change...****

Since it is difficult to quantify the diffusion length L, we will write it as a number of mean free paths of an ideal gas at the same conditions. That number is the reciprocal of the Knudsen number; therefore, the reciprocal of length is replaced by the Knudsen number divided by the mean free path of an ideal gas ($1/L = \sqrt{2}\,\pi\,d^2\,q\,\rho\,Kn$) [67]:

$$\dot{N} = \sqrt{2}\,\pi\,d^2\,q\,\rho\,Kn\,kA\left(\frac{\rho_g}{\eta_g} - \frac{\rho_{gc}}{\eta_{gc}}\right) \tag{3.200}$$

The first equation (3.50) is closely related to the Hertz-Knudsen equation. If we assume that the material resistivity is equal to the estimate from kinetic theory (Equation 3.109), then

$$\dot{N} = \frac{2kA}{3\pi d^2 q}\sqrt{\frac{1}{\pi m}}\left(\frac{\sqrt{T_g}}{L_g} - \frac{\sqrt{T_{gc}}}{L_{gc}}\right) \tag{3.201}$$

Writing the each length in terms of the Knudsen number ($1/L = \sqrt{2}\pi\,d^2\,q\,\rho\,Kn$, since the gas is ideal [67]),

$$\dot{N} = \frac{2kA}{3}\sqrt{\frac{2}{\pi m}}\left(Kn_g\rho_g\sqrt{T_g} - Kn_{gc}\rho_{gc}\sqrt{T_{gc}}\right) \tag{3.202}$$

If the area factor (k) is 3/4 (****justify):

$$\dot{N} = \frac{A}{\sqrt{2\pi m}}\left(Kn_g\rho_g\sqrt{T_g} - Kn_{gc}\rho_{gc}\sqrt{T_{gc}}\right) \tag{3.203}$$

If the Knudsen numbers are unity, then

$$\dot{N} = \frac{A}{\sqrt{2\pi m}}\left(\rho_g\sqrt{T_g} - \rho_{gc}\sqrt{T_{gc}}\right) \tag{3.204}$$

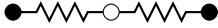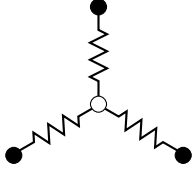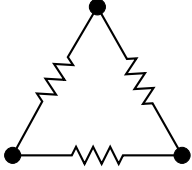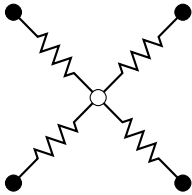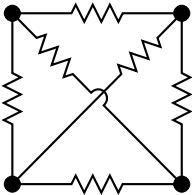which is the Hertz-Knudsen equation [41]. Otherwise since the gas is ideal,

$$\dot{N} = \frac{A}{\sqrt{2\pi m}}\left(\frac{Kn_g p_g}{\sqrt{T_g}} - \frac{Kn_{gc} p_{gc}}{\sqrt{T_{gc}}}\right) \tag{3.205}$$

which is the Hertz-Knudsen-Langmuir equation [68] with Kn_g as the condensation coefficient and Kn_{gc} as the evaporation coefficient.

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3.11.1.3   Maxwell-Stefan Equations

The model describes the same phenomena as the Maxwell-Stefan equations—drag between species in multicomponent flow—but in a different manner. The model uses a configuration where each species only interacts directly with a hypothetical mediation node. The first graphic column of Table 3.4 shows the configuration of the model for two-, three-, and four- component systems. The resistors represent friction between the species (filled circles). The central node (outlined circle) exists at the mediation velocity and imposes conservation of translational momentum without other forces or transients. The Maxwell-Stefan equations represent binary interactions directly between the species, as shown in the second graphic column. Thus the model has n_{spec} generalized resistors in a system with n_{spec} species whereas the Maxwell-Stefan equations have $n_{\mathrm{spec}}(n_{\mathrm{spec}} - 1)/2$ generalized resistors for the same system.

Table 3.4: Structure of the model vs. the Maxwell-Stefan equations.

Number of Species (n_{spec})	Model	Maxwell-Stefan
2		
3		
4		

To show the relation analytically, we first substitute the mediation velocity (Equation 3.65) into the equation for translational diffusive exchange (3.63). With some algebraic manipulation this is:

$$m\dot{\Phi}_{i\mathrm{DE}} = \sum_{j\in\mathrm{spec}} \frac{N_i N_i}{\mu_i \mu_i}(\phi_i - \phi_i) \Big/ \sum_{j\in\mathrm{spec}} \frac{N_i}{\mu_i} \tag{3.206}$$

This indicates that although the drag forces are calculated in the model via a hub arrangement (see Table 3.4), they may be cast in a binary form. However, the model has only n_{spec} properties of the form N_i/μ_i whereas the Maxwell-Stefan equations have $n_{\text{spec}}(n_{\text{spec}} - 1)/2$. This means that for greater than three species ($n_{\text{spec}} > 3$) the relation between the model and the Maxwell-Stefan equation places additional constraints on the binary diffusion coefficients D_{ii} used in the Maxwell-Stefan equation. With this caveat, the binary diffusion coefficients may be established by

$$D_{ii} = \frac{pV}{N_{\text{tot}}^2} \mu_i \mu_i \sum_{k \in \text{spec}} \frac{N_k}{\mu_k} \tag{3.207}$$

If we introduce this relation into Equation 3.206, then

$$\dot{m\Phi}_{i\text{DE}} = \frac{pV}{N_{\text{tot}}^2} \sum_{j \in \text{spec}} \frac{N_i N_i}{D_{ii}} \left(\phi_j - \phi_i \right) \tag{3.208}$$

We will make the following assumptions to relate the intra-regional drag force ($\dot{m\Phi}_{i\text{DE}}$) to the thermodynamic force: (i) SSSF conditions, (ii) no body forces, (iii) no chemical reactions, (iv) no shear forces, and (v) no drag due to other phases (e.g., solid).[xv] Then, the conservation of translational momentum reduces to $A\Delta p_{\text{T}i} = \dot{m\Phi}_{i\text{DE}}$. Making this substitution, taking the limit as length goes to zero, and generalizing to three dimensions,

$$\nabla p_i = -\frac{p}{N_{\text{tot}}^2} \sum_{j \in \text{spec}} \frac{N_i N_i}{D_{ii}} \left(\boldsymbol{\phi}_j - \boldsymbol{\phi}_i \right) \tag{3.209}$$

which is the form of the Maxwell-Stefan equations [52]. At uniform total pressure (p), this can be written in terms of concentration [52]:

$$\nabla \left(\frac{N_i}{N_{\text{tot}}} \right) = \frac{1}{N_{\text{tot}}^2} \sum_{j \in \text{spec}} \frac{N_i N_i}{D_{ii}} \left(\boldsymbol{\phi}_i - \boldsymbol{\phi}_i \right) \tag{3.210}$$

If the mixture is of ideal gases [50, 69], then this can be written in terms of chemical potential (here, g):

$$\nabla g_i = \frac{T}{N_{\text{tot}}^2} \sum_{j \in \text{spec}} \frac{N_i N_i}{D_{ii}} \left(\boldsymbol{\phi}_i - \boldsymbol{\phi}_i \right) \tag{3.211}$$

The ii term reduces to zero.

[xv]Note, however, that the shear forces and drag due the solid may be reintroduced when the final redundant and consistent Maxwell-Stefan equation is replaced; see below.

The factor of $N_1 N_2$ is based on that "the more molecules of both types that are present in the unit volume, the higher the number of collisions will be" [52, p. 15].

Maxwell-Stefan diffusion is based on the assumption that after collision, on average, each particle has the velocity of the center of mass of the pair before the collision. However, an empirical parameter/property is still necessary to account for the frequency at which the particles collide (assumed proportional to the product of the molar concentrations of the interacting components; the remaining factor is included in the binary diffusion coefficient) [52].

Derivation of the rate of collisions: (Rate of transfer of momentum from component 1 to component 2 due to collisions between 1 and 2) = (average amount of momentum exchanged in a single collision)*(rate of collisions between 1 and 2) (Rate of transfer of momentum from component 1 to component 2 due to collisions between 1 and 2) = -Gradp1*V [52, p. 16] (average amount of momentum exchanged in a single collision) $= m1*m2*(u_1-u_2)/(m_1+m_2)$ [52, p. 14] therefore $Grad p1 = -(u_1-u_2)*m1*m2*(rate of collisions between 1 and 2)/(m1+m2)/V$ The Maxwell-Stefan form is: $Grad p1 = -(u_1 - u_2)*p*x1*x2/D_S M12$ therefore $(rate of collisions between 1 and 2) = (m1+m2)*p*V*x1*x2/(m1*m2*D_S M12)$

Relation between momentum exchange rate and rate of collisions: $D_S M12 = (m1+m2)*p*V*x1*x2/(m1*m2*(rate of collisions between 1 and 2))$ $D_1 2 = (rate of collisions between 1 and 2)*T*m1*m2/((m1+m2)*p*L*m_1 2)$ If IG, then: $D_1 2 = (rate of collisions between 1 and 2)*m1*m2*A/((m1+m2)*M_1 2)$ Aside: $D_1 2 = (rate of collisions between 1 and 2)*A/((1/m1+1/m2)*(M1+M2))$ $D_1 2 = (rate of collisions between 1 and 2)*A/(N1+N_2+N1*m1/m2+N_2*m2/m1)$ $D_1 2 = (rate of collisions between 1 and 2)*A/(N1/m2+N_2/m1)/(m2+m1)$ $Deltam Phidot_i nter = (phi[i,:]-phi[j,:])*(rate of collisions between 1 and 2)*m1*m2/(m1+m2)$ $Deltam Phidot_i nter = (phi[i,:]-phi[j,:])*(rate of collisions between 1 and 2)/(1/m1+1/m2)$ If molecule 1 is much, much heavier than molecule 2, then $Deltam Phidot_i nter = (phi[i,:]-phi[j,:])*(rate of collisions between 1 and 2)*m2$ If the molecules are of equal mass $(m1 = m2 = m)$, then $Deltam Phidot_i nter = (phi[i,:]-phi[j,:])*(rate of collisions between 1 and 2)*m/2$ As the ratio of molar masses approaches 0 or 1, the transfer rate of momentum between components is increasingly limited by the mass of the lighter molecule, such that if one molecule has negligible mass, there is essentially no transfer of momentum.

The case is more complicated for collisions between particles of different types. $pij * A = (u1 - u2) * m1 * m2/(m1 + m2) * (rateof i - jcollisions)$ [52, p. 14] where ui is the thermal velocity of component i $pij * A = (sqrt(epsiloni) - sqrt(epsilonj)) * mi * mj/(mi + mj) * (rateof i - jcollisions)$

note that the model could be written in the form of binary interactions and still be linear, as long as there are momentum balances for each species. However, the hub arrangement makes the model implementation simpler and requires fewer parameters, which are only available for certain pairs of species (e.g., [57]).

The model has a translational momentum balance for every species (see Section 3.10.2), but as presented above and in the current literature the Maxwell-Stefan equations require a momentum balance for the fluid as a whole. The momentum balance of the mixture may be explicit or implicit via the assumption of SSSF, but it must relate the gradient of a driving property (e.g., total pressure) to the bulk flow rate of the mixture (e.g., velocity or molar flow rate). Since the sum of the partial pressure gradients ($\sum \nabla p_i$) is the total pressure gradient (∇p) and the binary diffusion coefficients are symmetric, a system of n_{spec} species has only $n_{\mathrm{spec}} - 1$ independent Maxwell-Stefan equations. Although the Maxwell-Stefan equations are symmetric, their implementation is inherently not. The choice of which equation to replace by the mixture momentum balance is arbitrary.[xvi]

The direct implementation of the $n_{\mathrm{spec}} - 1$ Maxwell-Stefan equations without individual momentum balances leads to a boot-strapping problem. The velocities are all coupled, yet to explicitly determine any one requires solving a nonlinear system of equations. In fact, "the Maxwell-Stefan equation is almost never used because it is difficult to solve mathematically, even in the simplest cases" [67, p. 54].

Due to the difficulty of implementing the Maxwell-Stefan equations and the inherent choices (of the momentum balance of the mixture and the Maxwell-Stefan equation to eliminate), many alternatives have been developed. Cussler [67] stated this more bluntly: "Because of an excess of theoretical zeal, many who work in this area have nurtured a glut of alternatives." Among

---

[xvi]The dusty-gas model circumvents this issue by adding a portion of the loss due to interaction with the solid (as characterized by Darcy's law) to each of the n_{spec} Maxwell-Stefan equations. However, Weber and Newman [33] have indicated that this is not rigorously correct and the Darcy's law itself should be introduced as the final equation.

these is the dusty-gas model, which has its own shortcomings [37, 70]. In fact, the current implementations may miss the original point, as stated by Kerkhof and Geboers [37]:

> "The vision of Maxwell, and very explicitly of Stefan, that one cannot treat a mixture as a single fluid, has also been obscured by the successful work of more recent authors on single-component fluids [...]"

Instead than attempting to cast the binary diffusion equations into a single-component framework, the proposed model embraces the multi-component nature. With a momentum balance and associated forces for every species, it avoids (i) the inherent asymmetry in the implementation, (ii) the difficulty in determining an appropriate momentum balance for the whole mixture complete with the pressure loss due to bulk flow, and (iii) the nonlinear problem in solving the individual velocities.

3.11.2   Heat Transfer

The following equations are discussed in the related sections of the model:

- Fourier's law: Section 3.7.3
- Newton's law of cooling: Section 3.7.3
- Nusselt number: Section 3.7.3
- Heat equation: Section 3.10.3

3.11.3   Solid-State Physics

The Einstein relation is discussed in Section 3.5.2. The model is related to the Shockley diode equation in Section 3.9. Below, it is related to charge drift/diffusion, Ohm's law, and the Einstein relation.

3.11.3.1   Charge Drift and Diffusion

If we assume that material is not stored along an axis through a region, then the total (advective plus diffusive) current is uniform across the region ($\dot{N}_n' = -\dot{N}_p' = JA$). Equation 3.110 implies that

$$2J = \frac{\dot{N}_n - \dot{N}_p}{A} + \phi_n \rho_n + \phi_p \rho_p \tag{3.212}$$

Using the material transport equation (3.108) and the normal force equation (3.106),

$$2J = \frac{k}{\eta L}\left(\left(\rho_n - \rho\right)\left(1 + e^{-\eta\phi L/2k}\right) + \left(\rho - \rho_p\right)\left(1 + e^{\eta\phi L/2k}\right)\right)$$
$$+ \frac{\beta L}{kA}\left(\frac{\rho_n m\dot{\Phi}_n}{\left(1 + e^{-\beta M\phi/2kA}\right)} + \frac{\rho_p m\dot{\Phi}_p}{\left(1 + e^{\beta M\phi/2kA}\right)}\right) + \left(\rho_n + \rho_p\right)\phi \quad (3.213)$$

We will assume that the material Péclet number is negligible (or the density gradient is uniform), the dynamic compressibility (β) is zero, and the area factor (k) is zero. Then,

$$J = \frac{\rho_n - \rho_p}{\eta L} + \rho\phi \quad (3.214)$$

We may write this in terms of electrical mobility, which is the product of the charge number and the bulk material velocity divided by the electric field ($\mu \equiv \phi/zE$).[xvii] Thus,

$$J = \frac{\rho_n - \rho_p}{\eta L} + \rho\mu zE \quad (3.215)$$

where J is the material transport rate. As length goes to zero ($L \to 0$) and generalizing to multiple dimensions,

$$\mathbf{J} = \rho\mu z\mathbf{E} - \frac{1}{\eta}\boldsymbol{\nabla}\rho \quad (3.216)$$

We can multiply this equation by the charge number (z) to write it in terms of electrical current density (zJ). For electrons ($z = -1$),

$$z\mathbf{J} = \rho\mu\mathbf{E} + \frac{1}{\eta}\boldsymbol{\nabla}\rho \quad (3.217)$$

and for holes ($z = 1$),

$$z\mathbf{J} = \rho\mu\mathbf{E} - \frac{1}{\eta}\boldsymbol{\nabla}\rho \quad (3.218)$$

These are the charge drift/diffusion equations, which are used to describe electron and hole transport in semiconductor devices [43, 71].

[xvii]Typically, electrical mobility is expressed in terms of charge drift velocity which is the product of the bulk material velocity and the charge number. The charge number is not explicit in that definition of mobility [71].

3.11.3.2 Ohm's Law

Ohm's law is the limiting case of charge drift/diffusion where drift current is much larger than diffusion current. As material resistivity goes to infinity ($\eta \to \infty$), the charge drift/diffusion equation (3.215) reduces to:

$$zJ = \rho\mu E \tag{3.219}$$

which is Ohm's law [43, 60, 71, 72]. The factor $\rho\mu$ is the electrical conductivity [71]. If we assume that the electric field is uniform ($v = EL$) and write this in terms of electrical current ($zI = zJA$) and electrical resistance ($R = L/A\rho\mu$),

$$v = zIR \tag{3.220}$$

which is the form of Ohm's law typically used in electrical circuit theory [43, 71–74]. This derivation may be generalized by superimposing the effects of the appropriate charge carriers (e.g., electrons and holes) [71].

Although Fick's law (Section 3.7.1) and Ohm's law have the same form (diffusivity:density::-conductivity:electrical potential), the modes of material transport are different. Fick's law describes material transport when it is dominated by diffusion or agitation (from high to low density). Ohm's law describes material transport (of charge carriers, cast as charge transport) when it is dominated by advection or translation. It happens that for electrical devices the rate of advection is often conveniently proportional to the electric field (high to low electrical potential).

3.11.3.3 Einstein Relation

**Reintroduce.

which is the Einstein relation [43, 71].

3.11.4 Electrochemistry

The following equations and topics are discussed in the section on electrochemical reactions (3.9):

- Butler-Volmer equation

- Tafel equation

- Nernst equation

CHAPTER 4

IMPLEMENTATION OF THE MODEL

CHAPTER 5

STATIC ANALYSIS

CHAPTER 6

DYNAMIC ANALYSIS

CHAPTER 7

COMPUTATIONAL PERFORMANCE

CHAPTER 8

CONCLUSIONS

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