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Exergetic Relationship between the Thermal Properties of Direct Contact Membrane Distillation

by

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Abstract

Direct contact membrane distillation (DCMD) is a process that has shown promise within the field of desalination due to its less energy intensive methods and widespread applications. DCMD is a thermally driven microfiltration separation process that operates on the principle of vapor-liquid equilibrium conditions where heat and mass transfer occur simultaneously. Fundamentally, DCMD is based on a porous hydrophobic membrane separating the hot solution (feed) from the cold solution (permeate) where desalinated water condenses. The temperatures at the membrane interface determine the vapor pressure difference across the membrane. Molecular simulation has been used to identify trends between the various parameters of the distillation process by holding one property constant to study the effect on the other components of the system. However, DCMD still requires more concentrated research to determine what is required of all vital system components to produce an ideal and maximized output.

In this work, a direct simulation Monte Carlo analysis is employed to investigate how the exergy of the system relates to other key thermal properties, namely, the temperature polarization coefficient and the thermal efficiency, as other parameters are changed, such as feed temperature, flow speed, and membrane porosity. Through molecular simulation, phase equilibrium was
reached by calculating the chemical potential at the membrane interface and the entropy of the system was found. Since exergy is a function of entropy, enthalpy, and temperature, the amount of useful work was calculated. Finally, exergy was compared to the TPC and TE as the flow rate and porosity was varied. We demonstrate that with these exergy calculations and the thermal relationship between microscopic and macroscopic scales, a probabilistic range for all parameters will improve future experimental work.
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Chapter 1

Introduction

1.1 Motivation

The global population is growing exponentially and is predicted to reach 8.5 billion by the year 2030 [4]. This growth suggests an increased demand for natural resources, in particular, access to clean water. Currently, the WHO/UNICEF reported that at least 1.8 billion people world-wide are estimated to drink water that is not protected against contamination from body waste [32, 34]. However, in a few decades, even water-rich countries will be affected. Therefore, tremendous efforts are needed to reduce the effects of this impending catastrophe, especially in overpopulated countries. Seventy percent of the earth is covered with water and only 3% of it is fresh. Additionally, only one third of that freshwater is liquid. The graphs in Figure 1.1 show that, over time, there will be an increase in the number of people in the world who will face water stress or water scarcity. Freshwater conservation is becoming increasingly important and hydrologists use the ratio between freshwater to population to identify which countries’ conditions are particularly challenging. Worldwide, desalination ac-
counts for only 0.2 percent of water used, but researchers are looking to expand
desalination applications [23]. Researchers are looking for solutions to utilize the
seemingly unuseable brackish water that has the potential to be an additional
water supply once converted into potable water.

![Figure 1.1: Prediction of population growth compared to freshwater availability
from 2000 to 2025 [4]](image)

Membrane distillation (MD) is a process that is being used across the world
as an alternative to other microfiltration processes. A major application of
membrane distillation is for seawater desalination. The more common separ-
ation processes such as electrodialysis reversal and reverse osmosis lack the
benefits of membrane distillation because they are more expensive and require
large amounts of energy. An increasing amount of research has been dedicated
to developing and advancing membrane distillation in all parts of the world to
utilize this untapped resource efficiently and effectively.

1.2 Literature Review

U.S. patent applications first describe the invention of MD. The first application
was submitted by Bruce R. Bodell in 1963 [3] and was described as an “apparatus
and methods for converting impotable aqueous fluids to a potable water.” Peter
K. Weyl filed a patent the following year for a similar desalination process and suggested that the feed and permeate be in direct contact with the membrane. This was approved by 1967 and stood out among other devices of this time that included an air-filled hydrophobic porous membrane [6].

In the same year that Weyl’s patent was accepted, the first MD paper was published by Marshall E. Findley, who provided theory and results for DCMD experiments. By the early 1980s, membrane manufacturing technologies began to flourish and interest grew in MD research. By 1983, the Swedish Development Co. patented a commercial MD system and published their theoretical models and results. This more academic approach did not capture the attention of the commercial MD market, but academic researchers were intrigued with the work and publications in this field have doubled since the 1990 [22].

Lawson et al. stated that a commonly accepted reason behind the increase of research in MD is thought to be because fundamental interdisciplinary engineering concepts are woven throughout the MD process [22]. This type of approach is the foundation for developing global solutions to environmental problems. Presently, there is a new generation of MD membrane materials such as carbon nanotubes fabricated with different polymers, solvents, and additives. Improved electro-spinning parameters are being used to improve membrane performance for desalination and volatile solute removal from water.

Figure 1.2 displays the four main methods of membrane distillation: Air Gap Membrane Distillation (AGMD), Vacuum Membrane Distillation (VMD), Sweeping Gas Membrane Distillation (SGMD), and Direct Contact Membrane Distillation (DCMD). Each of these processes are thermally driven, where heat and mass transfer take place simultaneously and a vapor pressure difference occurs due to a temperature difference across the membrane.

These four configurations, although similar, have different ways to process
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Figure 1.2: Different membrane distillation operation modes [19]

the cold side or permeate of the system. For example, in AGMD, an air gap exists between the membrane and the surface that collects the condensate. This configuration is highly energy efficient, yet produces a low output of useable water, or flux.

VMD subjects the vapor of the permeate side to a continuous vacuum chamber, which may require the condensation to collect in a separate device. It is beneficial to use this process for a volatile organic gas, but the external condenser adds additional cost. Similar to VMD, SGMD is also useful for removing volatile substances, as the produced vapor is carried by a sweeping gas from an aqueous solution. A large volume of this gas must be used to vaporize a small volume of permeate and this downfall limits the research dedicated to this configuration [35].

DCMD research has been increasing in the recent years due to its simple configuration and high water production rate. In this process, the hot brackish water, or feed, is in direct contact with the top side of the membrane while cold permeate lines the bottom side. Although a high flux is produced, this configuration has a low thermal efficiency because the permeate heat transfer
coefficient causes heat conduction losses. Nonetheless, 63% of papers published about the above four MD process have focused on DCMD [17], because of the potential promise of this method.

Most DCMD research has been conducted experimentally [12]. Over time, these experiments have been refined; however, the simultaneous heat and mass transfer is complex and the depth of the physics taking place has not fully been examined. Additionally, DCMD experiments are costly, so it is difficult to make the subtle changes necessary to isolate each parameter in the system while determining its relationship with all of the other components. Fortunately, computer-aided simulations possibly can assist in modelling systems and incorporating any design changes.

The first simulations were developed by Schofield et al., which laid the foundation for future work by the scientific community [30]. Mass transfer is well understood through macroscopic models such as the Schofield and dusty gas models, which bring together the transport mechanisms, Knudsen number, and molecular surface diffusions, as well as viscous flow. Models have also been able to determine Nusselt numbers and convective heat transfer coefficients by analyzing existing semi-empirical correlations. Finally, the effects of membrane physical properties can be characterized accurately with models that can simulate various materials and process operating conditions.

Several computational methods have been used to develop these models to fully understand the simultaneous mass and heat transfer in the MD process. Computational fluid dynamics has made two-dimensional modelling of this process possible, and results can also be determined via coupled finite difference and Runge-Kutta methods. The Monte Carlo method can simulate molecular flow moving in three dimensions, and energy efficiency has been improved by simulating novel possibilities such as varying external heat exchangers or solar
process designs \[11\].

\section*{1.3 Proposed Work}

As reviewed above, there have been several approaches used to evaluate the DCMD process, and many of these processes isolate and adjust one parameter at a time to provide a better understanding of its relationship to another parameter. This has helped the community gain a better understanding of what designs have room for improvement and what configurations have reached their potential. However, these studies have only covered the range of values for specific parameters in which system operation would be ideal. These discoveries still need to identify the effects those changes have on a holistic set of parameters for the entire system.

This work aims to define a relevant, related set of the thermal properties for the DCMD system. By using the Monte Carlo method, relationships between the inlet feed flow rate, temperature, and membrane porosity and the temperature polarization coefficient, and thermal efficiency are calculated from the simulations to pinpoint the ideal conditions for the DCMD process. Through molecular simulation, phase equilibrium was reached by calculating the chemical potential at the membrane interface and the entropy of the system was found. That entropy is used to calculate the exergy of the system and is compared to the temperature polarization coefficient and the thermal efficiency. This work demonstrates that a next useful step for this work could be the development of a Pareto frontier, under which the limitations of flux can be bounded, which will highlight the probabilistic range for improved future experimental work.
Chapter 2

DCMD Theory

2.1 Membrane Characteristics

A polymer is suitable for the MD process if it has porosity and cannot be wetted by process liquids [31]. Only vapor should be transported through the pores, and no capillary condensation can occur. The multicomponent vapor equilibrium must remain unaltered by the membrane and one side of that membrane must be in contact with the process liquid. Lastly, a partial pressure gradient of the vapor is the driving force of the MD process for each component.

In order to capture these requirements, extensive research has been targeted toward finding the membrane configurations that will make the MD process most efficient. There are two main configurations of membrane modules, tubular and plate and frame, as shown in Figure 2.1. The tubular system contains a high packing density of hollow fiber membranes where the shell or lumen side of the fibers receive the feed, and a cooling fluid, negative pressure, or sweeping gas can be added to the other side. The plate and frame system contains flat plate membranes and has a much smaller packing density for the same volume.
as the tubular configuration; however, layers of these membranes increase the effective area and this is widely used in laboratories to identify the parameters that increase flux and energy [8].

Of these two modules, there are key characteristics that determine how suitable the membrane is for the distillation process. Membrane thickness must be determined by balancing membrane permeability with thermal resistance. As thickness increases, the permeability rises and flux increases, though thermal resistance increases as well, which contributes to a reduction in thermal resistance. Membrane pores can also be considered a key characteristic. As previously stated in the definition of the MD process, the membrane must be porous, and should not be wetted by process liquids, which means that the hydrostatic pressure must be lower than the Liquid Entry Pressure (LEP). The wettability is defined by the Laplace (Cantor) equation given below [7]. This limitation requires a balance between pore size and pore distribution and introduces the need for ideal membrane material properties [6]:

$$LEP = \frac{-2B\gamma_l}{r_{max}} \cos(\theta) < P_{process} - P_{pore} \quad (2.1)$$

where $B$ is a geometric factor, $\gamma_l$ is the surface tension of the solution, $\theta$ is the contact angle between the solution and membrane surface, $r_{max}$ is the largest pore size, $P_{process}$ is the liquid pressure on either side of the membrane, and $P_{pore}$ is the air pressure in the membrane pore.

The three common materials used in MD are polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene fluoride (PVDF). These materials differ in thermal conductivity, hydrophobicity, and porosity, which affect the mechanical strength of the membrane under pressure and the overall membrane performance. Each configuration of the MD processes has different aspects that make one membrane material more advantageous than another. For example,
Figure 2.1: MD Module Configurations; a) plate and frame module used with flat sheet membranes; b) tubular module used with hollow fiber membranes [15]
PTFE is the most hydrophobic but also the most thermally conductive, making it a poor choice for DCMD, which experiences inherent conductive heat losses due to the latent heat of vaporization. PP and PVDF have similar thermal and chemical resistances, and there has been extensive research detailing the methods to fabricate such membranes with favorable thermal conductivity, hydrophobicity, and porosity. Two additional concerns about membrane fabrication are membrane fouling and wetting, which can cause flux to decrease. There are several published papers that discuss these challenges and suggest improved technology to address these issues, but they are outside of the scope of this thesis [14, 24, 28, 29, 33].

2.2 Heat Transfer across the Membrane and Boundary Layers

As mentioned above, the vapor pressure differential across the membrane is the driving force of this process, and is caused by a temperature difference on either side of the membrane. As illustrated in Figure 2.2, the total heat transfer includes (1) heat transfer across the membrane from the feed side to the permeate side as sensible and latent heat from the membrane, and (2) heat transfer from the bulk flow of the feed to the boundary layer by way of heat convection caused by part (1). Sensible heat is an exchange of heat that changes the system’s temperature, but not its volume or pressure, and is conducted through the membrane to the permeate. Latent heat is the energy required for a substance to change phase without changing its temperature and is carried by the water vapor [26].

The hot bulk feed solution is of temperature $T_f$ and meets the hydrophobic membrane at the membrane temperature $T_{m,f}$. The heat transfer rate of the
Figure 2.2: Heat and mass transfer mechanisms in the DCMD process [13]

feed side, $Q_f$, is:

$$Q_f = h_f(T_f - T_{mf})$$

(2.2)

where $h_f$ is the convective heat transfer coefficient of the feed solution. All heat transfer rates are on a per area basis.

Vaporization takes place at the membrane surface over the temperature range $\Delta T_m$ shown in equation 2.3 where $T_{mp}$ is the membrane temperature on the permeate side. Heat, $Q_m$, transfers through the membrane. This heat transfer includes both convection $Q_v$ and conduction $Q_c$:

$$\Delta T_m = T_{mf} - T_{mp}$$

(2.3)

$$Q_m = Q_v + Q_c$$

(2.4)

$$Q_v = h_v \Delta T_m$$

(2.5)
CHAPTER 2. DCMD THEORY

\[ Q_c = \frac{k_m}{\delta} \frac{dT}{dx} = \frac{k_m}{\delta} (T_{mf} - T_{mp}) \] (2.6)

\[ Q_m = h_v \Delta T_m + \frac{k_m}{\delta} (T_{mf} - T_{mp}) \] (2.7)

\[ Q_m = h_m \Delta T_m \] (2.8)

where \( h_v \) is the convective heat transfer coefficient of the vapor, \( k_m \) is the thermal conductivity of the membrane, and \( \delta \) is the membrane thickness. The variable \( h_m \) is defined in equation 2.9:

\[ h_m = \epsilon h_{mg} + (1 - \epsilon) h_{ms} \] (2.9)

where \( \epsilon \) is the membrane porosity, and \( h_{mg} \) and \( h_{ms} \) are the heat transfer coefficients of the vapor in the membrane pore and the solid material of the membrane, respectively.

Finally, the process ends with the water vapor condensing on the permeate side at \( T_p \) where the other side of the membrane pores interface with the cold permeate. The heat transfer rate of the permeate side, \( Q_p \) is:

\[ Q_p = h_p (T_{mp} - T_p) \] (2.10)

where \( h_p \) is the convective heat transfer coefficient of the permeate solution.

The bulk temperatures and the boundary layer temperatures tend to differ dramatically and considerably hinder the driving force. This effect is known as temperature polarization and explains the common, yet problematic, difference between theoretical flux and a much lower actual flux. Due to the boundary layer temperature differences, heat transfer occurs simultaneously with mass
transfer and additional complications emerge. The main hurdle is that most of the heat flux causes additional heat loss and only contributes a small portion of the heat flux, namely the latent heat of vaporization, to the mass transfer. The ratio between the latent heat and total heat flux is known as the thermal efficiency, and indicates quantity of heat transfer used to produce total flux [16].

There are two main methods to increase flux based on heat transfer. The first is by increasing the temperature difference between the feed and permeate and the second is to increase the temperature polarization coefficient (TPC, or \( \theta \)). TPC is defined as:

\[
\theta = \frac{T_{mf} - T_{mp}}{T_f - T_p}
\]  

(2.11)

The first method tends to require an energy-intensive external heat exchanger to boost the temperature of the feed.

The second method suggests the need to improve the convective heat transfer coefficient by reducing the thickness of the thermal boundary layer, so that the bulk temperature and membrane surface temperature would be closer in value, and the TPC would be close to one [2]. Taking a closer look at the energy balance of the closed system and the relationship between the heat transfer rate of the system and the flux, it can be considered that the heat transfer rate through the membrane must equal the heat transfer rates of the feed and permeate portions of the system, and can be defined as:

\[
Q_m = Q_f = Q_p
\]  

(2.12)

By substituting the above definitions of heat transfer rates throughout the system into equation (2.8), a total heat transfer rate can be written as:
CHAPTER 2. DCMD THEORY

\[ Q_m = h_m T_m = h_f (T_f - T_{mf}) = h_p (T_{mp} - T_p) \] (2.13)

Recall that heat and mass transfer occur simultaneously in the DCMD process. Equation (2.14) couples the heat transfer with mass transfer:

\[ Q_v = h_v T_m = J \Delta H_v \] (2.14)

where \( J \) is the rate of mass transfer or vapor flux and \( \Delta H_v \) is the heat of vaporization.

Generally, then, the heat transfer rate for the system can be written as:

\[ Q = J \Delta H \{T\} + h \Delta T \] (2.15)

Here it is important to note that \( \Delta H \{T\} \) represents the enthalpy of the liquid at a particular temperature for either the feed or permeate side, or the enthalpy of saturated vapor, to distinguish it from \( h \), the convective heat transfer coefficient.

2.3 Mass Transfer through the Membrane Pores

The mass transfer process starts with the hot feed evaporating at the vapor-liquid interface and ends with the resulting vapor pressure differential through the pores causing the water to condense on the cold permeate side. This process, shown in Figure 2.3, is often visualized as an electrical circuit for a multi-pore size model, as discussed below [26].

This process is driven by the difference in chemical potential and depends on temperature, pressure, and concentration. This implies that the vapor pressure differential and the membrane permeability are the two main contributing
factors that affect mass transfer. Water vapor permeability through the membrane is based on the kinetic theory of gases [27], where the main mass transport mechanisms are Knudsen diffusion and molecular diffusion. Viscous flow is negligible because the total pressure of the membrane is constant, as the feed and permeate are in direct contact with the membrane under atmospheric pressure [20].

The vapor flux can be calculated as a linear function of the vapor pressure difference across the membrane as shown below:

\[ J = C(P_f - P_p) \]  

(2.16)

where \( P_f \) and \( P_p \) are the vapor pressures of the transporting fluid at the membrane feed and permeate sides, respectively, and \( C \) is the membrane distillation coefficient for Knudsen flow. That coefficient is defined as:

\[ C = -\frac{2}{3l} \left( \frac{8\pi}{RT_{avg}M_i} \right)^{\frac{1}{2}} r^3 \]  

(2.17)

where \( l \) is the characteristic length of the pore channel, \( R \) is the gas constant, \( T_{avg} \) is the average temperature of the solution, \( M_i \) is the molecular weight of the species, \( i \), and \( r \) is the radius of the pore.
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The Knudsen number determines which transport mechanism should be used given a membrane pore and is defined by the mean path of the water molecule, \( \lambda \), divided by the membrane pore size, \( d_p \):

\[
Kn = \frac{\lambda}{d_p}
\]  

(2.18)

The free mean path can be calculated by:

\[
\lambda = \frac{k_B T_{p,avg}}{P \sqrt{2\pi \sigma^2}}
\]  

(2.19)

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature (K), \( P \) is the total pressure (Pa), and \( \sigma \) is the collision diameter (m).

Knudsen flow is the dominant transport mechanism when the free mean path is much higher than the pore size [17]. When this happens, the significance of the molecule-pore wall collisions dominate the molecule-molecule collisions. If the Knudsen number is small, the mean free path is much smaller than the pore size because the pore has captured idle air that was not dissolved in the water. A transition mechanism can exist that combines Knudsen and molecular diffusion when a mean pore size is used to theoretically determine flux. However, this was shown experimentally to be inaccurate and a log-normal pore size distribution better predicted experimental results [25].

In this chapter, heat transfer and mass transport have been described in detail on both the continuum and the molecular level. This theory is the basis for the system design and simulation model explained in the next chapter. Chapter 3 discusses the approach for executing the Monte Carlo simulation to incorporate the physical aspects of the system with a numerical analysis. The model system has been developed based on the data available in the current literature and has unique characteristics that will be discussed in the results section of Chapter 4.
Chapter 3

Methodology

3.1 System Design

Previously, the Monte Carlo model has been implemented for the DCMD process to describe the heat and mass transfer on a molecular level [35, 21, 12, 17, 6, 22]. In this study, a similar approach was adopted in order to account for membrane pore distribution and vapor flux without using adjustable parameters. The Monte Carlo approach also enables examination of how exergy changes with other thermal properties in the system. A porous membrane is represented by a simple two-dimensional rectangular network where the pore channels are represented by the bonds of the network referred to as elements. This network is shown in Figure 3.1. The effective pore diameter was distributed according to a statistical distribution function of log-normal probability density, and imitates several experimental results. The size of the membrane pore bodies, referred to as the nodes of the network, allow molecules to transport through the channel, but the pressure or temperature remains unaffected by the pore size. The pore length, $l$, remains a constant length, and given the pore size and pore length,
Figure 3.1: On the left is a simple two-dimensional rectangular membrane network, and on the right is a face centered cubic lattice of molecules the effective pressure and temperature fields can be calculated.

The following assumptions were made during the development of the simulation:

- membrane wetting did not occur and there was 100% salt rejection;
- DCMD is considered to be a steady-state process;
- the fluid flow is laminar and fully developed; and
- no heat loss to the environment occurs.

3.1.1 Calculating the Nodal Pressures and Temperature Profiles

With these bounding parameters, the vapor flux through the membrane can be determined. A variation of the Hardy-Cross method [5] was used to find the flows through the network, and the subsequent pressure drop across the pore. Assuming only purely water vapor is being transported, a mass balance for each node would be:
\[ \sum_j C_{ij} \Delta P_{ij} = 0 \quad (3.1) \]

where \( \Delta P_{ij} \) is the pressure drop across the pore and \( C_{ij} \) is defined by equation (2.17), and the sum is over all pores \( ij \) that are connected to the \( i \)th node.

The Newton/Raphson method was the iterative process chosen to compute the initial nodal temperature using the Antoine equation. At this point, with calculated vapor pressure and temperature at each node of the network, the molecular mean free path was found based on the average pressure and temperature. As mentioned earlier, viscous flow can be ignored due to constant atmospheric pressure, so therefore Knudsen flow is dominant. Using equation (2.16) for flux, and identifying the proper transport mechanism, a corresponding temperature distribution was calculated from the Antoine equation for each pore:

\[ P = \exp \left[ A - \frac{B}{C + T} \right] \quad (3.2) \]

where \( A, B, \) and \( C \) are empirical constants for a given species [18].

Once these values are determined for the system on the macroscopic level, the next stage requires a deeper look at equilibrium at the molecular level to fully understand the simultaneous mass and heat transfer.

As stated previously, the difference in chemical potential causes mass transfer. The chemical potential, \( \mu \), is the change in Gibbs free energy, \( G \), with respect to the change in amount of the component with constant pressure, temperature, and the amount of the other components, \( N_{AX} \):

\[ \mu_{AX}^{solution} = \left( \frac{\partial G_{solution}}{\partial N_{AX}} \right)_{T,P,N_{H_2O}} \quad (3.3) \]

The chemical potential could also be rewritten as \( \mu_i = \mu_{io}(T,P) + RT \ln(x_i, \gamma_i) \)
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Figure 3.2: FCC lattice before Monte Carlo Simulation

and its variables are defined in Appendix B.

The kinetic theory of gases is the basis for the calculations throughout the simulation model. After finding the temperature and pressure at each pore, an initial configuration was established to simulate a face centered cubic (FCC) lattice of 3000 particles within each pore in MATLAB, as shown in Figure 3.2.

3.1.2 Molecular Thermodynamics

This simulation is for an N-body system, a collection of particles that are in constant motion in all directions. The total energy, or the Hamiltonian, is a function of the linear momenta, $p$, and the center of mass positions of the particles, $r$, and is the total of the kinetic and potential energies of the system. The kinetic energy is determined by the particle motions that can be separated
CHAPTER 3. METHODOLOGY

into translational, rotational, and vibrational energies. The potential energy is associated with particle interactions between particles and their environment and depends on spacial variables instead of particle motion. Details of the equations of motion can be found in [35].

Using periodic boundary conditions, the coordinate vectors of each particle were stored, and the pair potential between each interaction was calculated, which depends only on the magnitude of the pair separation. The pair potential gives the particle interaction and potential energy of two interacting particles. The total potential energy is given by summing two-body energies called the pairwise additivity assumption, which is valid for dilute fluids. Real molecule interaction potentials are obviously more complicated, but there are a few common potentials that simplify models for theoretical work [27]. The potential, $u$, chosen for this simulation was the Lennard-Jones potential, due to its robustness and its computational simplicity:

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

(3.4)

where $\epsilon$ is the well depth and $\sigma$ is the collision diameter.

Thermodynamics has governing rules that state, for a closed system, that as the system undergoes changes from one equilibrium state to another, there will also be changes in the system energy, pressure, enthalpy, etc. The first law states that:

$$dU = \delta Q - \delta W$$

(3.5)

meaning that the change in internal energy of the closed system must equal the heat absorbed minus the work done on the environment. This is true for a system undergoing a change of state from one equilibrium to another. The
second law states that:

\[ dS \geq 0 \]  \hspace{1cm} (3.6)

which means that for an isolated system, the change in entropy is always positive. In classical thermodynamics, the entropy is defined as:

\[ dS = \frac{\delta Q_{\text{rev}}}{T} \]  \hspace{1cm} (3.7)

for a reversible system. However, due to the probabilistic nature of molecular simulations, information entropy better defines the kind of entropy suited for statistical discussion, and is defined as:

\[ S \equiv -k \sum_{i=1}^{n} p_i \ln(p_i) \]  \hspace{1cm} (3.8)

where \( k \) is the proportionality constant and \( p_i \) is the probability that a phase point is found in cell \( i \). To find the equilibrium distribution, entropy must be maximized and an understanding of statistical ensembles helps construct all states in which a system could possibly be to arrive at an average property that corresponds to a macroscopic state of the system. Ensembles, introduced by Gibbs in 1902 [9], can be conceived as a large number of identical independent systems that differ only in their configuration and velocity distribution. This collection of all the systems in \( 6N \)-dimensional phase space form a cloud or ensemble. There are five main ways to vary the systems to obtain specific macroscopic constraints to yield the below list of ensembles, such as number of particles (\( N \)), volume (\( V \)), energy (\( E \)), pressure (\( P \)), temperature (\( T \)), and chemical potential (\( \mu \)):

1. Microcanonical Ensemble (at constant \( N,V,E \)),

2. Canonical Ensemble (at constant \( N, V, T \)),

3. Grand canonical Ensemble (at constant \( N,V,E,\mu \)),

4. Isokinetic Ensemble (at constant \( N,V,E,T \)),

5. Isoenergetic Ensemble (at constant \( N,V,E,\mu \)).
3. Grand Canonical Ensemble (at constant V, T, \( \mu \)),

4. Isothermal - Isobaric Ensemble (at constant N, P, T), and

5. Gibbs Ensemble (a combination of the canonical, grand canonical and isothermal-isobaric ensembles).

The canonical ensemble was used for this work, since this is a closed and isolated system. As noted in equation (3.8), informational entropy is defined and the normalization of probabilities is:

\[
\sum_{i=1}^{M} p_i = 1
\] 

(3.9)

so that the average energy is defined as:

\[
\sum_{i=1}^{M} p_i \varepsilon_i = < E >
\] 

(3.10)

where \( \varepsilon_i \) is the value of the Hamiltonian at the \( i \)th point, and \(< E >\) is the internal energy. Based on the above constraints, \( S \), the thermodynamic entropy, can be maximized by using the Lagrangian method, which also gives the probability, the partition function of the canonical ensemble \( Z_N \), and uses \( \beta \) as the reciprocal temperature multiplied by Boltzmann’s constant. The relationships between these variables can be seen in equations (3.11), (3.12), (3.13), shown below:

\[
p_i = \frac{\exp(-\beta \varepsilon_i)}{Z_N}
\] 

(3.11)

\[
Z_N = \sum_{i=1}^{M} \exp(-\beta \varepsilon_i)
\] 

(3.12)
\[ S = k \ln(Z_N) + k\beta <E> \] (3.13)

From the fundamentals of thermodynamics a few additional relationships can be stated:

\[ S = -\frac{A}{T} + \frac{<E>}{T} \] (3.14)

\[ \beta = \frac{1}{kT} \] (3.15)

\[ A = -kT \ln(Z_N) \] (3.16)

where the partition function is a function of the Helmholtz free energy, \( A \), which relates the microscopic distributions to the macroscopic thermodynamic functions, namely the Boltzmann-Maxwell distribution.

### 3.1.3 Implementing the Monte Carlo Method to Find Chemical Potential

With the above statistical discussion in mind, a Monte Carlo simulation was implemented for each node, as seen in Figure 3.3. For the first node, a structure was created to store the data for the following parameters: the number of particles, the number of cells that contain the particles, and an index to match which particle number with the cell in which it is located. This helps to identify the particles for later calculations. After initializing all of the variables, thermal velocities were assigned using a random Gaussian distribution random number generator provided by MATLAB and the Euler method was used to store the original position and new positions of each particle as they move about the pore. Based on the new position, the program records if the particle strikes a wall or does not strike a wall. If a particle does strike a wall on the left or the right, the change in position and velocity is saved. When this is completed, the program
counts the number of particles that are now in each cell after the move and the cross reference list is created.

The program continues to loop over each cell and have the particles collide. As long as a cell has more than one particle in it, a number of candidate collision pairs are selected in each cell. Looping over the number of candidate collision pairs that were selected in the previous step, two particles are chosen randomly. The pair’s relative velocity is then calculated. If the ratio of the relative speed to the maximum relative velocity is greater than the random number generated by MATLAB, then the pair collides, post-collision velocities are calculated, and there is an updated maximum relative speed. The process continues for many random particles in each cell for all of the cells.

For a large number of trials, a test particle is added into the Monte Carlo
simulation and assigned a position. With the same periodic boundary conditions, the initial potential energy of the test particle is calculated. The test particle is randomly displaced and a potential energy is calculated. The original particles in the system are moved randomly as well, and their potential energies are also calculated. The acceptance criteria for moving the test particle depend on whether the change in potential energy is greater than the given random value.

If that condition fails, then a Widom test particle is used. The Widom test particle will calculate and sum the potential energy of just the inserted test particle, and not the original particles. This potential energy, plus the value of the long range cut off, calculates the value of the chemical potential for this system, since that point is where equilibrium is reached. From this, the average energy of each cell for all of the particles and all twelve nodes is calculated. Informational entropy is a function of energy, which was obtained by the previous explanation, as well as temperature and pressure, which were obtained through the modified Hardy-Cross approach.

3.2 DCMD Model

3.2.1 Exergy of the System

Exergy, denoted as \( Ex \), is the maximum useful work in a thermodynamic process achieving equilibrium with a heat reservoir to its environment. This work uses exergy analysis to observe how changing macroscopic properties influences microscopic properties. The combined mass and heat transport through the membrane is the thermodynamic process whose useful work may increase or decrease depending on other thermal properties such as inlet feed temperature, flow speed, and porosity.
The pressure-driven DCMD system that is induced by a temperature difference across the membrane has been simulated as stated above and several parameters have been determined that will be useful in calculating the exergy of the system. As shown in equation 3.17, exergy is a function of temperature, pressure, and composition:

\[ Ex = Ex^T + Ex^P + Ex^C \]  

\[ Ex^T = \dot{m}c_p \left[ (T - T_o) - T_o \ln \left( \frac{T}{T_o} \right) \right] \]  

\[ Ex^P = \dot{m} \left( \frac{P - P_o}{\rho} \right) \]  

\[ Ex^C = -\dot{m}(N_sRT_o \ln x_i) \]  

\[ \dot{m} = \frac{Q}{H} \]  

where \( \dot{m} \) is the mass flow rate, the subscript, \( o \), indicates the reference state of the temperature and pressure of pure water, \( c_p \) is the specific heat capacity, \( \rho \) is the density of the solution, and \( N_s \) is the number of moles of solvent per mass unit of the solution and is defined as:

\[ N_s = \left( \frac{1000 - \sum \frac{\omega_i}{\rho}}{MW_s} \right) \]  

The mole fraction, \( x_i \), is expressed as:

\[ x_i = \frac{N_s}{N_s + \sum \left( \frac{\beta_i c_i}{\rho MW_i} \right)} \]
where \( \beta_i \) is the number of generated particles from the dissociation of species \( i \), \( c_i \) is the mass concentration of the \( i \)th chemical per liter solution, \( MW_s \) is the molecular weight of the solvent, and \( MW_i \) is the molecular weight of the \( i \) chemical component. The total exergy destroyed and transformed into irreversible entropy production, \( R_s T_o \), is shown in equation 3.24:

\[
R_s T_o = Ex_{\text{electrical}} + Ex_{\text{thermal}} - \Delta Ex
\]  (3.24)

where the electrical and thermal components of the total exergy are written in equations 3.25 and 3.26 respectively, and the total exergy variation between outlet and inlet streams is given in equation 3.27:

\[
Ex_{\text{electrical}} = \frac{\dot{m} \Delta P}{1000 \eta_{\text{pump}}}
\]  (3.25)

\[
Ex_{\text{thermal}} = Q \left( 1 - \frac{T_o}{T} \right)
\]  (3.26)

\[
\Delta Ex = \sum Ex_{\text{inlet}} - \sum Ex_{\text{outlet}}
\]  (3.27)

3.2.2 System Efficiency

There are two main parameters that help determine the efficiency of the DCMD system. As stated previously in Chapter 2, the temperature polarization coefficient can give an approximation of how much heat is being lost through the membrane. The numerator is the temperature difference between the membrane surfaces and the denominator is the difference between the bulk temperatures of the feed and permeate. The more similar these differences in temperature are, the less energy is being lost through the membrane and the value of TPC is close to one. The thermal efficiency also depends on the membrane surface
temperatures and thermal properties. The thermal efficiency equation is shown below:

\[
\eta(\%) = \frac{J \Delta H}{\left( \frac{1}{h_f} + \frac{1}{(km/s)} + \frac{1}{h_p} \right)^{-1} \frac{T_{mf} - T_{mp}}{T_{mf} - T_{op}}} \times 100 \tag{3.28}
\]

In order to calculate this value and the TPC of the system, it is important to make sure that the mass transport and heat transport directions are accurate in two dimensions. Figure 3.4 shows that vapor flux passes through the membrane pores and the temperature profile color illustrates the heat flux through the membrane in the vertical direction. The horizontal direction incorporates the cross-membrane water flux and the vapor flux links both processes. Figure 3.5 then translates that physical process into a flow chart of the interaction of the various governing equations that must be resolved in the simulation process.

To start the simulation, several variables need to be initialized with guess values to begin the iterative process needed to compute the feed and permeate membrane temperatures. The temperature difference between the membrane feed temperature and membrane permeate temperature is estimated. The bulk feed temperature, \(T_{bf}\), is calculated by taking the average between inlet feed temperature and the initial outlet feed temperature, which is initially 1.5°C less than the given feed inlet temperature. \(T_{bf}\), \(T_{mf}\), and \(T_{if}\) are used to calculate a more accurate \(T_{of}\). The same process is used to calculate the permeate outlet temperature, \(T_{op}\), using a given permeate inlet temperature. With all of these values initialized, the membrane feed temperature is calculated and is the link between the simultaneous heat and mass transport.

As shown in the flow chart, several variables rely on \(T_{mf}\) as thermal properties are calculated through the discretized portion of the membrane, and mass
Figure 3.4: Schematic representation of DCMD model
Figure 3.5: DCMD Flow Chart for Computer Simulation, where the numbers refer to equations in Tables 3.1 and 3.2
transport properties are calculated across the membrane. As this process iterates, all variables related to thermal properties are constantly updating within a subloop until the convergence criteria is reached. The criteria is that the new $T_{op}$ must be within 2% of the original $T_{op}$. The simulation then stops and moves on to the next discretized portion using the previous output values as input values until the entire length of the membrane is analyzed. The average of this information provides the variables needed to calculate the TPC and thermal efficiency.

The equations that correspond to the numbered boxes in the flow chart can be seen in the table below. The definition of the variables are in the Appendix. Using the results of the simulation, the next chapter presents the relationship between exergy within the membrane pores and the thermal efficiency and TPC. These variables will be analyzed based on changes in the inlet temperature, porosity, and flow speed.
CHAPTER 3. METHODOLOGY

\[ T_{of} = \frac{m_{if}c_{pf}T_{if} - h_f A(T_{bf} - T_{mf})}{m_{of}c_{pf}} \]  
(3.29)

\[ T_{bf} = \frac{T_{if} + T_{of}}{2} \]  
(3.30)

\[ T_{if} = \frac{m_{of}c_{pf}T_{of} - h_f A(T_{bf} - T_{mf})}{m_{if}c_{pf}} \]  
(3.31)

\[ T_{op} = \frac{m_{ip}c_{pp}T_{ip} - h_p A(T_{bp} - T_{mp})}{m_{op}c_{pp}} \]  
(3.32)

\[ T_{bp} = \frac{T_{ip} + T_{op}}{2} \]  
(3.33)

\[ T_{ip} = \frac{m_{op}c_{pp}T_{op} - h_p A(T_{bp} - T_{mp})}{m_{ip}c_{pp}} \]  
(3.34)

\[ T_{mf} = \frac{\alpha(T_{ip} + \beta - T_{if}) + h_f T_{if} - JH_f}{\alpha + h_f + \alpha \beta} \]  
(3.35)

\[ T_{mp} = \frac{\alpha(T_{if} + \beta^{-1} - T_{ip}) + h_p T_{ip} - JH_p}{\alpha + h_p + \alpha \beta^{-1}} \]  
(3.36)

\[ T_{ffilm} = \frac{T_{of} + T_{mf}}{2} \]  
(3.37)

\[ T_{pfilm} = \frac{T_{op} + T_{mp}}{2} \]  
(3.38)

\[ k_f = 1 - (2.3434 \times 10^{-3} - 7.924 \times 10^{-6}(T - 273.15) + 3.924 \times 10^{-8}(T - 273.15)^2)S' + (1.06 \times 10^{-5} - 2 \times 10^{-8}(T - 273.15) + 1.2 \times 10^{-10}(T - 273.15)^2)S'^2 \]  
(3.39)

\[ C_{pf} = 4190 + (-13.81 + 0.1938(t_{ffilm} - 273.15) - 0.0025(t_{ffilm} - 273.15)^2)CL + (0.43 - 0.0099(t_{ffilm} - 273.15) + 0.00013(t_{ffilm} - 273.15)^2)CL^{1.5} \]  
(3.40)

\[ \mu_f = 0.0428i_s + 0.00123i_s^2 + 0.000131i_s^3 + (-0.03724i_s + 0.01859i_s^2 - 0.00271i_s^3) \times \log(10^3(2.414 \times 10^{-5} \times 10^{(247.8/(T_{ffilm} - 140))})) \]  
(3.41)

\[ k_p = -0.92247 + 2.8395 \left( \frac{t_{pfilm}}{273.15} \right) - 1.8007 \left( \frac{t_{pfilm}}{273.15} \right)^2 \]

\[ + 0.52577 \left( \frac{t_{pfilm}}{273.15} \right)^3 - 0.07344 \left( \frac{t_{pfilm}}{273.15} \right)^4 \]  
(3.42)

Table 3.1: Flow Chart Equations Group 1
\[ C_{pp} = 4217.4 - 3.72(t_{pfilm} - 273.15) + 0.141(t_{pfilm} - 273.15)^2 \\
- 2.654 \times 10^{-3}(t_{pfilm} - 273.15)^3 + 2.093 \times 10^{-5}(t_{pfilm} - 273.15)^4 \] (3.43)

\[ \mu_p = 2.414 \times 10^{-5} \times 10^{(247.8/(t_{pfilm} - 140))} \] (3.44)

\[ Pr_f = \frac{\mu_f C_{pf}}{k_f} \] (3.45)

\[ Re_f = \frac{dhV\rho}{\mu_f} \] (3.46)

\[ Pr_p = \frac{\mu_p C_{pp}}{k_p} \] (3.47)

\[ Re_p = \frac{dhV\rho}{\mu_p} \] (3.48)

\[ Nu_f = 0.664Pr_f^{1/3}Re_f^{1/2} \] (3.49)

\[ Nu_p = 0.664Pr_p^{1/3}Re_p^{1/2} \] (3.50)

\[ h_f = \frac{Nu_f k_f}{dh} \] (3.51)

\[ h_p = \frac{Nu_p k_p}{dh} \] (3.52)

\[ P_{sat}^{mf} = x_w a_w P_{sat}^{w} \] (3.53)

\[ J_f = AC_m P_{sat}^{mf} \] (3.54)

\[ H_f = 1000(1.7535T_{mf} + 2024.3) \] (3.55)

\[ P_{sat}^{mp} = 133.322 \times 10^{(8.10765 - (1450.286/(T_{mp} + 235)))} \] (3.56)

\[ J_p = AC_m P_{sat}^{mp} \] (3.57)

\[ H_p = 1000(1.7535T_{mp} + 2024.3) \] (3.58)

Table 3.2: Flow Chart Equations Group 2
Chapter 4

Results and Validation

This chapter will present the results of the Monte Carlo simulation applied for a DCMD system. It will also show the relationships between exergy, changes in porosity, temperature, and flow rate, as well as how these parameters compare with the temperature polarization coefficient (TPC) and thermal efficiency (TE). The model includes two modes of transport, heat and mass transfer through the membrane and across the length of the membrane. Using a concurrent flow pattern, where the feed and permeate fluids flow in the same direction across the length of the membrane, the simulation discretizes the membrane, and at each location calculates the inlet, outlet, and membrane temperatures on the feed and permeate sides. Once this is complete, the output values become the input values for the next section and the loop continues. After the system temperatures are calculated, parameters are isolated to see how they effect the TPC and TE.

It is common practice in DCMD research to vary the feed temperature between 20°C and 90°C and the permeate temperature between 10°C and 40°C. It is also well known that the feed temperature is the parameter that appears to
CHAPTER 4. RESULTS AND VALIDATION

4.1 Porosity Relationship to Feed Temperature, TE, TPC

This simulation identifies the trends that thermal properties have along the membrane. For example, Figure 4.1 shows that the feed temperature decreases across the membrane at different porosities. The figure shows that varied membrane porosity has little effect on the temperature of the feed solution across the membrane. There is a slight gap between the line that represents 0.3 porosity and the lines that represent 0.5 and 0.7 porosities. Although the values are similar, a porosity of 0.3 has a higher value for feed temperature across the membrane.

This is also the case when analyzing the effect varied porosity has on the thermal efficiency over increasing temperature. Figure 4.2 shows that while the thermal efficiency increases with increasing temperature, the porosity variation
Figure 4.2: Thermal Efficiency vs. Increasing temperature with varying porosity does little to shift the thermal efficiency. One difference between this figure and the previous figure is that there is a gap between the line that represents 0.7 porosity and the lines that represent 0.5 and 0.3 porosities. This gap means that the rate of increase of thermal efficiency as temperature increases is faster at a 0.7 porosity than at either of the lower porosities.

The final plot in this section is Figure 4.3 and shows the temperature polarization coefficient (TPC) decreasing with increasing temperature at varying porosities. When the porosity is 0.3, the TPC has a higher value and when the porosity is 0.7, the TPC has the lowest value. The decrease does not appear to be uniform since the gap between the 0.3 and 0.5 porosities is larger than the gap between 0.5 and 0.7 porosities. This may be because a high porosity has a higher impact on the membrane surface temperatures causing there to be a smaller temperature difference between the membrane on the feed side and the membrane on the permeate side. This is to be expected because porosity affects the thermal conductivity of the membrane and can hinder membrane tempera-
4.2 Mass Flow Rate Relationship to Feed Temperature, TE, TPC

Next, examining how changes of mass flow rate affected the feed temperature, TE and TPC, it can be observed that changing the mass flow rate had a larger effect than changing the porosity. An example of this is seen in Figure 4.4, where the feed temperature decreases across the membrane. The slower flowrate, 0.35 kg/s, causes the temperature to decrease faster than the flow rate of 0.55 or 0.75 kg/s. There is also a larger gap between the line that represents 0.35 kg/s and the lines that represent 0.55 and 0.75 kg/s than between the lines that represent 0.55 and 0.75 kg/s. This could mean that the decrease in flow rate does not lead to a decrease in feed temperatures uniformly.

Thermal efficiency of the system in Figure 4.5 does not appear to change much with increasing mass flow rate. The most distinct change appears to be a shift in the graphy from 0.35 kg/s to 0.75 kg/s. The temperature range at 0.35
Figure 4.4: Feed Temperature across the membrane with varying mass flow rate kg/s is from approximately 323 K to almost 333 K, which is approximately a ten degree difference. The temperature range at 0.55 kg/s is also almost a ten degree difference, however, that difference is shifted to the right. This is also the case for 0.75 kg/s. This implies that with a faster flow rate, the temperature of the feed increases but the increase is no more than a ten degree difference.

Similarly to Figure 4.3, the plot of TPC with varied porosity, in Figure 4.6, TPC decreases with increasing feed inlet temperature and increases with increasing mass flow rate. This trend may exist because the slower flow rate causes the membrane temperatures to have a smaller temperature difference than the feed and permeate temperatures. As the flow rate increases, the temperature difference between the membrane begins to reflect a value closer to the temperature difference between the feed and permeate temperatures.

This is an expected result since the flow rate is a parameter that influences the system’s temperatures. These temperatures are then used to calculate TPC and TE, as shown in equations 2.11 and 3.28. The relationship between the TE and TPC can be summarized that as the inlet feed temperature rises, the thermal efficiency increases but the temperature polarization coefficient decreases.
CHAPTER 4. RESULTS AND VALIDATION

Figure 4.5: Thermal efficiency across the membrane with varying mass flow rate

Figure 4.6: TPC at different feed temperatures with varying mass flow rate
4.3 Porosity and Mass Flow Rate Relationship to Exergy

Next, exergy, the useful energy of the system, is observed to determine if there is a relationship with either porosity and/or flow rate. Exergy is a function of the changes in enthalpy, entropy, and temperature. It is expected that the exergy of the system increases with increasing feed inlet temperature because a larger temperature difference between the feed and the permeate increases the pressure. The additional effects of porosity and mass flow rate can be seen in Figures 4.7 and 4.8, respectively. It is observed that exergy is not greatly affected by porosity, but it is by mass flow rate.

Recalling all of the relationships from the flow chart in Section 3.2.2, the mass flow rate is directly connected to a multitude of other variables. When mass flow rate changes, that changes would affect other variables throughout the system such as temperature. In accordance with equation 3.17, a decrease in temperature and pressure will decrease the total change in exergy. As the feed temperature gets cooler throughout the length of the membrane, the amount of
useful energy of the system also decreases. The lower flowrate produces a lower value for exergy and the higher flowrate produces a higher value for exergy.

Figure 4.9 provides another way to observe that exergy decreases with a temperature decrease along the length of the membrane. The feed inlet temperature is decreasing along the membrane. This is in agreement with exergy also decreasing along the membrane. The results of membrane temperatures can be validated based on Figure 4.10 from [11]. Their plot shows that as the temperatures of the feed and permeate approach each other, so do the membrane temperatures on the feed and permeate sides. By understanding how the temperature changes across the membrane, it becomes clear that variables that are a function of temperature would behave in similar ways to this plot.

4.4 Exergy relationship to TPC and TE

As stated previously, the two main parameters that determine the efficiency of the DCMD system are the thermal efficiency and the temperature polarization coefficient. In addition to analyzing how the exergy changes with varied porosity and varied mass flow rate, this section will observe how exergy changes with
Figure 4.9: Membrane temperatures across each slice of the membrane
Figure 4.10: Membrane temperature across the length of the membrane [11]
First, Figure 4.11 shows how exergy changes with increasing feed temperature and also shows how exergy varies with porosity. The previous section revealed that a change in porosity does not cause exergy to change dramatically. Nonetheless, it is clear that as the feed temperature increases, the exergy increases as well. This is an expected result. Again, there is a slight shift to the right in temperature when exergy experiences a change in mass flow rate, a result that was similar to TE with varying mass flow rate in Figure 4.5. This is still the case when exergy is compared to the feed temperature as shown in Figure 4.12. However, one noticeable difference is that the exergy is lower at a lower flow rate and is higher at a higher flow rate.

Next, the TE will be compared with exergy at varying porosities and mass flow rates. Figure 4.13 shows that, again, porosity has a very small effect on TE regardless if the plot is compared to exergy or temperature. This is a consistent result. There is a small intersection point in this figure similar to Figure 4.11
CHAPTER 4. RESULTS AND VALIDATION

Figure 4.12: Exergy vs. Feed Temperature with varying mass flow rate and takes place near the same value for exergy.

Figure 4.14 compares exergy to TE with varied mass flow rate. The TE value for different mass flow rates does correlate to different exergy values. The lower the flow rate, the lower higher the TE is for a given value of exergy. This is a different result for TE and mass flow rate relationships since Figure 4.5 shows very little change in TE regardless of the value of the mass flow rate. This may be because the rate of increase of exergy is larger than the rate of increase of temperature so the changes in mass flow rate propagate on a larger scale.

The last comparison of data from the simulation proposed in this work is determining the relationship between the TPC and exergy over varying porosities and flow rates. Recall Figure 4.3 that shows there is a difference in TPC when porosity is varied. Figure 4.15, below, shows a very similar plot, that if the porosity is high, the TPC is low with increasing exergy and the TPC is high at lower porosity with increasing exergy. This again relates back to the temperatures at the membrane and bulk locations on either the feed and per-
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Figure 4.13: Thermal efficiency vs. Exergy with varying porosity

Figure 4.14: Thermal efficiency vs. Exergy with varying mass flow rate
An increase in porosity makes the temperature difference between the membranes closer in values than the temperatures of the bulk solutions, and causes a low TPC value.

As similar result can be observed in Figure 4.16. This plot mirrors the result obtained in Figure 4.6 where the increase in mass flow rate increases the TPC and a lower mass flow rate results in a lower TPC. This trend is true for TPC compared to feed temperature and TPC compared to exergy. It appears as if the rate of increasing exergy is higher than the rate of increasing feed temperature because the rate of decrease of TPC when the mass flow rate is 0.35 kg/s when compared to exergy is much steeper than the same data compared to feed inlet temperature. The faster rate between exergy and temperature is a trend also seen in Figure 4.14.
4.5 Validation with Current Literature

The analysis completed in this work is fairly new to the field and there is not much data regarding the parameters investigated in this simulation. However, there are a few strong correlations between common parameters that suggest the data on exergy is correct. This section will conclude this chapter by showing four plots that agree with a few of the plots produced in the previous sections. The figures below will show that the simulation has reproduced trends that are common in DCMD research and that will serve as basis for validating the trends seen for exergy.

Results from several published papers will be examined to ensure that the proposed model is in good agreement with other simulations and experiments. First, Mohamed Khayet and Takshi Matsuura published a membrane distillation book in 2011 that has become the canonical reference for simulation calculations and experiments [21]. This can be used to compare the temperature polarization coefficient against temperature, as well as the thermal efficiency. Chapter 10 of the book discusses direct contact membrane distillation at length and identifies
CHAPTER 4. RESULTS AND VALIDATION

trends of TPC and TE. The book states that the temperature polarization coefficient will decrease with increasing feed temperature. It also plots a graph of different membrane types and shows what the TPC values would be over the feed temperature. Below in Figure 4.17, that plot is compared to Figure 4.3 from the simulation results and shows that this relationship is true.

Next, F. Macedonio et al. have published work about the relationship between increased flow rate and temperature as well as the flow rate and the position on the module [1]. The decreasing feed temperature in red in the plot on the left in Figure 4.18 matches the results of the simulation. This is seen in Figure 4.4 where the lower the mass flow rate, the lower the feed temperature. This plot also shows how the flow rate decreases across the length of the membrane. Both of these parameters are in good agreement with literature.

The research group of Macedonio et al. did additional work that helps validate the results of this research. On the left side of Figure 4.19 the thermal efficiency is plotted against feed temperature for a series of different membranes. These types of membranes and their properties are outside of the scope of this research; however, the trend of thermal efficiency increasing with increasing temperature is prevalent. This plot is compared to Figure 4.5 where the thermal efficiency is also increasing with increasing feed temperature.

Finally, there is published literature on the effects of thermal efficiency and porosity. Elimelech et al. recently published a paper about the relationship between porosity and thermal efficiency. In Figure 4.20, the Elimelech et al. plot is on the left and the plot from this simulation is on the right. Both plots show that there is a trend of increasing porosity with an increase in thermal efficiency.

The foundation of the feed temperature, TE, and TPC have been compared to common parameters, such as porosity and mass flow rate. The comparisons
Figure 4.17: Feed temperature vs. TPC from Khayet and Matsuura [21].
Figure 4.18: Flow rate and position [10]
Figure 4.19: Thermal efficiency vs. Feed Temperature from Macedonio et al. [1]
Figure 4.20: Porosity vs. thermal efficiency [13]
have been validated by current literature and show that the simulation has reasonable results. For this reason, the calculation of exergy compared to these values must also be valid as the equations have been taken from literature and used against the simulation validated by literature. Exergy calculations for DCMD are new and preliminary results have been published over the past two years. Those results define the control volume to be the entire DCMD system with mechanical components and complete exergy equations based off of this definition. This work sets itself apart by analyzing the control volume of individual membrane pores. At each pore, the energy, entropy, enthalpy, and temperature is calculated to determine the exergy of the membrane. This microscopic-scale analysis has been applied to other applications, but not DCMD applications that would produce results applicable to this simulation. Nevertheless, the very well-known parameters mentioned above that have been calculated and validated against current literature have laid the foundation for exploration into this unique niche of the DCMD field.
Chapter 5

Conclusions and Future Work

5.1 Conclusions

In this work, a direct contact membrane distillation system was simulated microscopically and macroscopically. On the microscopic level, a direct simulation Monte Carlo method was executed to evaluate the useful work in the particle network which is described here as exergy. This calculation was possible by determining the chemical potential when the system was at equilibrium. By calculating the energy in each cell, the entropy in each cell became an output in the simulation. Since exergy is not only a function of entropy, the macroscopic analysis of the DMCD system was used to gather information about enthalpy and temperature to complete the exergy calculation. Exergy was used to understand its relationship with other thermal properties such as the temperature polarization coefficient, the thermal efficiency, and the feed temperature. Physical parameters such as porosity and mass flow rate were considered in the
CHAPTER 5. CONCLUSIONS AND FUTURE WORK

analysis to see how much of an effect they had on the thermal properties.

The porosity had little effect on the feed temperature and the exergy of the system, but as it increased it caused the TPC and TE values to increase as well. Mass flow rate had more of an impact on all of the thermal properties. The faster the mass flow rate, the higher the TE, feed temperatures, and exergy. The opposite was true for the TPC, where having a slower mass flow rate is more beneficial when trying to reduce that value. The TPC decreases with increasing feed inlet temperature, and TE increases with increasing temperature which is aligned with other results in the current literature.

This research is similar to other published simulations in the membrane distillation field in that it compares thermal properties and physical properties. The concept that sets this work apart is the relationship to exergy at the microscopic level as opposed to an entire system with external heat sources and other mechanical components. Including this exergetic relationship provides information to the scientific community about where useful work is in the microscale system and to see how that impacts the larger system.

5.2 Future Work

Several cases have been analyzed in this paper to gain a better understanding of the interconnected relationships between the thermal and physical properties of DCMD in the microscopic and macroscopic scales. There are a number of additional configurations that could be isolated to gain additional useful information. Furthermore, vacuum, air gap, and sweeping gas membrane distillation configurations may have similar or vastly different relational properties based on the intricacies of the systems. A Pareto frontier is a widely used tool to understand the best possible values for parameters while ensuring that other components/parameters are not adversely changed. Taking the current infor-
information in this work and optimizing each parameter would be useful for further DCMD experimentation. For example, other published work in the literature suggests that a counter-current flow has a better permeate flux output than the concurrent flow which was studied in this work. It may be useful to change the direction of the flow and vary the types of membranes used instead of comparing all thermal properties for one membrane with one thermal conductivity value.

Additionally, DCMD research is moving in the direction of renewable energy as an external heat source instead of customary sources like heat exchangers fueled by consumption of primary fuels. There is current work in solar DCMD where an electro-spun carbon black nanoparticle coating is layered on top of the membrane to increase the temperature difference between the feed and permeate sides, which should positively influence the flux. This research is widely carried out experimentally which is costly. The cost of DCMD experimentation has had an impact on the pace of the research in this field. The ability to simulate this interface would provide invaluable information at a much smaller cost. Moving forward, continued computational research will provide a good foundational understanding of the DCMD process to guide future experimental work.
Appendix A

Variables in the Flow Chart from Tables 3.1 and 3.2

$cp$, Specific Heat Capacity
$h$, Convective Heat Transfer Coefficient
$H$, Enthalpy
$J$, Vapor Flux
$k$, Thermal Conductivity
$\mu$, Dynamic Viscosity
$Nu$, Nusselt
$Pr$, Prandtl
$P_{sat}$, Saturated Pressure
$Re$, Reynolds
$T_b$, Bulk Temperature
$T_{film}$, Film Temperature
$T_i$, Inlet Temperature
$T_m$, Membrane Temperature
$T_o$, Outlet Temperature

subscripts

$f$, Feed side of the membrane
APPENDIX A. VARIABLES IN THE FLOW CHART FROM TABLES ?? AND ??68

\( p \) Permeate side of the membrane

Greek Symbols

\( \alpha \) Ratio of membrane properties (thermal conductivity over thickness)

\( \beta \) Ratio of convective heat transfer coefficients (feed over permeate)
Appendix B

Alternative equation for chemical potential

\[ \mu_i = \mu_o(T, P) + RT \ln(x_i, \gamma_i) \]

\( \mu_i \) Chemical Potential of species \( i \)
\( \mu_o \) Chemical Potential of reference species
\( T \) Temperature
\( P \) Pressure
\( R \) Universal Gas Constant
\( x_i \) Mole Fraction of species \( i \)
\( \gamma_i \) Activity Coefficient of species \( i \)
Bibliography


