Extreme Liquid Superheating and Homogeneous Bubble Nucleation in a Solid State Nanopore

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Extreme Liquid Superheating and Homogeneous Bubble Nucleation in a Solid State Nanopore

A DISSERTATION PRESENTED
BY
EDLYN VICTORIA LEVINE
TO
THE SCHOOL OF ENGINEERING AND APPLIED SCIENCES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
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Extreme Liquid Superheating and Homogeneous Bubble Nucleation in a Solid State Nanopore

ABSTRACT

This thesis explains how extreme superheating and single bubble nucleation can be achieved in an electrolytic solution within a solid state nanopore. A highly focused ionic current, induced to flow through the pore by modest voltage biases, leads to rapid Joule heating of the electrolyte in the nanopore. At sufficiently high current densities, temperatures near the thermodynamic limit of superheat are achieved, ultimately leading to nucleation of a vapor bubble within the nanopore.

A mathematical model for Joule heating of an electrolytic solution within a nanopore is presented. This model couples the electrical and thermal dynamics responsible for rapid and extreme superheating of the electrolyte within the nanopore. The model is implemented numerically with a finite element calculation, yielding a time and spatially resolved temperature distribution in the nanopore region. Temperatures near the thermodynamic limit of superheat are predicted to be attained just before the explosive nucleation of a vapor bubble is observed experimentally.

Knowledge of this temperature distribution is used to evaluate related phenomena including bubble nucleation kinetics, relaxation oscillation, and bubble dynamics. In particular, bubble nucleation is shown to be homogeneous and highly reproducible. These results are consistent with experimental data available from electronic and optical measurements of Joule heating and bubble nucleation in a nanopore.
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TO MY PARENTS
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The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.

Herbert B. Callen

1

Introduction

We recently discovered that an aqueous electrolyte can be strongly superheated within a solid-state nanopore by electrical means. In the present work, I explain our investigations into understanding this discovery. Using experimental and theoretical methods, we show that the nanopore enables the focusing of thermal energy, allowing for the creation and manipulation of highly excited, metastable states of the liquid electrolyte in the nanopore. This superheated liquid can ultimately undergo a transition to the vapor phase by means of a bubble nucleating homogeneously within the nanopore.

We have found that the electrical method for superheating within a nanopore is a finely controlled and highly reproducible manipulation of the liquid state. As such, it opens many exciting avenues of research, including the development of useful applications for superheated liquids.
On a fundamental level, this method enables our studying the properties of the superheated state of the most important liquid in nature: water. The extreme localization of bubble nucleation within the nanopore also affords us unprecedented temporal resolution in elucidating the creation and evolution of a new phase.

This chapter describes the experiments that motivated our study of heating in nanopores. I begin with an introduction to the solid state nanopore as a tool for investigating physics on the nanoscale and subsequently describe the motivating experiments. In the context of explaining our results, we were interested in determining the temperature of the electrolyte in the nanopore. Experimental measurement of the temperature within the pore was not possible, necessitating my work in theoretical modeling that I present in this thesis. The maximum level of superheat that I calculated to be attained within the pore was extreme: over 200 K above the equilibrium boiling point of water at atmospheric pressure. This is a remarkable result that we did not anticipate, and explains many interesting effects we observe in the experiments.

In the latter half of this chapter, I discuss the physics behind superheating of a liquid, explaining how it is thermodynamically possible to occur. I find this to be one of the most important concepts required to understand the underlying physics involved in the extreme heating of the electrolyte. It sets the stage for why superheating a liquid is possible to begin with before delving into the particular circumstance of superheating in a nanopore.

This chapter concludes with an outline of the organization of this thesis. The objective of this thesis is to explain heating and bubble nucleation caused by focused currents induced to flow through a nanopore. My focus is on the theoretical modeling I have done in conjunction with the experiments performed in our group. In the ensuing chapters, I will answer the questions of how superheating can be brought about in a nanopore, what extreme temperatures are achieved, what unique properties the superheated state has in the nanopore environment, and how, ultimately, the nucleation, growth, and collapse of the vapor phase occurs.
1.1 **Solid State Nanopores**

All of the experiments and modeling described in this work involve solid state nanopores. A solid state nanopore is a small, nanometer-sized hole that has been fabricated in a thin, free-standing membrane of insulating material such as silicon dioxide, SiO\textsubscript{2}, or silicon nitride, Si\textsubscript{3}N\textsubscript{4}. Current techniques for fabricating such a pore include using either ion sculpting\textsuperscript{2} or a focused electron beam.\textsuperscript{3} A nanopore is approximately cylindrical in shape, however the exact geometry of each nanopore will vary between different fabricated samples.\textsuperscript{4}

The Golovchenko Group at Harvard University has a long history of using these nanopores to study physics on the nanoscale.\textsuperscript{2,4–7} A particular focus of the group has been the application of nanopores to DNA sequencing.\textsuperscript{8,9} These studies require mounting the membrane in a flow cell that is then flushed with the liquid of interest, wetting the nanopore.\textsuperscript{4} The membrane therefore separates two reservoirs of the liquid, connected only by the fluid in the nanopore. The liquid is typically an aqueous electrolyte, with DNA or other polymers in solution. A voltage is subsequently applied across the insulating membrane, generating an ionic current through the pore. The resistance to the flow of ions in the system primarily results from the electrical resistivity of the solution combined with constricted geometry of the nanopore.\textsuperscript{4,10,11} Therefore, the behavior of the liquid (and polymers if included) in and around the region of the nanopore can be carefully monitored by measurement of the ionic current.

1.2 **Experimental Investigation of Joule Heating in a Nanopore**

The experiments that led to our discovery of superheating in solid state nanopores were initially aimed at exploring the consequences of extreme current densities in these pores. Typical voltage biases used in the DNA experiments are approximately 100 mV.\textsuperscript{8} Our initial question was quite simple: in the absence of DNA, what happens when increasingly large voltage biases are applied
across the membrane?

To explore this question, we used the experimental setup shown in Figure 1.1. This consists of a single nanopore, fabricated with a focused ion beam in a free-standing silicon nitride membrane. The membrane is affixed to a frame of silicon dioxide and silicon. Silicon nitride was chosen as the membrane material because it is highly wettable and has a higher thermal conductivity than the aqueous electrolyte. These properties will prove to be important characteristics needed for extreme superheating because they minimize the likelihood of heterogeneous nucleation occurring on the walls of the nanopore.

![Figure 1.1: Cross sectional schematic (not-to-scale) of the experimental setup used to measure ionic current in the nanopore for different applied voltages. The compensation circuit on the left hand side of the figure is used to minimize the initial effect of capacitive charge build up across the membrane.](image)

The membrane and frame were mounted in a fluidic cell in which the membrane separated two fluid chambers connected electrically only through the pore. An aqueous 3M NaCl solution prepared in deionized, degassed water was added to each chamber and contacted with Ag/AgCl electrodes. A pulse generator (HP 8110A), current sensing resistor, and high bandwidth (500 MHz) oscilloscope are connected to the fluidic cell with a compensation circuit to minimize the
effect of capacitance between the two fluidic chambers.

Figure 1.2 plots the time-dependent nanopore conductance observed when 11 $\mu$s voltage pulses, ranging from 4 to 8.22 V, with 30 ns rise time were applied across a 53.5 nm radius, 71 nm thick nanopore. The initial nanopore conductance is 1.15 $\mu$S (aside from an initial capacitance spike due to imperfect compensation) and increases with time and applied voltage to a value of 3.5 $\mu$S and a current density of $3.3 \times 10^9$ A/m$^2$ for 8.22 V applied. We expected this rise due to time dependent Joule heating of the electrolyte in and near the pore and the positive temperature dependence of electrolyte conductivities, which are strongly influenced by the temperature dependence of the water viscosity. The noise in the data belongs to the oscilloscope amplifiers.

![Figure 1.2: The conductance of a 53.5 nm radius, 71 nm thick nanopore at 4, 5, 6, 7, and 8.22 volts. The data are filtered at 13 MHz from 0 to 1 $\mu$s and 20 MHz from 1 to 10 $\mu$s by an eight pole Bessel filter.](image)

Figure 1.3 plots a continuation of the conductance data for the applied 8.22 V pulse from
Figure 1.2(a) beyond 10 $\mu$s. A rapid drop in the conductance occurs at 10.4 $\mu$s. This is the result of a bubble nucleating and growing explosively within the nanopore. In so doing, the bubble blocks the conduction of ions through the pore, contributing to the rapid drop in conductance. The bubble ultimately collapses and the conductance rapidly returns to its previous level as Joule heating resumes. The electrolyte within the pore consequently re-heats, triggering another bubble nucleation event. This cycle repeats, and subsequent bubble events are seen to occur with quasiregular periodicity after the first event. The duration of each bubble event is approximately 16 ns with about 120 ns between events. The behavior is that of a relaxation oscillator whose time constant is shown in Ch. 7 to be determined by the relevant thermal and fluid dynamics.

Figure 1.3: Continuation of the 8.22 V conductance data after 10 $\mu$s. The data are filtered at 200 MHz; the faded line in the background is the unfiltered measured conductance data.

Our interpretation of these data was that rapid Joule heating of the electrolyte in and near the nanopore results, elevating the temperature of the electrolyte until a vapor bubble nucleates in
the nanopore, blocking conductance. However, we did not know how hot the liquid in the pore became or whether the bubble nucleation events were homogeneous, occurring in the center of the pore, or heterogeneous, occurring on the edge of the pore. Experimental determination of the spatial extent and temporal evolution of the temperature distribution within the pore are difficult. Therefore, we rely heavily on model calculations to interpret results.

1.3 The Superheated Liquid: A State of Metastable Equilibrium

My initial calculations of focused Joule heating in the nanopore indicated that the temperature of the liquid was becoming much hotter than the equilibrium boiling point well before nucleation events were observed to occur. This led us to the realization that the liquid in the nanopore was likely being superheated; i.e. heated above its boiling point while still remaining a liquid. I therefore set out to establish for myself how superheating is thermodynamically possible. In this section, I share my understanding of these concepts which I applied to the question of heating a liquid in a nanopore.

A superheated liquid is a liquid that has been heated to a temperature above its boiling point at a given pressure without converting to a vapor. Vaporization of this liquid has not occurred due to the energetic barrier required to form an initial liquid-vapor interface. This energy barrier prevents the system from transitioning to the more energetically favorable vapor state and is the reason that superheating can occur.

In the framework of thermodynamics, a superheated liquid is a metastable equilibrium state. Thermodynamic equilibrium is defined by states for which the entropy, $S$, of the system is an extremum: $dS = 0$. In order for such an equilibrium to be stable, the extremum in entropy must be a maximum: $d^2S < 0$. This entropy maximum principle is subject to the constraint of a given total internal energy, $U$, for a closed composite system. These statements can be reformulated using the energy representation requiring $dU = 0$ and $d^2U > 0$ for stable equilib-
This energy minimum principle is subject to the constraint of a given total entropy for a closed composite system. A metastable equilibrium state is defined as a local minimum in energy, whereas a fully stable equilibrium state is the global minimum in energy for that system. A liquid at atmospheric pressure is in stable thermodynamic equilibrium when its temperature is below its boiling point, but is in metastable thermodynamic equilibrium when its temperature is above its boiling point. In the latter case, the fully stable equilibrium state is the vapor phase.

These concepts can be illustrated very simply by the example of a single-component, van der Waals fluid. The van der Waals equation of state approximates the behavior of a non-ideal gas and captures the qualitative features of a liquid-vapor phase transition. The equation proposed by van der Waals is

\[
P = \frac{Nk_bT}{V - Nb} - \frac{N^2a}{V^2}
\]

where \(V\) and \(N\) are the extensive parameters volume and particle number, \(P\) and \(T\) are the intensive parameters pressure and temperature, \(k_b\) is Boltzmann’s constant, and \(a\) and \(b\) are two empirical constants specific to the particular fluid. The stability criterion, \(d^2U > 0\), can be shown to require

\[
\left(\frac{\partial P}{\partial V}\right)_T < 0
\]

which is an expression of Le Châtelier’s Principle. However, the van der Waals equation violates this stability criterion over certain regions of the macroscopic configuration space. This becomes clear upon inspection of isotherms of the dimensionless form of Eqn. 1.1, plotted in Figure 1.4. The spinodal curve marks the boundary between stable and unstable fluid and is calculated by

\[\text{A Legendre transformation can be used to convert from } U, \text{ to the Helmholtz free energy, Gibbs free energy, or Enthalpy, depending on which thermodynamic parameters of the system are constrained.}\]

\[\text{Note that although only one equation of state is needed in this discussion on stability, complete thermodynamic specificity of a single component system requires three equations of state: one equation for each of the intensive parameters, } P, T \text{ and the chemical potential } \mu, \text{ in terms of the extensive parameters, } V, N, \text{ and the entropy } S. \text{ This is in the energy representation. When considering the entropy representation, the extensive parameters are } V, N, \text{ and the internal energy } U.\]
determining the points at which $\partial P/\partial V$ are equal to zero. All states below the spinodal are thermodynamically unstable and cannot physically occur. This unstable region separates the incompressible, liquid-like phase on the left-hand side of the spinodal from the compressible, vapor-like state on the right-hand side of the spinodal. For temperatures below the critical temperature, $T_c$, approach of the unstable region from the left causes the system to undergo a phase transition from liquid to vapor, whereas approach of the unstable region from the right causes a phase transition from vapor to liquid. The unstable region does not extend above $T_c$, therefore no distinction can be made between liquid and vapor above that isotherm.

![Figure 1.4: Isotherms of the non-dimensional van der Waals equation of state for temperatures above and below the critical temperature, $T_c$. The isotherm of this critical temperature is that of $T/T_c = 1$. Below the critical temperature, isotherms pass through a region that violates the stability criterion of Le Châtelier, Eqn. 1.2. The boundary of this region is the dashed line called the spinodal.](image)

For temperatures below $T_c$, the phase transition that occurs upon approach of the unstable region will typically take place well before the stability limit has been reached. The reason for this is elucidated by consideration of the Gibbs free energy along a given isotherm. For a single
component system, the Gibbs free energy per mole, \( g \), is equivalent to the chemical potential, \( \mu \). Therefore, Eqn. 1.1 can be used in the Gibbs-Duhem relation to calculate \( g \). The Gibbs-Duhem equation states the relationship between the intensive parameters

\[
d\mu = -s\,dT + v\,dP
\]  
(1.3)

where \( s = S/N \) and \( v = V/N \). At constant temperature, \( v(P) \) can be integrated to obtain the Gibbs potential

\[
\mu(P,T) = \int v(P)dP + f(T)
\]  
(1.4)

within an additive integration constant that is a function of \( T \). By assigning a chemical potential to a reference state, this can be rewritten

\[
\mu - \mu_0 = \int v(P)dP
\]  
(1.5)

The result of this integration gives \( \mu \) as a function of \( P \). Figure 1.5(a) shows the isotherm \( v(P) \) for \( T/T_c = 0.9 \). Integration of this gives the form for \( \mu(P) \) shown in Figure 1.5(b) for the \( T = 0.9T_c \) isotherm.

It is evident that \( \mu(P) \) is triple-valued over a region of pressure as a consequence of \( v(P) \) being likewise triple-valued. This key feature of the system’s energy as a function of its extensive parameters allows for determining the exact conditions under which a phase transition becomes energetically favorable to occur. In Figure 1.5(b), \( \mu \) is single-valued when decreasing pressure from from A to B. As pressure drops below B, \( \mu \) becomes triple valued, two values of which belong to the stable equilibria and one to the unstable equilibrium. Of the two values of \( \mu \)

---

\(^\dagger\)The Gibbs potential, \( G \), is a Legendre Transformation of the internal energy, \( U \): \( G = U - TS + PV \). According to the Euler Equation, \( U = TS - PV + \mu N \) for a single component system. Therefore, \( G = \mu N \), and \( \mu = g = G/N \).
corresponding to stable equilibria, the one belonging to the liquid state (green curve) is lower in energy than the one belonging to the vapor state (blue curve). The liquid state is therefore favorable since it is the global energy minimum. However, at C, with pressure $P/P_c = 0.647$, the Gibbs potential intersects itself: the liquid curve and the vapor curve cross over. Dropping below this pressure, from C to D, the vapor state is lower in energy than the liquid state, and therefore more favorable. Thus, the phase transition from liquid to vapor normally occurs at C, called the boiling point, which is far from the limit of stability at D. This pressure condition is plotted as a dashed line along with $v(P)$ in Figure 1.5(a). In converting from liquid to vapor, the phase transition along this constant pressure line (called a Maxwell Construction) splits the system into two regions, one liquid and one vapor, the extent of each region determined by the Lever Rule.\footnote{12}

![Figure 1.5: (a) A van der Waals isotherm for $T = 0.9T_c$ is shown, plotted with volume as a function of pressure. The conventional representation is shown in the inset. The vapor phase is plotted in blue, the liquid phase in green, and the unstable region in red. (b) The Gibbs free energy per mol (equivalent to the chemical potential for a single component system), is shown as a function of pressure. The Gibbs potential crosses itself at $P/P_c = 0.647$; this is the point at which a phase transition becomes energetically favorable.}

If a phase transition does not occur at C as the pressure is dropped along the isotherm, the system will continue to remain in the liquid state between C and D in Figure 1.5(b). In this case, the state of the system is metastable: it is in a local, not global energy minimum.
Determining whether the system remains metastable or changes phase at C requires understanding the mechanism underlying the phase transition. The energetic barrier to converting from liquid to vapor is the energy cost of creating an interface between the two phases. If an interface is already present in the system, a phase transition will occur exactly at C. If no interface exists, there is an energy cost to creating it, and the system will remain a metastable liquid at pressures below C. In this latter case, the conversion of the system to the lower energy, vapor phase occurs by a mechanism understood through the lens of statistical mechanics. A macroscopic equilibrium state is thermodynamically defined to be static and unchanging, but statistically, the microstate of the system is perpetually changing. It undergoes rapid fluctuations on length and time scales much smaller than those characteristic of macroscopic measurement. In the case of the liquid to vapor transition, the microstate fluctuations are those corresponding to fluctuations of local density of the liquid.\textsuperscript{12} For a metastable superheated liquid, a density fluctuation of sufficient magnitude will ultimately occur to overcome the energy barrier of creating a liquid-vapor interface, thereby allowing the transition to the vapor phase. The formal theory accounting for the surface-tension-induced energy barrier, as well as the fluctuations driving transition of phase will be treated in Ch. 6.

Dropping the pressure along an isotherm is only one of many possible thermodynamic pathways that can be used to create a metastable liquid. In the case of superheating, the pathway used to create a metastable liquid is increasing the temperature of an isobaric system. The pressure-temperature phase diagram is useful in considering this approach, and is generated by projecting $\mu(P, T)$ of Eqn. 1.4 onto the $P-T$ plane. Figure 1.5(b) shows a cross section of the $\mu(P, T)$ surface at a single temperature; this plot has an additional perpendicular axis for $T$ that is not shown. The point C for phase conversion, as well as the spinodal points B and D for the limits of stability, are therefore curves in the $\mu, P, T$ configuration space. Projection of these curves onto the $P-T$ plane gives the pressure-temperature phase diagram in Figure 1.6. Keep in mind that not all
thermodynamic information is known from the single equation of state (i.e., the van der Waals equation of state is not a fundamental relation) as evidenced by the fact that the integration factor \( f(T) \) in Eqn. 1.4 is still unknown.

![Pressure-temperature phase diagram for a van der Waals fluid. The region above the blue spinodal curve is only stable liquid. The region between the blue curve and red saturation (or phase coexistence) curve can either be stable liquid or metastable vapor, the region between the red curve and the green spinodal curve can either be metastable liquid or stable vapor, and the region below the green curve can only be stable vapor. The dashed lines show two thermodynamic pathways that create the same metastable liquid at point Q. The spinodal and saturation curves all disappear at the critical point, in accordance with the phase behavior observed in Figure 1.4. The dotted lines indicate the boiling point temperature and the temperature of the thermodynamic limit of superheat at a given pressure.](image)

In the pressure-temperature phase diagram, the red curve is the phase coexistence curve corresponding to the location of the pressure temperature coordinates where the \( \mu \) surface intersects itself. This is the location a phase transition will happen if an interface is already present in the system. Thus, the red curve gives the boiling point temperature at a given pressure. Without an interface it is possible to create a metastable liquid, as indicated by the point, Q, in the region between the red saturation curve and green spinodal curve. The vertical dashed line shows the isothermal pathway, and the horizontal dashed line shows the isobaric pathway that can be taken.
to create a thermodynamically identical, metastable liquid. The term superheated liquid refers specifically to a metastable liquid that has been created by increasing the temperature along an isobaric path. The boiling point temperature along this isobaric path is indicated with a dotted line in Fig. 1.6, as is the temperature of the thermodynamic limit of superheat. The former temperature is that at which a phase transition occurs if an interface is present, and the latter temperature is the limiting value of superheat that the liquid can sustain at that pressure before it becomes unstable.

The physical principles behind creating a metastable, superheated liquid are now clear. A system can be heated above its boiling temperature at constant pressure if no liquid-vapor interfaces are present. However, this is quite uncommon in everyday experience: usually there are impurities in the bulk of the liquid or at the interface between the liquid and its solid container. These provide interfaces or energetically favorable nucleation sites for the liquid-vapor phase transition to occur at the boiling temperature. It is evident therefore that a very special environment devoid of nucleation sites must be created in order to superheat a liquid. This is what we discovered is possible using a solid state nanopore.

1.4 Organization of Thesis

In this thesis, I explain the relevant heating dynamics, nucleation kinetics, and hydrodynamics of the bubble lifetime that underlie the experimental data just presented. Organization of the chapters is as follows:

Chapter 2 presents a derivation all of the relevant equations governing Joule heating in nanopores. The chapter begins with physical description of the electrolyte at equilibrium. Application of an applied electric field to this electrolyte gives rise to ion transport which is shown

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§The interested reader is encouraged to consult with the large body of texts and review articles concerning the thermodynamic of metastable liquids. These include, but are not limited to, those consulted for writing this section.12–19
to be described by the Nernst-Planck equation. Finally, the heat equation is derived from considerations of entropy balance.

Chapter 3 discusses the development of a Finite Element Method (FEM) model using the governing equations from the Ch. 2. This requires simplifying the governing equations and the geometry of the nanopore system and incorporating reasonable approximations for the temperature dependent material properties of the superheated electrolyte. The chapter concludes with a description of the numerical implementation of the FEM model using COMSOL Multiphysics.

Chapter 4 presents results from the FEM model. These include the temperature dependent conductivity of the aqueous 3M NaCl solution and the space- and time-dependent temperature distribution in the nanopore. The calculated temperature is compared to the limit of superheat of pure water, measurements of which have been taken using other methods. Calculated results are also shown indicating induced charge densities occur in the region of the nanopore due to the strong temperature gradients there.

Chapter 5 investigates analytical approaches to approximately solve the problem of Joule heating in a nanopore. These results are compared to those of the FEM model, emphasizing how these solutions build intuition and confidence in the FEM modeling results as well as important differences that necessitate using the FEM model.

Chapter 6 applies kinetic theory to determine the nucleation rate in the nanopore. The surface tension induced barrier to nucleation and the concept of reversible work of bubble formation are introduced. The distribution function for nuclei of different sizes along with its governing dynamical equation is derived. The solution to this equation is the temperature dependent nucleation rate, which is applied to the case superheating in a nanopore. The results indicated that homogeneous nucleation of a single vapor bubble occurs at the center of the nanopore. Experimental results from optical experiments are presented, verifying this conclusion.

Chapter 7 discusses the quasiperiodic nucleation events that occur after the first bubble
nculeates as well as the lifetime of the bubble. The former is show to be determined by temperature dynamics of Joule heating in the nanopore. The latter is dictated by the hydrodynamics of bubble growth and lifetime subsequent to nucleation. The governing hydrodynamical equations for the bubble dynamics are derived and discussed. A simplified model and solution for Rayleigh-Plesset growth of the bubble is presented and shown to describe the initial growth of the bubble.

Chapter 8 concludes with a recapitulation of results and remarks on the future work for superheating an aqueous electrolyte within in a solid state nanopore.
There is an obvious objection to the Boltzmann equation, the so-called Umkehreinwand. Any system obeying the laws of mechanics should also obey time reversal, and the Boltzmann equation does not. To this objection the research of Poincaré in mechanics has added a second, the so-called Wiederkehrreinwand, the objection of recurrence in time.

Gregory H. Wannier

The Dynamics of Joule Heating in a Solid State Nanopore

Joule heating of an electrolytic solution in a nanopore involves the simultaneous flow of electric current and heat in the system. The voltage bias that is applied across the membrane during experiments acts to perturb the equilibrium state of the electrolyte. In response, an ionic current is established, which is focused in the nanopore. This focused current leads to resistive heating of the solution in and around the nanopore. Due to the difficulty of measuring the temperature experimentally, I use mathematical modeling to determine the spatial extent and temporal evolution of the temperature distribution within the pore.
My objective for this chapter is to derive the equations governing the dynamics of Joule heating of the liquid in the nanopore. In so doing, I derive and discuss the underlying physics that gives rise to what we observe in the experimental data.

At the onset of the experiments, before application of a voltage bias, the electrolyte is at equilibrium. I therefore begin by describing the equilibrium state of the 3M NaCl solution in terms of Debye-Hückel theory and discuss the properties of the equilibrium state that effect ion transport. I proceed to consider the application of an electrical potential, which acts to perturb the equilibrium state resulting in an ionic current response. The motion of ions results from two contributions: drift due to the electric potential gradient and diffusion due to gradients in chemical potential. Together, these give rise the Nernst-Planck expression for current density.

Lastly, I consider the effect of this ionic current resistively heating the electrolytic solution. The intensity of heating will be strongest in the region of the nanopore due to focusing of the current there. I treat the electrical and thermal dynamics in the context of entropy balance that must be maintained during the course of this irreversible process. This results in a system of coupled differential equations, consisting of the charge continuity equation and heat equation, which govern the behavior of the system. I conclude this chapter with a summary of the governing equations.

2.1 Aqueous 3M Sodium Chloride Solution

Our choice of 3 M NaCl resulted from the fact that NaCl is a common salt that is easy to work with. As such, it has been extensively studied and well characterized, making it easier for us to find material data that we needed for modeling of the electrolyte-nanopore system. We used a concentrated, 3 M solution in order to ensure that current densities were high enough for significant resistive heating to occur in the nanopore.

Before the voltage bias is applied, the NaCl solution is at equilibrium in the sense that no
net motion of the ions, \( \text{Na}^+ \) and \( \text{Cl}^- \), occurs. In this section, I address the properties of this equilibrium state, some of which impact the transport or electrodiffusion of ions once the voltage bias is turned on. The properties of aqueous electrolyte solutions arise primarily from three physical effects: ion hydration, ion-ion interactions, and electrodiffusion.\(^{20}\) Of these, ion-ion interactions dominate the equilibrium state of the electrolyte, and electrodiffusion dominates the behavior of the electrolyte subject to an external electric field. However, ion-ion interactions become important in electrodiffusion if conditions allow for ion-pair formation.

A physically accurate description of the electrolyte at equilibrium is not trivially obtained. Ions in solution present a many-body problem requiring a consistent solution for two co-dependent properties. The first is the distribution of the ions in solution relative to one another. The second is the net force acting on each ion due to the presence of all the other ions. These factors are not independent since the forces effect the ionic distribution and vise versa; this poses a challenge in determining either.

Debye and Hückel solved this problem in a self-consistent manner, thereby establishing the modern theory for electrolytes at equilibrium. They considered rigid, unpolarizable, spherical ions immersed in a continuum dielectric material of fixed permittivity. These ions interact with each other over long ranges by means of the Coulomb force. As such, an individual ion at a given location in the solution will effect the spatial distribution of the ions in its vicinity. For example, a single positive ion will attract negative ions and repel other positive ions, leading to a negative charge density in its direct surroundings. This charge density is referred to as the ionic atmosphere of the positive ion, and is assumed to be spherically symmetric about the positive ion.\(^{\ast}\) In the same way, a negative ion will have a spherically symmetric ionic atmosphere consisting of a local positive charge density.

\[^{\ast}\text{The ions are always in motion due to thermal effects. Therefore, this is the symmetry of the time-averaged distribution of ions in the vicinity of the ion under consideration.}\]
The Debye-Hückel theory uses the Poisson equation to solve for the potential assuming spherical symmetry. This gives the mutual dependence of the forces and distribution of ions

\[ \nabla^2 \phi_j = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \phi_j(r) \right) = -\frac{q_j(r)}{\epsilon} \]  \hspace{1cm} (2.1)

where \( q_j(r) \) is the spherically symmetric charge density consisting of the \( j \)th ion at the origin and its ionic atmosphere, \( \phi_j(r) \) is the electrical potential from ion \( j \) and its ionic atmosphere, and \( \epsilon \) is the electrical permittivity of the solution.\(^1\) The charge density is then expressed in terms of the potential by means of the Boltzmann distribution giving

\[ q_j(r) = \sum_{i=1}^{s} z_i e n_i \exp \left( -\frac{z_i e \phi_j(r)}{k_b T} \right) \]  \hspace{1cm} (2.2)

where \( k_b \) is Boltzmann’s constant, \( T \) is temperature, \( s \) is the number of ionic species in solution, \( n_i \) is the concentration of ion \( i \), \( z_i \) is the valence of ion \( i \), and \( e \) is the elementary charge. The term \( z_i e \phi_j(r) \) is the potential energy of the \( i \)th ion a distance \( r \) from the \( j \)th ion. \( \phi_j(r) \) can then be solved for by using a linearized form of Eqn. 2.2 in the Poisson equation, Eqn. 2.1. This is done explicitly in Appendix A giving

\[ \phi_j(r) = \frac{z_j e}{4\pi \epsilon} \left( \frac{\epsilon^2}{r_j^0 k_D} + 1 \right)^{1/2} r e^{-k_D r} \]  \hspace{1cm} (2.3)

where \( r_j^0 \) is the distance of closest approach to ion \( j \) by another ion, and the quantity

\[ \Lambda_D = \frac{1}{k_D} = \sqrt{\frac{e k_b T}{e^2 \sum_{i=1}^{s} n_i z_i^2}} \]  \hspace{1cm} (2.4)

\(^1\)The Poisson equation is applied to the time-averaged charge distribution in this instance, ameliorating any difficulty in using Eqn. 2.1 here.\(^{21,22}\) Strictly speaking, the Poisson equation is valid for only a static distribution of charges, and not for charges in motion as in the case of ions in solution.
is the Debye screening length. $\Lambda_D$ characterizes the extent of the electric field due to the $j$th ion such that for $r > \Lambda_D$, the field resulting from ion $j$ is largely screened out by its ionic atmosphere. The Debye length varies inversely with the square root of the ionic concentrations, $n_i$. As $n_i$ increases, more ions are available in close proximity to a given ion $j$ to screen out its field over a shorter distance.

The 1:1 stoichiometry of NaCl results in equal concentrations of cations and anions in solution, so that $n_+ = n_-$. Used in Eqn. 2.4 along with the ionic valences $z_+ = -z_- = 1$, this gives the Debye screening length of aqueous NaCl solution

$$\Lambda_D = \frac{1}{\kappa_D} = \sqrt{\frac{\epsilon k_B T}{2n e^2}}$$

(2.5)

where $n$ is the concentration of NaCl in solution in units of number of ions per unit volume.

Fig. 2.1 plots $\Lambda_D$ as a function of temperature for different concentrations of NaCl solutions. For a 3 M solution, $\Lambda_D$ is predicted to be less than 0.2 nm. This distance is comparable to the crystalline radii of Na$^+$ and Cl$^-$, $r_+ = 0.096$ nm and $r_- = 0.181$ nm, respectively. As such, the predicted screening length is too small to be physically real, consistent with the fact that Debye-Hückel theory breaks down for concentrations above 0.01 M. The physical picture required to characterize a 3 M NaCl therefore has additional complications not included in Debye-Hückel theory.

Modeling solutions of higher concentration requires corrections to Debye-Hückel theory. Such corrections include incorporating ion hydration, breaking of spherical symmetry, and the polarization of ions due to asymmetric local fields. However, the primary reason for the breakdown of the Debye and Hückel theory at higher concentrations is the possibility for ions of opposite charge to form associated pairs in solution. A characterization of the ion-to-ion distance below which two ions form an associated pair can be found in the literature.
can be used to show that a certain amount of association of ions likely occurs in a 3 M NaCl solution.

Given how small the nanopores are, it helpful to consider the actual number of ions and water molecules per unit volume. Water, with a density of 1000 kg/m$^3$ at ambient temperature and pressure, has a concentration of 55.5 M which corresponds to approximately 33 water molecules per cubic nanometer. In comparison, 3 M NaCl contains less than 4 ions per cubic nanometer. The 3 M concentration is also less than the solubility limit of NaCl under ambient conditions of temperature and pressure. This limit is 36 g NaCl in 100 g water,$^{26}$ which is equivalent to a 4.5 M NaCl solution.

Despite its limitations, the Debye–Hückel theory still provides a useful physical picture for the equilibrium state of aqueous 3 M NaCl solution of ions and their associated ionic atmospheres. However, the exact values predicted for the screening length of ions are not valid at such a high concentration, and it should be expected that long range interactions and ion association
occur to some degree. This will effect the net number of charge carriers available to produce a current in response to the application of a voltage bias. Calculating the number of ion pairs and developing a theory for the overall conductivity of 3 M NaCl is a complicated many-body problem. However, it is also an unnecessary problem to consider here since the conductivity of the 3 M NaCl solution will be determined empirically by fitting experimental data as shown in Ch. 4.

2.2 Electrodiffusion of Ions: Applying a Voltage Bias to the Electrolyte

The section presents a derivation of the electrodiffusion equation, also called the drift-diffusion equation, for the current density that results from the application of a voltage bias. There are three dominant effects that impact the motion of ions: the force on the ions due to the applied field, the random thermal motions of the ions, and the convection of ions with the overall flow of the solution. Electrodiffusion concerns only the first two of these effects. The motion of ions due to electrodiffusion and convection must obey the charge continuity equation\(^\ddagger\)

\[
\frac{d\varrho_\pm}{dt} = \frac{\partial \varrho_\pm}{\partial t} + \mathbf{v} \cdot \nabla \varrho_\pm = -\nabla \cdot \mathbf{J}_\pm
\]

(2.6)

where \(\varrho_\pm\) is the charge density of positive and negative ions with dimension of charge per unit volume, \(\mathbf{v}\) is the velocity of the fluid and \(\mathbf{J}_\pm\) is the flux of positive and negative ions with dimension of charge per unit area per unit time. Only the electrodiffusion of ions is considered here, with the objective of deriving \(\mathbf{J}_\pm\) in the form of the drift-diffusion equation. In section 2.3, I discuss how experiment is tuned to have \(\mathbf{v} = 0\).

The application of an electric field causes each ion \(i\) to move in the direction opposite to its ionic atmosphere. So long as the applied field is sufficiently weak and of low frequency,\(^\ddagger\)

\(^\ddagger\)Derived in the same manner as the continuity equation for mass conservation in Appendix A.
this can be treated as a perturbation of the equilibrium state of the electrolyte in the method of Onsager,\textsuperscript{22} similar to Lindhard’s treatment of an electron gas.\textsuperscript{27} The drift-diffusion equation can also be derived from the statistical arguments by solving the Boltzmann transport equation using a relaxation time approximation.\textsuperscript{28} The treatment I present here derives the current densities from phenomenological arguments\textsuperscript{20} considering the empirical laws defining the response of ions to a concentration gradient and to a gradient in electrical potential.

In the absence of an electric field, ions will diffuse in a concentration gradient as a result of random motion according to Fick’s Law

\[
K_i = -D_i \nabla n_i
\]  

(2.7)

where \(K_i\) is the flux of ion \(i\) in units of number per unit area per unit time, \(D_i\) is the diffusion coefficient of ion \(i\) in unit area per unit time, and \(n_i\) is the concentration of \(i\) in number of ions per unit time. Multiplying \(K_i\) by the the charge per ion, \(z_i e\) gives the electric current density \(J_i\)

\[
J_i = z_i e K_i = -z_i e D_i \nabla n_i
\]  

(2.8)

This defines the diffusive current density resulting from net movement of ions responding to a concentration gradient, not to an applied electric field.

In the absence of a concentration gradient, the ions will migrate in an electric field (down an electric potential gradient). All the ions respond to the force exerted by the electric field according to Newton’s laws, i.e. acceleration is proportional to the force with mass as the proportionality constant. However, because the ions are moving in a medium and experience collisions hindering their movement in the direction of the applied force, their behavior is better approximated by assuming that the ion velocity, \(v_i\), is proportional to the field responsible for that force.
\[ \mathbf{v}_i = \bar{\mu}_i \mathbf{E} \]  

(2.9)

where \( \bar{\mu}_i \), the proportionality constant, is called the mobility of the ion species \( i \) and characterizes how easily the ion can move through the medium. Multiplying the single ion velocity by the concentration gives the molar flux resulting from the electric field

\[ \mathbf{J}_i = -\bar{\mu}_i n_i \nabla \varphi \]  

(2.10)

and again multiplying by the charge per ion gives the current density

\[ \mathbf{J}_i = -z_i e \bar{\mu}_i n_i \nabla \varphi \]  

(2.11)

This is the electrophoretic equation developed by Kohlrausch and others expressing the drift current density.\(^{20}\) This equation is in fact Ohm’s Law, with the conductivity contributed by ion \( i \) equal to \( \sigma = z_i e \bar{\mu}_i n_i \). The equivalent conductivity for ion \( i \) is defined as \( e \bar{\mu}_i \).

In the presence of both a concentration gradient and an electric field, the total current density will be given by the sum of the diffusive and drift components, Eqns. 2.8 and 2.11 respectively

\[ \mathbf{J}_i = -z_i e D_i \nabla n_i - z_i e \bar{\mu}_i n_i \nabla \varphi \]  

(2.12)

The diffusion coefficient and the mobility can be related by the Nernst-Einstein relation\(^ {20}\)

\[ D_i = \frac{k_b T}{z_i e \bar{\mu}_i} \]  

(2.13)

giving

\[ \mathbf{J}_i = -z_i e D_i \nabla n_i - \frac{z_i^2 e^2 D_i n_i}{k_b T} \nabla \varphi \]  

(2.14)
which is called the Nernst-Planck equation. This equation gives the flux of charge in response to a gradient in concentration and electrical potential, termed electrodiffusion, or drift-diffusion. The appearance of the valence $z_i$ in the first term indicates that ions of opposite charge will contribute in opposing ways to the diffusion term. Both positive and negative ions will diffuse down a concentration gradient, however, this contributes a positive charge flux in the case of negative ions and a negative charge flux in the case of positive ions. In contrast, $z_i^2$ in the second term means that both positive and negative ions contribute in the same manner for the drift in response to an electrical potential gradient. This is because positive ions will move down a potential gradient whereas negative ions will move up a potential gradient.

In the case of the 3M NaCl solution, there are two equations for current density, one for Na$^+$ and one for Cl$^-$, given by Eqn. 2.14 with $z_+ = -z_- = 1$

$$
J_+ = -eD_+ \nabla n_+ - \frac{e^2 D_+ n_+}{k_b T} \nabla \varphi
$$

$$
J_- = eD_- \nabla n_- - \frac{e^2 D_- n_-}{k_b T} \nabla \varphi
$$

(2.15)

The diffusion constants at ambient temperature and pressure are $D_+ = 1.33 \times 10^{-9}$ m$^2$/s for Na$^+$ and $D_- = 2.03 \times 10^{-9}$ m$^2$/s one for Cl$^-$.\textsuperscript{20} Eqns. 2.15 define the fluxes of ions in the nanopore system and must obey the continuity equation of Eqn. 2.6.

2.3 Electroosmotic Flow and the Convection of Ions

At the onset of the Joule heating experiments, we had to consider the possibility of electroosmotic flow of the NaCl solution occurring through the nanopore.\textsuperscript{29} This motion of fluid, $v \neq 0$, convects ions, leading to a non-zero contribution to ion transport and therefore impacts the current that is measured experimentally.

Electroosmotic flow is possible when the silicon nitride membrane possesses an overall sur-
face charge. This fixed charge is screened by ions to a depth characterized by the Debye screening length. The resulting accumulation of ions near to the membrane surface is referred to as an electrical double layer. An applied electric field induces this layer of charge to move, resulting in a net flow of the fluid, which is the electroosmotic flow.

In order to prevent this convection of ions, we designed the Joule heating experiments such that electroosmotic flow would not manifest. We did this by adjusting the pH of the 3 M NaCl solution to 4.6, equal to the isoelectric point of the silicon nitride membrane. At this pH, surface charge does not build on the membrane, meaning that the electric double layer and therefore electroosmotic flow are absent. Since \( v = 0 \), Eqn. 2.6 takes the form

\[
\frac{\partial q_\pm}{\partial t} = -\nabla \cdot \mathbf{J}_\pm
\]

which is the charge continuity equation applying to Joule heating for the nanopore system.

2.4 Entropy Balance of Thermoelectric Phenomena

The ionic current induced to flow through the nanopore by application of a voltage bias resistively heats the solution. This heating is a non-equilibrium process that results from the simultaneous flow of the ionic currents with the flow of heat. These dynamics are governed by entropy production, which is expressed in the form of the entropy balance equation.

In this section, I will show that the familiar dynamical equation, the heat equation with Joule heating source term, can be derived from the entropy balance equation. My motivation for doing this was to show the connection between the underlying mechanism of entropy production and the resulting heat equation, as well as to establish the proper dependence of the material properties in the heat equation (notably, why is \( \rho C_p \) outside of the time derivative of the heat equation). This discussion is not essential for the overall understanding of this thesis and readers
are invited to skip to section 2.5 which summarizes the governing equations and the conclusions from this chapter.

Thermoelectric phenomena resulting from this simultaneous flow were first considered in 1854 by Lord Kelvin in the context of empirical observation. However, they were not satisfactorily explained until Onsager presented his theory on the reciprocal relations relating fluxes to their driving forces in 1931 for which he was awarded the 1968 Nobel Prize. In this section, application of entropy balance and Onsager’s theorem are used to complete the derivation of the system of differential equations which govern the system.

The Onsager reciprocity theorem is a central pillar of irreversible thermodynamics; another being the fluctuation dissipation theorem of Callen and Welton. Irreversible thermodynamics is concerned with explaining time-dependent processes that occur when a system is not at equilibrium, in contrast to thermo-statics which concerns only equilibrium. This is an expression of the second law of thermodynamics: thermo-statics considers only the cases for which $dS = 0$, whereas irreversible thermodynamics is concerned with $dS > 0$. As such, an equation accounting for entropy change, called the entropy balance equation, plays the central role in the theory of irreversible processes. This equation expresses the fact that entropy of a small volume under consideration changes for two reasons:

- Entropy flows into or out of the bounding surface of the volume element
- Entropy is produced as a result of irreversible processes occurring within the volume element

This latter contribution is called an entropy source. Taken together, these can be expressed by

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§Examples of thermoelectric phenomena include Joule heat (heat produced by the flow of electric current), Thomson heat (heat absorbed from connected heat reservoirs when current transverses a temperature gradient), the Sorret effect (motion of particles in response to a temperature gradient), and the Dufour effect (flow of heat in response to a concentration gradient; reciprocal of the Sorret effect).
writing the variation in entropy as the sum of two parts\textsuperscript{35}

\[ dS = d_e S + d_i S \quad (2.17) \]

where \( d_e S \) is the entropy supplied to a volume by its external surroundings, and \( d_i S \) is the entropy produced internally within the volume. \( d_i S \) will equal zero for reversible transformations and will be greater than zero for irreversible transformations. \( d_e S \) can be positive, negative, or zero. For example, in an adiabatically isolated system, closed off to heat and particle flow, \( d_e S = 0 \), yielding the following relation for the second law

\[ dS = d_e S + d_i S = d_i S \geq 0 \quad (2.18) \]

For a closed system, restrictive only to particle flow, \( d_e S = dQ/T \), which is the Carnot-Clausius relation. In this case, the second law reads

\[ dS = d_e S + d_i S \geq \frac{dQ}{T} \quad (2.19) \]

If the flow of both heat and particles into and out of the system is non-restrictive, then the \( d_e S \) can be negative. This case is not considered in the Carnot-Clausius theorem, and a simple inequality cannot be written.

The entropy balance equation is arrived at by converting Eqn. 2.17 into its local form.\textsuperscript{8} To

\textsuperscript{8}Conversion to the local form is consistent with the treatment of irreversible thermodynamics as a macroscopic field theory with parameters that depend continuously on time and spatial coordinates. This same method is applied to the related theories of fluid mechanics and electro-magnetics of continuous media.
do so, consider the rate of change of the total entropy in an infinitesimally small volume \(^1\)

\[
\frac{dS}{dt} = \frac{d}{dt} \int_V \rho s \, dV = \int_V \frac{\partial (\rho s)}{\partial t} \, dV
\]  

(2.20)

where \(s\) is the entropy per unit mass. The time integral can be placed within the volume integral according to Reynold’s transport theorem for a stationary test volume. This must be equal to the entropy that flows into or out of the bounding surface of the volume, \(A\), given by

\[
\frac{dS}{dt} = - \int_A J_{S,tot} \cdot dA
\]  

(2.21)

in addition to any entropy produced within the volume element

\[
\frac{dS}{dt} = \int_V \Sigma_S \, dV
\]  

(2.22)

The entropy flux, \(J_{S,tot}\) in Eqn. 2.21, is the amount of entropy that flows out of the bounding surface per unit time per unit volume, and the negative sign indicates that the flux is defined as positive when directed outward from the volume element (in the same direction as \(A\)). In Eqn. 2.22, \(\Sigma_S\) is the entropy source strength, which is the entropy produced per unit volume per unit time. Taken together

\[
\int_V \frac{\partial (\rho s)}{\partial t} \, dV = - \int_A J_{S,tot} \cdot dA + \int_V \Sigma_S \, dV
\]  

(2.23)

With the help of the divergence theorem, and recognition that the integral holds over arbitrary

\(^1\)This is infinitesimal in the macroscopic sense: the volume \(V\) is small compared to the system size but still contains a macroscopic number of particles.
volume, this can be written in differential, or local form

\[ \frac{\partial (\rho s)}{\partial t} = -\nabla \cdot J_{S,\text{tot}} + \Sigma_S \quad (2.24) \]

This equation gives the entropy balance that is upheld during any irreversible process. The barycentric substantial time derivative can be used with mass continuity\textsuperscript{**} to rewrite this as

\[ \frac{ds}{dt} \rho = -\nabla \cdot J_S + \Sigma_S \quad (2.28) \]

where \( J_S = J_{S,\text{tot}} - \rho s v \), which is the total entropy flux minus a convective term, \( \rho s v \), where \( v \) is the velocity of the material of the system (e.g. fluid or molecular components). What now remains is to determine the appropriate forms of the entropy source, \( \Sigma_S \), and the entropy flux, \( J_S \).

An expression for the entropy source, \( \Sigma_S \), can be arrived at by considering the first differential of entropy. The equilibrium entropy per unit mass, \( s \), is a function of the internal energy per unit mass, \( u \), the specific volume, \( v = \rho^{-1} \), and the mass fractions, \( c_k \), of the components of the system

\textsuperscript{**}These relationships are derived in Appendix B and quoted here for convenience. The barycentric (enter of mass) derivative is

\[ \frac{d}{dt} = \frac{\partial}{\partial t} + v \cdot \nabla \quad (2.25) \]

which along with conservation of mass

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0 \quad (2.26) \]

gives

\[ \frac{\rho}{dt} \frac{dx}{dt} = \frac{\partial}{\partial t} (x \rho) + x \rho v \quad (2.27) \]

for any vector \( x \).
in the absence of external fields. Thus \( s = s(u, v, c_k) \), and we have for the first differential

\[
ds = \frac{1}{T} du + \frac{P}{T} dv - \sum_k \frac{\mu_{k,\text{tot}}}{T} dc_k
\]

(2.29)

where \( \mu_{k,\text{tot}} \) is the total electrochemical potential from component \( k \). To proceed, the assumption is made that a state of local equilibrium exists within each small mass element even though the system is not in equilibrium. As such, it is assumed that Eqn. 2.29 is valid for a mass element followed along its center of mass motion, giving

\[
\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} + \frac{P}{T} \frac{dv}{dt} - \sum_k \frac{\mu_{k,\text{tot}}}{T} \frac{dc_k}{dt}
\]

(2.30)

This assumption of local equilibrium is justified macroscopically only by means of the validity of the conclusions drawn from it. From microscopic models, the assumption can be shown to be valid for deviations from equilibrium that are not too large\(^35\). It is possible to derive criteria for how far from equilibrium a system can be for the assumption to remain valid.

The continuity equation for the mass fraction of component \( k \) is derived in Appendix B, Eqn. B.35, and takes the form

\[
\rho \frac{dc_k}{dt} = -\nabla \cdot J_k
\]

(2.31)

Similarly, the continuity of internal energy was shown in Appendix B, Eqn. B.32, to equal

\[
\rho \frac{du}{dt} = -\nabla \cdot \left( J_q + \sum_k \mu_k J_k \right) - \rho P \frac{dv}{dt} + \bar{D} : \nabla v + \sum_k F_k \cdot J_k
\]

(2.32)

where \( J_q \) is the heat flux density, \( \bar{D} \) is the viscous stress tensor, \( J_k \) is the mass flux density of component \( k \), and \( F_k = -\nabla \psi_k \) is the conservative body force acting on component \( k \) (for example gravity or Lorentz force). In this case, \( \psi_k = z_k e \phi \) where \( \phi \) is the electrical potential.
Inserting these in Eqn. 2.30 gives

\[ \rho T \frac{ds}{dt} = -\nabla \cdot \left( J_q + \sum_k \mu_k J_k \right) + \overline{D} : \nabla \mathbf{v} + \sum_k F_k \cdot J_k + \sum_k \mu_k \nabla \cdot J_k \] (2.33)

This equation can be reorganized

\[ \rho \frac{ds}{dt} = \frac{1}{T} \left[ -\nabla \cdot J_q - \sum_k J_k \cdot \nabla \mu_k - \sum_k J_k \cdot \nabla \psi_k + \overline{D} : \nabla \mathbf{v} \right] \]

\[ = -\nabla \cdot \left( \frac{J_q}{T} \right) + J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \cdot \nabla (\mu_k + \psi_k) + \frac{1}{T} \overline{D} : \nabla \mathbf{v} \] (2.34)

The last term associated with dissipation due to internal friction in the fluid can be dropped since the electrolyte present in the nanopore has no overall velocity, \( \mathbf{v} = 0 \). This gives

\[ \rho \frac{ds}{dt} = -\nabla \cdot \left( \frac{J_q}{T} \right) + J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \cdot \nabla \mu_{k,tot} \] (2.35)

where \( \mu_{k,tot} = \mu_k + \psi_k \) is the electrochemical potential. Comparing this with Eqn. 2.28 shows that the flux density of entropy is equal to

\[ \mathbf{J}_S = \frac{J_q}{T} \] (2.36)

and the entropy source strength is equal to

\[ \Sigma_S = J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \cdot \nabla \mu_{k,tot} \] (2.37)

Eqn. 2.36 for the entropy flux is consistent with the Carnot-Clausius relation \( dS = dQ/T \). From
Eqn. 2.30, the substitution \( \mathbf{J}_q = T \mathbf{J}_S = \mathbf{J}_u - \mu_{k,\text{tot}} \mathbf{J}_k \) can also be made in Eqn. 2.37 giving \(^\text{12}\)

\[
\Sigma_S = \mathbf{J}_u \cdot \nabla \left( \frac{1}{T} \right) - \sum_k \mathbf{J}_k \cdot \nabla \left( \frac{\mu_{k,\text{tot}}}{T} \right)
\]  

(2.38)

The entropy source strength is therefore equal to the product of the fluxes with their associated affinities. The fluxes are those of the entropic extensive parameters, \( u \) and \( c_k \), and the affinities are defined as the gradients of their associated entropic intensive parameters, \( \nabla (1/T) \) and \( \nabla (\mu_{k,\text{tot}}/T) \) respectively.

The affinities are the thermodynamic driving forces that drive a thermodynamic process. This includes all thermoelectric processes involved in Joule heating of an electrolyte in a nanopore. The production of entropy is the physics that underlies the heat equation. To proceed in deriving the heat equation, a form for the fluxes, \( \mathbf{J}_n \), in terms of the affinities is required. In any thermodynamic process, the fluxes vanish if the thermodynamic driving forces, or affinities, are equal to zero. Conversely, non-zero affinities result non-zero fluxes. Therefore, for a system with \( i \) unconstrained extensive parameters, the flux of parameter \( n \) will take the form

\[
\mathbf{J}_n = \mathbf{J}_n(\tilde{\mathbf{\xi}}_0, \tilde{\mathbf{\xi}}_1, \tilde{\mathbf{\xi}}_2, \ldots \tilde{\mathbf{\xi}}_i)
\]  

(2.39)

for which \( \tilde{\mathbf{\xi}}_i \) is the affinity (gradient of the intensive parameter) associated with the \( i \)th extensive parameter. It is important to note that the flux of the \( i \)th extensive parameter depends on all affinities in the system; however, it will have the strongest dependence on its own affinity. Eqn. 2.39 also assumes that the fluxes at any instant in time depend only on the values of the affinities at that given instant, meaning the system has no memory. \( \mathbf{J}_n \) can be expanded as

\[
\mathbf{J}_n = \sum_i L_{i,n} \tilde{\mathbf{\xi}}_i + \frac{1}{2!} \sum_{i,j} L_{i,j,n} \tilde{\mathbf{\xi}}_i \tilde{\mathbf{\xi}}_j + \ldots
\]  

(2.40)
A constant term is not required since $J_j = 0$ when the affinities vanish. $L_{i,n}$ are the kinetic coefficients equal to $\partial J_n / \partial \tilde{\xi}_i$, and $L_{i,j,n}$ are the second-order kinetic coefficients equal to $\partial^2 J_n / \partial \tilde{\xi}_j \partial \tilde{\xi}_j$. These coefficients are functions of the local intensive parameters$^{12}$. Third order and higher coefficients are similarly defined.

If the affinities are small, the higher order terms of the expansion can be neglected. These cases are referred to as linear processes for which

$$J_n = \sum_i L_{i,n} \tilde{\xi}_i \quad (2.41)$$

This equation takes the form of the familiar phenomenological laws: Fick’s first law of diffusion, Fourier’s law of heat transfer, Ohm’s law of conduction, and the Nernst-Planck law of ion conduction. However, Eqn. 2.41 is more general in that it relates the fluxes to all affinities in the system. Onsager’s reciprocity theorem states that $L_{i,n} = L_{n,i}$ in the absence of angular velocity or an applied magnetic field$^{35}$. This theorem is based on the principle of time reversal invariance of the equations of motion of the constituent particles of the system$^{12-35}$, and expresses a symmetry between the effect of the $n$th affinity on the $i$th flux, and the $i$th affinity on the $n$th flux.

Applying this derivation to the electrolyte in the nanopore system requires accounting for all components of the system. These include the individual ionic species Na$^+$, and Cl$^-$, water molecules, associated pairs of NaCl in solution, and dissociated water in the form of hydronium and hydroxyide groups. However, the behavior of the electrolyte is dominated by the charge carriers Na$^+$ and Cl$^-$ alone. Therefore, the simplifying assumption is made that the other components do not contribute significantly to fluxes in the system. In this case Eqn. 2.37 can be

$^{††}$Note that the concentrations of the ionic species cannot be adjusted independently of each other. For example, a solution cannot contain 1 M Na$^+$ and 2 M Cl$^-$, rather they must have equal concentrations. Therefore, ionic species are not independent thermodynamic components of a system as defined formally by Gibbs.$^{22}$
written
\[ \Sigma_S = J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} K_+ \cdot \nabla \mu_{+tot} - \frac{1}{T} K_- \cdot \nabla \mu_{-tot} \] (2.42)

Here, \( K_+ \) is the flux of Na\(^+\) ions, \( K_- \) is the flux of Cl\(^-\) ions with units of number per unit area per unit time. This notation is meant to distinguish particle flux from current density \( J_\pm = z_\pm e K_\pm = \pm e K \) for Na\(^+\) and Cl\(^-\). Note that these are in units of number of ions per unit time per unit area, not charge per unit time per unit area. The electrochemical potentials are

\[ \mu_{+tot} = \mu_+ + e \phi \quad , \quad \mu_{-tot} = \mu_- - e \phi \] (2.43)

where \( e \) is magnitude of the elementary charge, and \( \phi \) is the electrical potential field resulting from the applied voltage bias. Eqn. 2.42 indicates three affinities in the system

\[ \delta_q = \nabla \left( \frac{1}{T} \right) \quad , \quad \delta_+ = \frac{\nabla \mu_{+tot}}{T} \quad , \quad \delta_- = \frac{\nabla \mu_{-tot}}{T} \] (2.44)

According to Eqn. 2.41 thermodynamic fluxes are therefore

\[ J_q = L_{1,1} \nabla \left( \frac{1}{T} \right) + L_{1,2} \frac{\nabla \mu_{+tot}}{T} + L_{1,3} \frac{\nabla \mu_{-tot}}{T} \]
\[ -K_+ = L_{1,2} \nabla \left( \frac{1}{T} \right) + L_{2,2} \frac{\nabla \mu_{+tot}}{T} + L_{2,3} \frac{\nabla \mu_{-tot}}{T} \] (2.45)
\[ -K_- = L_{1,3} \nabla \left( \frac{1}{T} \right) + L_{2,3} \frac{\nabla \mu_{+tot}}{T} + L_{3,3} \frac{\nabla \mu_{-tot}}{T} \]

where Onsager’s reciprocal theorem has been applied to the kinetic coefficients. As already mentioned, the strongest dependence of a flux will be on its associated affinity, and for simplicity this it is assumed that all other dependencies are negligible. This gives for the flux density of heat

\[ J_q = L_{1,1} \nabla \left( \frac{1}{T} \right) = -\frac{L_{1,1}}{T^2} \nabla T = -\kappa \nabla T \] (2.46)
where the kinetic coefficient, $L_{1,1}$, has been related to the thermal conductivity, $L_{1,1} = T^2 \kappa$, yielding the familiar Fourier’s Law. The flux densities of the ions likewise become

$$J_+ = eK_+ = -eL_{2,2} \frac{\nabla \mu_{+,\text{tot}}}{T} = -\frac{eL_{2,2}}{T} \nabla (\mu_+ + e\varphi)$$

$$J_- = -eK_- = eL_{3,3} \frac{\nabla \mu_{-\text{tot}}}{T} = \frac{eL_{3,3}}{T} \nabla (\mu_- - e\varphi)$$ \tag{2.47}

where the factor $e$ for charge per unit ion has been included to change the units of the fluxes from number per unit volume per unit time to charge per unit volume per unit time. In order to relate $L_{2,2}$ and $L_{3,3}$ to the familiar quantities of the diffusion coefficients, $D_+$ and $D_-$, the current densities in Eqn. 2.47 must be put in the same form as the Nernst-Planck equations in Eqn. 2.15. This is done by using the relation between chemical potential and concentration $\mu_\pm = \mu_\pm^0 + k_b T \ln a_\pm$, where $\mu_\pm^0$ is the chemical potential of a reference state, and $a_\pm$ is the activity of the anions and cations. The chemical potential depends on the activity in the same manner that it would depend on concentration for an ideal solution. As such, $a_\pm$ can be understood as an effective concentration and is equal to $a_\pm = \gamma_\pm x_\pm$ where $\gamma$ is the activity coefficient and $x_\pm = n_\pm / n$ is the number fraction of the ion. This gives $\mu_\pm = \mu_\pm^0 + k_b T (\ln x_\pm + \ln \gamma_\pm)$. Taking the gradient of the chemical potentials, $\mu_\pm$, gives

$$\nabla \mu_\pm = k_b T \left( \frac{\nabla x_\pm}{x_\pm} + \frac{\nabla \gamma_\pm}{\gamma_\pm} \right) = k_b T x_\pm \left( 1 + \frac{x_\pm}{\gamma_\pm} \frac{\partial \gamma_\pm}{\partial x_\pm} \right) \nabla x_\pm = k_b T \frac{n_\pm}{n} \left( 1 + \frac{n_\pm}{\gamma_\pm} \frac{\partial \gamma_\pm}{\partial n_\pm} \right) \nabla n_\pm$$

If the solution is dilute, $\gamma_\pm$ is constant according to Henry’s Law, and if it is ideal, $\gamma_\pm = 1$. In either case, $\partial \gamma_\pm / \partial x_\pm = 0$ which shall be assumed here. Using this in Eqn. 2.47 gives

$$J_+ = -\frac{eL_{2,2}}{T} \left( \frac{k_b T}{n_+} \nabla n_+ + e \nabla \varphi \right) = -eD_+ \left( \nabla n_+ + \frac{en_+}{k_b T} \nabla \varphi \right)$$

$$J_- = \frac{eL_{3,3}}{T} \left( \frac{k_b T}{n_-} \nabla n_- - e \nabla \varphi \right) = -eD_- \left( \nabla n_- - \frac{en_-}{k_b T} \nabla \varphi \right)$$ \tag{2.48}
where comparison with the Nernst-Planck equation in Eqn. 2.15 gave $L_{2,2} = n_+ D_+ / k_b$ and $L_{3,3} = -n_- D_- / k_b$.

The fluxes in the Entropy Balance equation of Eqn. 2.35 are now defined and can be used to derive the familiar form of the heat equation. Using the expression for $J_q$ from Eqn. 2.46 in Eqn. 2.35 gives

$$\rho \frac{d\dot{s}}{dt} = -\nabla \cdot \left( \frac{1}{T} \mathbf{L}_{1,1} \nabla \left( \frac{1}{T} \right) \right) + \mathbf{L}_{1,1} \nabla \left( \frac{1}{T} \right) \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \mathbf{K}_+ \cdot \nabla \mu_{+tot} - \frac{1}{T} \mathbf{K}_- \cdot \nabla \mu_{-tot}$$

$$= -\frac{1}{T} \nabla \cdot \left( \mathbf{L}_{1,1} \nabla \left( \frac{1}{T} \right) \right) - \frac{1}{T} \mathbf{K}_+ \cdot \nabla \mu_{+tot} - \frac{1}{T} \mathbf{K}_- \cdot \nabla \mu_{-tot}$$

(2.49)

The time derivative of entropy can be rewritten

$$\rho \frac{d\dot{s}}{dt} = \rho \left( \frac{ds}{dT} \right) \frac{dT}{dt} = \rho C_p \frac{dT}{dt}$$

(2.50)

where the definition of the heat capacity at constant pressure, $C_p$, has been used. The material derivative, Eqn. 2.25, with fluid velocity equal to zero, gives $dT/dt = \partial T/\partial t$. In Eqn. 2.49

$$\rho C_p \frac{dT}{dt} = -\nabla \cdot \left( \mathbf{L}_{1,1} \nabla \left( \frac{1}{T} \right) \right) - \mathbf{K}_+ \cdot \nabla \mu_{+tot} - \mathbf{K}_- \cdot \nabla \mu_{-tot}$$

(2.51)

The gradients of chemical potentials can be written in terms of the ion fluxes using Eqn. 2.47. This gives $\nabla \mu_{+tot} = -T \mathbf{K}_+/L_{2,2}$ and $\nabla \mu_{-tot} = T \mathbf{K}_-/L_{3,3}$ which can be used in Eqn. 2.50

$$\rho C_p \frac{dT}{dt} = \nabla \cdot (\kappa \nabla T) + \frac{k_b T}{n_+ D_+} K_+^2 + \frac{k_b T}{n_- D_-} K_-^2$$

(2.52)

where $L_{1,1} = \mathbf{L}^2 \kappa$, $L_{2,2} = n_+ D_+/k_b$, and $L_{3,3} = -n_- D_- / k_b$ have been substituted. Using
\[ J = \pm eK, \text{ this gives} \]

\[ \rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \frac{k_b T}{e^2 n_+ D_+} J_+^2 + \frac{k_b T}{e^2 n_- D_-} J_-^2 \]  \hspace{1cm} (2.53)

This is the equation I will use for calculating the effects of Joule heating of the electrolyte in a nanopore, discussed in the subsequent chapter. However, as demonstrated in its derivation, many simplifying assumptions have been made, most notably the reduction of the fluxes in Eqn. 2.45 to depend only their associated affinities. This simplification is justified so long as the affinities are small, as confirmed by the phenomenological laws of Ohm, Fourier, and Fick. However, when the affinities are large, this is not necessarily true, and the full linear laws of Eqn. 2.45 may become necessary. In extreme cases, the assumption of linearity itself, Eqn. 2.41, may not be valid.

2.5 SUMMARY OF GOVERNING EQUATIONS

The primary result of this chapter is the system of dynamical equations governing Joule heating of the aqueous NaCl solution in the nanopore. These consist of the charge continuity equation and the heat equation along with the definition of the ion current densities. In the quasistatic approximation, the charge densities relate to the electrical potential via the Poisson equation

\[ \nabla^2 \varphi = -\frac{\varrho_+ + \varrho_-}{\epsilon} \]  \hspace{1cm} (2.54)

and obey the charge continuity equation, Eqn. 2.16

\[ \frac{\partial \varrho_+}{\partial t} = -\nabla \cdot \mathbf{J}_+ , \quad \frac{\partial \varrho_-}{\partial t} = -\nabla \cdot \mathbf{J}_- \]  \hspace{1cm} (2.55)
The heat equation has the form of Eqn. 2.53

\[
\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \frac{k_b T}{e^2 n_+ D_+} J_+^2 + \frac{k_b T}{e^2 n_- D_-} J_-^2
\]  

(2.56)

and the current densities are given by the Nernst-Planck equation of Eqn. 2.15

\[
\begin{align*}
J_+ &= -eD_+ \nabla n_+ - \frac{e^2 D_+ n_+}{k_b T} \nabla \varphi \\
J_- &= eD_- \nabla n_- - \frac{e^2 D_- n_-}{k_b T} \nabla \varphi
\end{align*}
\]  

(2.57)

it should be noted that \( \rho \pm = \pm en \pm \). Together, Eqns. 2.54, 2.55, and 2.56 are four differential equations, for which the scalar fields of \( T, \varphi, n_+ \), and \( n_- \) can be solved.
Many bubble chamber physicists have turned their attention toward developing automatic pattern recognition, measuring, and computing machines. Some day it is dreamed that such a machine, armed with a memory filled with full knowledge of all known processes occurring in high-energy physics, will devour miles of film each day, duly noting the numbers, characteristics, and types of all the known processes it recognizes. [Nobel Lecture, 1960]

-Donald A. Glaser

Model of Joule Heating in a Nanopore:

Finite Element Method (FEM)

The system of differential equations summarized at the end of the previous chapter (Eqns. 2.54, 2.55, 2.56, and 2.57) govern the dynamics of Joule heating that will occur in the nanopore system. This chapter discusses the Finite Element Method (FEM) model that I developed in order to solve this system of equations.

Obtaining a solution is complicated by the fact that the material properties of the electrolyte are temperature dependent. This makes the equations highly nonlinear. In addition, the geometry of the current-focusing nanopore must be accounted for with appropriate boundary conditions.
An FEM model is therefore highly advantageous compared to an analytical approach since the latter would require vast over-simplifications of the relevant physics.

This chapter presents the necessary steps that I had to implement in order to build and solve the FEM model using COMSOL Multiphysics software. These steps include simplifying the system of differential equations, building the geometry of the nanopore system, determining the appropriate temperature dependent material properties, defining appropriate initial and boundary conditions, meshing the system, and establishing the solver method.

3.1 Simplifying the Governing Equations

The equations governing the dynamics of Joule heating were summarized at the end of Chapter 2. They include the Poisson equation, Eqn. 2.54, the charge continuity equation, Eqn. 2.55, the heat equation, Eqn. 2.56, and the Nernst-Planck equations, Eqn. 2.57. These form a system of four coupled differential equations, for which the scalar fields of temperature, \( T(r, t) \), electrical potential, \( \phi(r, t) \), cation concentration, \( n_+(r, t) \), and anion concentration, \( n_-(r, t) \) can be solved.

As indicated, each of these scalar fields is dependent on space and time.

To proceed with simplifying these equations, the assumption is made that the concentration of cations and anions is everywhere equal and independent of \( r \) and \( t \). This assumption requires \( n_+ = n_- \), and \( \nabla n_+ = \nabla n_- = 0 \), which reduces the Nernst Planck equation for the current densities, Eqn. 2.57 as follows

\[
\begin{align*}
J_+ &= -\frac{e^2 D_+ n}{k_B T} \nabla \phi \\
J_- &= -\frac{e^2 D_- n}{k_B T} \nabla \phi
\end{align*}
\]

(3.1)

where \( n_+ = n_- \) has been replaced by \( n \). Thus, no diffusive currents are assumed to occur.

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Adding these together gives the total current density

\[ \mathbf{J} = -\frac{e^2 n}{k_b T} (D_+ + D_-) \nabla \varphi \] (3.2)

which has the form of Ohm’s law

\[ \mathbf{J} = \sigma \mathbf{E} \] (3.3)

where it is assumed that the quasi-static approximation \( \mathbf{E} = -\nabla \varphi \) holds for relating the electric field to the electrical potential. The factor \( (D_+ + D_-) e^2 n / k_b T \) is the electrical conductivity of the electrolyte, \( \sigma \), with units of S/m. The dependence of \( \sigma \) on \( T \) and the temperature dependent diffusion coefficients, make \( \sigma \) a function of \( \mathbf{r} \) and \( t \).

Not surprisingly, \( \sigma \) is also dependent on the concentration of ions \( n \). Recall that \( n \) is not necessarily equal to the concentration of NaCl in solution. As discussed in the previous chapter, at 3 M concentration NaCl, it is highly likely that associated ion pairs form in solution. However, these ion pairs do not contribute to the current, and therefore do not need to be considered. In the context of this calculation, determining the fraction of ions that form associated pairs is not important since ultimately, the conductivity of the solution will be determined by fitting experimentally measured conductance data, which I discuss in the next chapter.

The total current will also obey the continuity equation which can be obtained by adding the individual continuity equations for cations and anions in Eqn. 2.55 giving

\[ \frac{\partial q}{\partial t} = -\nabla \cdot \mathbf{J} \] (3.4)

where \( q = q_+ + q_- \) is the total density of free charge carriers.

The heat equation in Eqn. 2.53 is also simplified by using the current densities of Eqn. 3.1.
to give
\[ \rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \frac{e^2 n}{k_b T} (D_+ + D_-) |\nabla \varphi|^2 \] (3.5)

The factor \((D_+ + D_-) \frac{e^2 n}{k_b T}\) is the electrical conductivity of the electrolyte, \(\sigma\). Thus, the heat equation becomes
\[ \rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \sigma |\nabla \varphi|^2 \] (3.6)

Using \(E = -\nabla \varphi\) and Ohm’s law in Eqn. 3.3 gives
\[ \rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + \mathbf{J} \cdot \mathbf{E} \] (3.7)

which is the familiar form of the heat equation with a Joule heating source term, assuming Ohm’s law applies to the current densities.

This form of the heat equation together with the continuity equation in Eqn. 3.4 compose the system of coupled differential equations that I use in the finite element modeling. These equations are summarized in Table 3.1. The assumption that \(n_+ = n_-\) simplified a system of four differential equations with four unknown scalar fields into a system of two differential equations with two unknown scalar fields, \(T(r, t)\) and \(\varphi(r, t)\). The electric field, current density, and spatial dependence of material properties can all be subsequently calculated from these scalar fields.

The FEM model solves these equations over all material domains of the nanopore system, which includes the liquid electrolyte and the electrically insulating, solid membrane materials. The Joule heating source term, \(\mathbf{J} \cdot \mathbf{E}\) is only nonzero in the conducting electrolyte. It should also be emphasized that in the material properties of the electrolyte are all dependent on the temperature distribution and therefore depend on \(r\) and \(t\). These material properties include the material density \(\rho(r, t)\), the heat capacity \(C_p(r, t)\), the thermal conductivity \(\kappa(r, t)\), and the electrical conductivity \(\sigma(r, t)\).
System of Differential Equations for Joule Heating

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho C_p \frac{\partial}{\partial t} T(r, t) = \nabla \cdot (\kappa \nabla T(r, t)) + J(r, t) \cdot E(r, t) )</td>
<td>Heat equation, Eqn. 3.7</td>
</tr>
<tr>
<td>( \frac{\partial}{\partial t} \varrho(r, t) = -\nabla \cdot J(r, t) )</td>
<td>Continuity, Eqn. 3.4</td>
</tr>
<tr>
<td>( J(r, t) = \sigma E(r, t) )</td>
<td>Ohm’s Law, Eqn. 3.3</td>
</tr>
<tr>
<td>( E(r, t) = -\nabla \varphi(r, t) )</td>
<td>Electrical potential</td>
</tr>
</tbody>
</table>

Table 3.1: Summary of the system of equations for Joule heating that will be solved in the COMSOL finite element model. The heat equation and the continuity equation form a system of partial differential equations. Ohm’s Law and the definition of electric potential relate the quantities of electric potential to electric field and current density.

It is necessary at this point to comment on the validity of the assumption of charge neutrality, \( n_+ = n_- \). At the onset of the Joule heating experiments, the concentrations of cations and anions are everywhere equal, meaning charge neutrality is exact. However, the simulated results discussed in the subsequent chapter indicate that charge neutrality does not hold in the neighborhood of the nanopore as a result of the extreme temperature gradients obtained there. The effect however is very small, and it will later be shown that the resulting correction is negligible. Thus, the assumption of charge neutrality remains valid even in the region of the localized temperature distribution.

3.2 Geometry and Boundary Conditions of the Nanopore System

The experimental nanopore system that is being modeled consists of an insulating membrane of amorphous silicon nitride suspended on a silicon-dioxide, silicon frame, separating between two reservoirs of aqueous, 3M NaCl solution. Electrical contact between the two reservoirs is maintained by the presence of a single pore present in the membrane. This experimental setup
was introduced in section 1.2.

Finite element modeling allows for inclusion of the detailed geometric features of the nanopore system with dimensions taken from the experiments. Fig. 3.1 depicts a cross-section of the model geometry. The nanopore is slightly conical in shape due to the process of fabrication using ion beam sculpting. The computational domain is half the size of the image in Fig. 3.1, taking advantage of the axial symmetry of the nanopore as labeled in the figure. All dimensions are given in Table 3.2.

![Figure 3.1: Schematic of the nanopore system. A two-dimensional axi-symmetric model of the system was developed. The axis of symmetry is shown down the center of the model, with boundary conditions indicated on the edges of the computational domain with \( T_0 = 273.15 \text{K} \). For clarity, the system is reflected across the axis of symmetry, and an inset shows the dimension of the nanopore to scale.](image)

The initial condition for temperature is assumed everywhere to be equal to the ambient temperature measured at the time of the experiment, 293.15K. This temperature is imposed on the boundary of the domain, far from the nanopore. As shown in Fig. 3.1, the voltage \( V \) is set to the experimental value on the lower boundary of the computational domain, and zero on the upper
### Dimensions of the Nanopore System

<table>
<thead>
<tr>
<th></th>
<th>Thickness</th>
<th>Radial distance from $r=0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$ membrane</td>
<td>71nm</td>
<td>53.5nm$^a$</td>
</tr>
<tr>
<td>SiO$_2$ layer</td>
<td>1.6μm</td>
<td>2.4μm</td>
</tr>
<tr>
<td>Si frame</td>
<td>53.74$^b$</td>
<td>53.12 μm</td>
</tr>
</tbody>
</table>

Table 3.2: This table summarizes dimensions of the nanopore system that are used in the finite element model. $^a$ This is the radius of the nanopore. $^b$ This is the angle the Silicon makes with the layer of silicon-dioxide, labeled as $\theta$ in Fig. 1 from wet etching in KOH.

boundary, corresponding to electrodes. The boundary condition on the vertical boundary is zero normal current density $J_n$, as presented in Fig. 3.1.

### 3.3 Material Properties

The values used for the properties of the membrane materials are reported in Table 3.3. Using constant values is a reasonable approximation since the temperature of the membrane changes only slightly.

<table>
<thead>
<tr>
<th>Material Properties of the Membrane$^a$</th>
<th>$\rho$ [kg/m$^2$]</th>
<th>$C_p$ [J/kg·K]</th>
<th>$\kappa$ [W/m·K]</th>
<th>$\sigma$ [S/m]</th>
<th>$\epsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>3100</td>
<td>700</td>
<td>3.2$^b$</td>
<td>0</td>
<td>9.7</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2200</td>
<td>730</td>
<td>1.4$^c$</td>
<td>0</td>
<td>4.2</td>
</tr>
<tr>
<td>Si</td>
<td>2329</td>
<td>700</td>
<td>130</td>
<td>10</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Table 3.3: Material data for the Si$_3$N$_4$ membrane, the SiO$_2$ layer, and the Si frame. $^a$Data from COMSOL material library, unless otherwise indicated. $^b$Thermal conductivity is for Low Pressure Chemical Vapor Deposition (LPCVD) silicon nitride films [27, 28]. $^c$Thermal conductivity of silicon-dioxide thin films [29].

In contrast, the material properties of the electrolyte must include their temperature dependence in order to accurately account for the effects of heating. However, material data for metastable superheated aqueous 3M NaCl solution at atmospheric pressure are not available for the extremely high temperature regime that is reached experimentally. Therefore, the values of...
\( \rho, C_p, \) and \( \kappa \) used in the model are those available from the IAPWS-95 formulation for the equation of state of water, shown in Fig. 3.2. \(^{41-43} \) Also shown is the temperature dependence of the relative permittivity, \( \epsilon_r = \epsilon / \epsilon_0 \), of water. \(^{24} \)

The IAPWS-95 formulation for the equation of state is an industrial and scientific standard for the material properties of water over the entire liquid and vapor ranges. \(^{41} \) The formulation is an empirical description of the Helmholtz free energy that was fit to an amalgamation of experimental data for thermophysical properties of water, including in the superheated metastable region. \(^{41,44,45} \) The Helmholtz free energy is a fundamental thermodynamic relation, and all thermodynamic properties can be derived from it if it is known for a given substance such as water. Obtaining the temperature dependences of the material properties in Fig. 3.2 required extrapolating the IAPWS-95 formulation into the metastable regime for which there is no available

---

**Figure 3.2:** Temperature dependence of the material properties of water. The density \( \rho \), thermal conductivity \( \kappa \), and heat capacity \( C_p \), are calculated from the IAPWS equation of state for superheated water at 1 atm. \(^{41-43} \) The electrical permittivity \( \epsilon_r = \epsilon / \epsilon_0 \) is saturation curve data for water. \(^{24} \)
The presence of ions in solution will also affect the material properties of the solvent water as a result of ion-ion and ion-solvent interactions. We were unable to find data available for the material properties of 3M NaCl solution in the superheated regime; therefore, the use of water properties was substituted. The electrical conductivity of the 3M NaCl solution is the most significant property that changes when ions are dissolved in pure water. Outside of auto-ionization into hydronium and hydroxide groups, pure water is almost insulating. However, experimental data for the solution’s electrical conductivity at such high temperatures under atmospheric pressure are also not available. This is addressed by fitting the electrical conductivity to the experimentally measured conductance curves as discussed in the subsequent chapter.

3.4 Numerical Implementation: Meshing and Solvers

The system of governing equations was solved using the commercial finite element software COMSOL 5.0 (Comsol, Inc.), with the geometry and materials of the nanopore system. The model geometry, illustrated in Fig. 3.1, was chosen to be two-dimensional, and axisymmetric along the axis through the pore center. This symmetry drastically reduces the computational domain of the problem from that of a fully three dimensional model. The modeled domain extends 100 μm from the nanopore. This distance is sufficiently large such that the room temperature boundary condition does not impact the solution anywhere in the domain. As a result, the shape of the boundaries also has no impact on the solutions, and the rectangular domain of Fig. 3.1 was used interchangeably with a circular domain.

Mesh resolution and time stepping were adjusted such that no variation in the solution occurred with changing of the spatial and time discretization parameters. This was accomplished by running mesh refinement studies on the mesh sizing parameters. A fine triangular mesh was required in the neighborhood of the nanopore due to its small dimension. Mesh elements in and
around the nanopore had a width on the order of a nanometer. The mesh element size was scaled up for regions of the domain far away from the pore, reflecting the small variation of the fields being solved and the courser geometrical features in that region of the domain. An initial time step of \(10^{-5}\) ns was used to initiate the time dependent calculation, with a maximum time step of \(10^{-2}\) ns.

A time-dependent study modeled the dynamics of heating. The calculation is started just after a voltage pulse is turned on at \(t=0\). The electrical potential, \(\varphi(r,0)\), everywhere in the domain was calculated using COMSOL’s Electric Currents (ec) module. This module solves the steady-state form of the continuity equation, Eqn. 3.4, along with Ohm’s Law, Eqn. 3.3, by implementing an affine invariant form of the damped Newton method. The result of this calculation was then used as the initial condition in the time-dependent study of the Joule Heating (jh) module. This module solves the coupled system of equations, Eqns. 3.7, 3.4, and 3.3 using variable-order, variable-step-size backward differentiation formulas.
It does not make any difference how beautiful your theory is; it does not make any difference how smart you are. If the theory disagrees with experiment it is wrong. That is all there is to it.

-Richard P. Feynman

FEM Model Results and Discussion

The solution of the system of differential equations for Joule heating along with appropriate initial and boundary conditions is presented in this chapter. The equations were summarized in Table 3.1, and the solution was calculated using the FEM model presented in the previous chapter. The primary result of the calculation is the spatially and temporally resolved temperature distribution in the nanopore.

The results from the calculation are truly remarkable. The maximum temperature calculated to be achieved in the center of the nanopore is $603 \pm 10$ K which is about 5% greater than the theoretical limit of pure water. The temperature distribution is highly localized, rising by almost 130 K from the edge of the pore to the center 53.5 nm away. The heating also occurs rapidly within only a few microseconds after the voltage pulse is turned on for the 53.5 nm
radius pore. Comparison of these results with experimental observations are consistent with
bubble nucleation events, which are discussed in chapters 6 and 7.

The sections of this chapter are organized in the following manner. In the first section, the
temperature dependence of the electrical conductivity of the 3 M NaCl solution is determined
by fitting experimental data. In the second section, the calculated temperature distribution is
presented and discussed, including consideration of the amount of thermal energy stored by the
heated electrolyte in the nanopore. In the third section, the calculated temperature is compared
with the experimental and theoretical values known for the limit of superheat of pure water. In
the fourth section, consideration is given to the induced charge densities resulting from extreme
temperatures in and around the nanopore. The assumption of negligible diffusive current, made
for the current density, Eqn. 3.3, is shown to be valid.

4.1 ELECTRICAL CONDUCTIVITY OF THE SUPERHEATED ELECTROLYTE

Calculating the dynamics of nanopore heating requires ascertaining the temperature dependence
of the electrical conductivity $\sigma(T)$ of the aqueous 3 M NaCl solution at atmospheric pressure.
The temperature distribution $T(r, t)$, in the nanopore there leads to a spatially varying electrical
conductivity $\sigma(T(r, t))$. In Fig. 4.1, we show conductivity data taken of a bulk sample of 3 M
NaCl solution for $T < 373$ K at atmospheric pressure. Above this temperature and pressure, the
bulk sample boils, rendering further data acquisition difficult. However, I was able to determine
an appropriate form $\sigma(T)$ by fitting the experimentally measured nanopore conductance curves
for the case in which the solution does superheat. These data were obtained by applying voltage
pulses ranging from 4 to 8.22 V across a 53.5 nm radius, 71 nm thick nanopore. $^1$ $\sigma(T)$ is assumed
to take the form

$$\sigma(T) = mT - b - \frac{(T - T_0)^\alpha}{\beta}$$

(4.1)
Figure 4.1: The temperature-dependent behavior of the conductivity of aqueous 3M NaCl solution. We calculated our fit for $\sigma(T)$ at 1 atm using our own data for bulk conductivity measured below 373 K, and by comparing to conductivity measurements taken at much higher pressures by Bannard. \(^\text{48}\)

with $T_0 = 293.15$ K. The linear trend for $T < 373$ K is expressed by the first two terms on the right hand side. The constants $m$ and $b$ were determined by fitting the bulk solution conductivity data of Fig. 4.1, and are equal to $0.391 \pm 0.002$ S/(m K) and $96.9 \pm 0.06$ S/m respectively. The third term on the right hand side is a corrective factor accounting for the high temperature behavior of $\sigma(T)$ beyond the boiling point. The parameters $\alpha$ and $\beta$ were treated as free parameters in calculations to fit the shape of the measured time-dependent nanopore conductance, $G(t)$, plotted in Fig. 1.2. This plot is reproduced in Fig. 4.2 for convenience. The conductance is the result of the surface integral

\[ G(t) = \int \sigma(T(\mathbf{r}, t)) d^2r \]  \hspace{1cm} (4.2)
over the cross sectional area of the nanopore. Fitted values of $\alpha = 2.7 \pm 0.01$ and $\beta = 5.6 \times 10^4 \pm 0.1 \times 10^4$ resulted in the computed pore conductance curves shown in red in Fig. 4.2. A plot of $\sigma(T)$ with these parameter values is shown in Fig. 4.1 in comparison with our measured conductivity as well as data collected by Bannard at higher pressures. \textsuperscript{48} It is evident that in the superheated temperature regime, the electrical conductivity of aqueous NaCl solution ultimately starts to decrease with increasing temperature.$^*$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{conductance_trace.png}
\caption{Data for the measured nanopore conductance traces taken for different applied voltages are shown in blue with the calculated conductance curves in red. \textsuperscript{1} The predicted peak temperature obtained within the nanopore is reported for each curve. The reported uncertainties in the maximum temperatures attained for the 7 V and 8.22 V pulses were calculated based on the uncertainty in the parameters $\alpha$ and $\beta$ used to fit the conductance data. The calculated uncertainties for the maximum temperatures attained for the 6 V, 5 V and 4 V pulses were below the number of significant digits reported here.}
\end{figure}

\textsuperscript{*}The fact that the electrical conductivity ultimately decreases with increasing temperature prevents thermal runaway from occurring in the nanopore. \textsuperscript{49,50} Thermal runaway can occur in systems with conductivity of positive temperature coefficient if connected to a voltage source (heating source term behaves as $\sigma E^2$), and in systems with conductivity of negative temperature coefficient is connected to a current source (heating source term behaves as $J^2 / \sigma$). In either case heating increases with increasing $T$. \textsuperscript{51}
The high temperature behavior of $\sigma(T)$ is an expected consequence of decreasing density and dielectric constant of water with increasing temperature.\textsuperscript{48,52} At lower temperatures, $\sigma(T)$ increases linearly with increasing $T$. This is a result of increased mobility of the ions due to decreasing water viscosity as the temperature increases. However, the density and dielectric constant of water also decrease with increasing temperature. The decreasing density decreases the number of ions per unit volume; the decreasing dielectric constant increases the number of ion pairs that form, reducing the number of unassociated charge carriers. Both effects reduce the conductivity of the solution and dominate the temperature dependence of $\sigma$ at very high temperatures.\textsuperscript{†52}

4.2 Extreme Superheating within the Nanopore

The calculated temperature attained at the pore center after 10 $\mu$s for each applied voltage is indicated for each conductance trace in Fig. 4.2. Fig. 4.3 shows the contour plots of the temperature field within the nanopore at 10 $\mu$s for 4V, 5V, 6V, 7V, and 8.22V applied. In the case of 8.22V, extreme superheating is calculated to occur, strongly localized at the pore center. A maximum of 603 K $\pm$ 10 K is obtained at the center of the pore, dropping by 130 K to the edge of the pore, 53.5 nm from the center. The $\pm$ 10 K uncertainty in the maximum temperature results from the uncertainty in the parameters $\alpha$ and $\beta$ used to fit the conductance data. The maximum temperature attained in the nanopore for each applied voltage is plotted as a function of time in Fig. 4.4 demonstrating the rapid heating that occurs.

It is evident from the temperature contour that the region of superheated liquid extends to 230 nm from the pore center. The amount of stored thermal energy available for bubble formation and expansion in this superheated region is approximately 5 pJ. This is determined by integrating

\textsuperscript{†This is in part due to the fact that there is a decline in the rate of decrease of viscosity with increasing temperature at high values of $T$.\textsuperscript{52}}
Figure 4.3: Contour plots showing the calculated temperature distribution in the nanopore after application of a 4V, 5V, 6V, 7V, and 8.22V pulse for 10.4 μs.

\[ E_{\text{thermal}} = \int C_p(T(r))\rho(T(r))(T(r) - T_b) d^3r \]  

(4.3)

where \( T(r) \) is the temperature distribution at 10.4 μs, and \( T_b \) is the boiling temperature at atmospheric pressure. The integration domain is defined by the region for which \( T(r) > T_b \). The upper limit for the radius of a spherical bubble corresponding to this energy is 620 nm, accounting for latent heat of vaporization and assuming no thermal losses due to thermal diffusion.

As yet, it has not been possible to experimentally measure the temperature; therefore we are completely reliant on these results for our determination of what temperatures are attained in the pore. The predicted temperature for the 8.22 V pulse when bubble nucleation occurs is consistent with the required temperature for homogeneous nucleation, discussed in Ch. 6. This consistency lends confidence to the calculated values.

Error in the calculated value of \( T \) is therefore difficult to determine. There are two main sources of error in the calculation for \( T \): first, the assumed form of the temperature dependent material properties of the electrolyte; second, the assumption that the nanopore is circular. For the latter, the nanopores used in the experiment are only approximately circular. Variation in
the shape of the pore effects the temperature distribution due to the comparatively high thermal conductivity of the membrane.

4.3 **Comparison with the Limit of Superheat of Pure Water**

The maximum temperature of 603 K is about 5% greater than the theoretical limit of pure water, 580 K.\textsuperscript{19} It should be noted that this theoretical value calculated for water assumes an equation of state for water, which is an open area of research. The high concentration of NaCl in solution may contribute to this increase in a manner similar to boiling point elevation in electrolyte solutions.\textsuperscript{53}

Other studies have focused on measuring the limit of superheat of pure water. A variety of experimental methods have been used in these studies. Among the most successful are micro-
capillary boiling, heating in a host liquid, and pulse heating of a filament or film heater. A brief summary of selected values from these different methods is provided in Table 4.1 in order to compare with our result. These values are, to my knowledge, the highest temperature obtained using each of the different methods.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Limit of Superheat [K]</th>
<th>Experimental Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous 3M NaCl</td>
<td>603 ± 10</td>
<td>Heating in a Nanopore</td>
</tr>
<tr>
<td>Water</td>
<td>543</td>
<td>Capillary Boiling</td>
</tr>
<tr>
<td>Water</td>
<td>552.5</td>
<td>Heating in a Host Liquid</td>
</tr>
<tr>
<td>Water</td>
<td>576</td>
<td>Filament Heating</td>
</tr>
<tr>
<td>Water</td>
<td>573</td>
<td>Film Heater</td>
</tr>
</tbody>
</table>

Table 4.1: This table summarizes values measured for the limit of superheat using other methods to compare with our result. Note that all other studies were done on pure water.

The reproducible focusing of heating to the center of the nanopore is one of the main differences between our experiment and the other methods of superheating. Capillary boiling, filament boiling, and film boiling all rely on temperature distributions with peak temperatures closest to the liquid-solid interface. This can effect the measured limit of superheat by allowing for heterogeneous nucleation to occur. I discuss why this is unlikely for the nanopore heating experiments in Chapter 6. The method of heating in a host liquid requires injecting water droplets into another immiscible liquid which is heated. This eliminates liquid-solid interfaces, but miscibility increases with temperature and it is not always clear that the water and host fluid do not mix.

Another significant difference is the requirement for charge carriers to be present in solution for our experimental method. The self ionizing property of water gives it a conductivity of only $0.75 \times 10^{-4}$ S/m at room temperature. Therefore, although it is possible to study the limit of superheat of increasingly dilute aqueous salt solutions, it is unlikely that the method can be translated to study pure water.
4.4 **Induced Charge Densities Near the Nanopore**

The sharply peaked temperature distribution in the region of the nanopore results in a spatially dependent electrical conductivity $\sigma$, and electrical permittivity $\epsilon$. The non-zero gradients of these material properties result in induced charge densities consistent with $\nabla \cdot \mathbf{J} = 0$. This is evident upon inserting Ohm’s Law, Eqn. 3.3, giving

$$\nabla \cdot \mathbf{J} = \nabla \sigma \cdot \mathbf{E} + \sigma \nabla \cdot \mathbf{E}$$

(4.4)

This shows that divergence of the electric field in the neighborhood of the nanopore is not zero due to the non-zero gradient in the electrical conductivity. We can further solve for the free charge density, $\varrho$

$$\epsilon_0 \nabla \cdot \mathbf{E} = \varrho + \varrho_{pol}$$

(4.5)

where $\varrho_{pol}$ is the polarization charge density. Using Eqn. 3.3, and $\varrho_{pol} = -\nabla \cdot (\epsilon_0 \chi_e \mathbf{E})$ we can solve for the free charge density in terms of the current density

$$\varrho = \frac{\epsilon}{\sigma} \left( \frac{\nabla \epsilon}{\epsilon} - \frac{\nabla \sigma}{\sigma} \right)$$

(4.6)

where the electrical susceptibility $\chi_e$, has been written in terms of the $\epsilon$, by the relation $\epsilon = \epsilon_0(1 + \chi_e)$. The variation of the conductivity of the material, expressed in the second term on the right hand side, allows for charging of the spatially varying dielectric in the first term, such that a net free charge density results.

Fig. 4.5 shows the calculated free charge density and polarization charge density plotted along the central axis of the nanopore. The polarization charge density is seen to only be partially screened by the free charge, leading to a total, non-zero charge density near the pore.
Figure 4.5: The calculated free charge density $\varrho$, and polarization charge density $\varrho_{\text{pol}}$, plotted along the central axis of the nanopore. The total charge density $\varrho + \varrho_{\text{pol}}$ is also plotted and is nonzero in the region of the nanopore. The gray band indicates the location of the nanopore.

It is important to note that this treatment is approximate since it does not include the diffusive current resulting from the gradient in density of the free charge carriers. This diffusive current will act to reduce the build-up of charge reported in Fig. 4.5. However, since this density is very small, with a maximum corresponding to $4 \times 10^{-4}$ M, the inclusion of the diffusive term would be a correction to what is already a minor effect.
For partial differential equations, only two generally practicable methods of solution are known, the integral solution and the separated solution. Integral solutions have the advantage of generality, for once the Green's function is found, any desired solution of the homogeneous or inhomogeneous equation may be found, in principle.

Philip M. Morse & Herman Feshbach

Analytical Approaches to the Joule Heating Problem

This chapter presents an analytical approach to the problem of Joule heating in a nanopore. This investigation ensures that the FEM model is behaving in accordance with the analytical behavior of the equations governing heating dynamics. Due to the numerical complexity of FEM modeling, this study of analytical behavior is essential to building confidence in the FEM model results. In addition, the intuition provided by the analytical approach further supports our interpretation of the experimental results.

The analytical approach presented here cannot serve as the sole model of the system since
it requires an overly simplified form of the Joule heating problem. The temperature dependence of the material properties as well as the geometrical details of the nanopore must be neglected. The impact that these simplifying assumptions have on the calculated temperature highlights the importance of inclusion of these details by use of FEM modeling for the calculation.

The chapter begins by introducing the simplified, analytically solvable model for Joule heating. This model is solved using the method of Green’s functions, the solutions of which are then compared to the temperature distribution computed by the FEM model.

5.1 Dimensionless Form of the Governing Equations for a Simplified Model

The system of differential equations governing Joule Heating in the nanopore were presented in Table 3.1. These equations are highly nonlinear due to the temperature dependence of the material properties and must be solved over the detailed geometry of the nanopore system consisting of membrane materials and the electrolyte. Therefore, in order to analytically solve these equations, the following simplifying assumptions must be made:

1. The system is assumed to be homogeneous, consisting only of the electrolyte,
2. The material properties of the electrolyte are treated independent of temperature,
3. The Joule heating source term is assumed to be constant and of finite extent,
4. The system is assumed to be spherically symmetric.

This section seeks to explain the rational behind these assumptions, discussing why they present a reasonable approximation of the nanopore system.

The first two assumptions concern the material constituents of the system: the electrolyte and the membrane materials. These materials have different electrical and thermal conductivities which drastically impact the behavior of the system. Assuming that the system is homogeneous
neglects the presence of membrane materials and the impact they have on the solution. Of these, the Si$_3$N$_4$ is the most important because it is the only layer of the solid state membrane through which the nanopore is fabricated. This layer serves to cool the electrolyte within the pore because of the relatively high thermal conductivity, 3.2 W/(m K), of amorphous Si$_3$N$_4$ in comparison to water’s 0.6 W/(m K). In order to neglect the Si$_3$N$_4$, one must therefore assume a higher effective thermal conductivity for the homogeneous system. In contrast, the SiO$_2$, and Si, can be reasonably neglected because they are farther away from the pore, 2 μm and 50 μm from the edge of the nanopore respectively, and do not strongly impact the temperature in the pore. The electrically insulating property of Si$_3$N$_4$ is accounted for by having non-zero current density only within the nanopore as discussed below.

Assuming that the properties of the electrolyte are independent of temperature is the only tractable way to proceed with developing an analytical solution since doing so linearizes the governing equations. The temperature dependence of the electrical conductivity greatly impacts the ultimate temperature achieved necessitating the use of FEM modeling as described in the previous chapter.

The third simplification concerns the form of the Joule heating source term of the heat equation, $J(r,t) \cdot E(r,t)$. In this model, this term is assumed to be constant, denoted $Q$, equal to $J \cdot E = J^2/\sigma$ where the electrical conductivity, $\sigma$, and the current density, $J$, are both constant. $Q$ is also assumed to be nonzero within the nanopore, $r \leq r_p$ where $r_p$ is the radius of the nanopore, and zero outside of the nanopore, $r > r_p$. This is a physically reasonable assumption since the nanopore focuses the ionic current resulting in most of the Ohmic losses occurring within the pore volume. Outside of the nanopore, the current density is very small, contributing little to heating. Assuming this constant form for the source term removes the coupling between the heat equation and the charge continuity equation because a form is assumed for the electrical potential. All that remains is to solve the heat equation for the temperature distribution.
The geometry of the system is greatly simplified by assuming it is spherically symmetric. Although cylindrical symmetry or oblate spheroidal symmetry might appear more natural for the nanopore, localization of Joule heating to within the volume of the nanopore necessitates the use of spherical symmetry. This is because the Si$_3$N$_4$ is so thin that the diffusion of heat will mainly occur through the electrolyte in a spherically symmetric manner.

With these assumptions in place, the heat equation is simplified from Eqn. 3.7 to

$$\frac{\partial}{\partial t} T(r, t) = \zeta \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) T(r, t) + \frac{1}{\rho C_p} Q(r) \tag{5.1}$$

where $\zeta = \kappa / \rho C_p$ is the thermal diffusivity. The source term is $Q(r) = J^2 / \sigma$ for $r \leq r_p$. The magnitude of the current density, $J$, will be approximated by $I / \pi r_p^2$, which is the current divided by the cross-sectional area of the pore. The current is equal to the pore conductance* times the applied voltage $V$ which in the thin pore limit gives $J = 2\sigma r_p V / \pi r_p^2$. This gives for the source term

$$Q(r) = \begin{cases} 
\frac{4\sigma V^2}{\pi^2 r_p^2} & r \leq r_p \\
0 & r > r_p 
\end{cases} \tag{5.2}$$

The system is initially at room temperature. Since the temperature scale can be shifted by an arbitrary constant, room temperature can be set to zero, giving an initial condition of $T(r, 0) = 0$. The boundary of the system is located at $r = r_d$ such that $r_d \gg r_p$. The condition of room temperature is imposed on this boundary, $T(r_d, t) = 0$. A second boundary condition, $T(0, t) = \text{finite}$, is also imposed which serves to preclude the unphysical possibility of singular solutions for which the temperature distribution becomes infinite at $r = 0$. The parameters for the nanopore system used in this model, including both geometric quantities and material

*The conductance of the nanopore is assumed to be the conductivity times the pore diameter $2\sigma r_p$ which applies for the thin pore limit.\textsuperscript{10}
properties are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_p )</td>
<td>53.5 nm</td>
<td>Radius of Nanopore</td>
</tr>
<tr>
<td>( r_d )</td>
<td>1 ( \mu )m</td>
<td>Radius of Domain</td>
</tr>
<tr>
<td>( C_p )</td>
<td>4183 J/(kg K)</td>
<td>Heat Capacity (^a)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>1000 (kg/m(^3))</td>
<td>Liquid Density (^a)</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>0.9 W/(m K)</td>
<td>Thermal Conductivity (^b)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>21 S/m</td>
<td>Electrical Conductivity (^c)</td>
</tr>
<tr>
<td>( V )</td>
<td>8.22 V</td>
<td>Applied Voltage</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>293.15 K</td>
<td>Room Temperature</td>
</tr>
</tbody>
</table>

Table 5.1: This table summarizes the parameters used in the analytical model. \(^a\)Value for water at atmospheric pressure and room temperature. \(^b\) This is an average of the thermal conductivity of \( \text{Si}_3\text{N}_4, 3.2 \) W/m\(^\circ\)K, and water, 0.6 W/m\(^\circ\)K, obtained by integration over a sphere of radius \( r_p \) assuming a 71 nm thick layer of \( \text{Si}_3\text{N}_4. \) \(^c\) This is the electrical conductivity of aqueous 3M NaCl solution at atmospheric pressure and room temperature.

Eqn. 5.1 can be rewritten in natural units by nondimensionalizing the equation using the system’s characteristic length scale and time scale. The characteristic length scale is the radius of the pore, \( r_p \). The characteristic time scale can be obtained from combining this with the thermal diffusivity, \( \zeta \), yielding \( r_p^2/\zeta \). Using the values in Table 5.1 gives \( \zeta = 2.15 \times 10^{-7} \) m\(^2\)/s, a characteristic length scale of \( r_p = 53.5 \) nm, and a characteristic time scale of \( r_p^2/\zeta = 133 \) ns. The following dimensionless variables are defined with these quantities

\[
\tilde{r} = \frac{r}{r_p} \quad \tilde{t} = \frac{\zeta}{r_p^3} t \quad (5.3)
\]

Using the chain rule, the derivatives in Eqn. 5.1 can be redefined, giving

\[
\frac{\zeta}{r_p^2} \frac{\partial}{\partial t} T(\tilde{r}, \tilde{t}) = \frac{\zeta}{r_p^2} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r}^2 \frac{\partial}{\partial \tilde{r}} \right) T(\tilde{r}, \tilde{t}) + \frac{1}{\rho C_p} Q(\tilde{r}) \quad (5.4)
\]
which simplifies to
\[ \frac{\partial}{\partial t} T(\tilde{r}, \tilde{t}) = \frac{\partial}{\partial \tilde{r}} \left( \tilde{r}^2 \frac{\partial}{\partial \tilde{r}} \right) T(\tilde{r}, \tilde{t}) + \tilde{Q}(\tilde{r}) \] (5.5)

with
\[ \tilde{Q}(\tilde{r}) = \frac{r^2}{\zeta} \left( \frac{1}{\rho C_p} Q(\tilde{r}) \right) \] (5.6)

This equation still has units of temperature which can be removed by divided out a characteristic temperature. In the next section, the dimensionless variables \( \tilde{r} \) and \( \tilde{t} \) are written as \( r \) and \( t \) to keep notation simple.

5.2 Green’s Function Solution

In this section, the radially symmetric heat equation, Eqn. 5.1, will be solved using the Green’s function method. The result will be a solution for the temperature distribution equal to that calculated using the method of separation of variables presented in Appendix C. However, the advantage to using this method is that it yields a closed function solution, the Green’s Function, which gives physical insight the behavior of the system in response to the stimulus of a unit point heat source.

In order to derive the Green’s function, the general form for the heat equation is first considered and solved without the assumption of radial symmetry. The radial dependence is then isolated by integrating out the angular coordinates. The general form is for the heat equation is

\[ \frac{\partial}{\partial t} T(r, t) - \zeta \nabla^2 T(r, t) = 4\pi q(r, t) \] (5.7)

where the source term is \( q(r, t) = Q(r, t)/(4\pi \rho C_p) \) from Eqn. 5.1. The initial condition is \( T(r, 0) = 0 \), and boundary conditions are \( T(0, t) = \text{finite} \), and \( T(\infty, t) = 0 \). The external boundary is at infinity, \( r_d = \infty \), since the Green’s function method can be applied to an infinite
domain. The corresponding equation satisfied by the Green’s function for this problem is

\[
\frac{\partial}{\partial t} G(r, t| r_0, t_0) - \zeta \nabla^2 G(r, t| r_0, t_0) = 4\pi \delta(r - r_0) \delta(t - t_0) \tag{5.8}
\]

Thus, \(G\) is the response of the system measured at \(r\) at time \(t\) to an impulse introduced at \(r_0\) at time \(t_0\). Causality therefore requires that \(t > t_0\). It can be shown\(^6\) that the solution takes the form

\[
T(r, t) = \int_0^{t^+} dt_0 \int dV_0 q(r_0, t_0) G(r, t| r_0, t_0)
+ \frac{\zeta}{4\pi} \int dt_0 \int dS_0 \cdot [G \nabla_0 \varphi - \varphi \nabla_0 G] + \frac{1}{4\pi} \int dV_0 [\psi G]_{t_0=0} \tag{5.9}
\]

where the first term on the right hand side incorporates the volumetric source term, the second term incorporates the boundary conditions and the third term incorporates the initial conditions.

This solution is only useful if the form for \(G\) is known. This is obtained by considering the Green’s function for an infinite domain, called \(g(R, \tau)\), where \(R = |r - r_0|\) and \(\tau = t - t_0\). Eqn. 5.8 is solved for \(g\) by expanding it in a three dimensional Fourier integral

\[
g(R, \tau) = \frac{1}{(2\pi)^3} \int e^{i\mathbf{p} \cdot \mathbf{R}} \gamma(p, \tau) dV_p \tag{5.10}
\]

Using this form in Eqn. 5.8 gives

\[
\frac{\partial g}{\partial t} - \zeta \nabla^2 g = \frac{1}{(2\pi)^3} \int e^{i\mathbf{p} \cdot \mathbf{R}} \left[ \frac{\partial \gamma}{\partial t} + \zeta p^2 \gamma \right] dV_p \tag{5.11}
\]

and

\[
\delta(\mathbf{R}) = \frac{1}{(2\pi)^3} \int e^{i\mathbf{p} \cdot \mathbf{R}} dV_p \tag{5.12}
\]
from which is obtained a differential equation for $\gamma$

$$\frac{\partial \gamma}{\partial t} + \zeta p^2 \gamma = 4\pi \delta(\tau)$$

(5.13)

Away from $\tau = 0$, this has the form

$$\frac{\partial \gamma}{\partial t} + \zeta p^2 \gamma = 0$$

(5.14)

with a solution

$$\gamma = Ae^{-\zeta p^2 \tau}$$

(5.15)

This can be used to study the behavior close to $\tau = 0$. In that limit, one cannot assume that the coefficient $A$ is independent of $\tau$. Plugging $\gamma$ back into its differential equation (Eqn. 5.13), and letting $\tau$ goes to zero gives

$$\frac{\partial A}{\partial t} = 4\pi \delta(\tau)$$

(5.16)

The derivative of a Heaviside function is a delta function, giving the conclusion that

$$A = 4\pi u(\tau)$$

(5.17)

where $u(\tau)$ is the Heaviside function. Thus,

$$\gamma(\vec{p}, \tau) = 4\pi e^{-\zeta p^2 \tau}u(\tau)$$

(5.18)

and the Green’s function therefore has the form

$$g(R, \tau) = \frac{4\pi}{(2\pi)^3} \int e^{i\vec{p} \cdot \vec{R}} e^{-\zeta p^2 \tau}u(\tau) dV_p = \frac{1}{2\pi^2} u(\tau) \int e^{i\vec{p} \cdot \vec{R} - \zeta p^2 \tau} dp$$

(5.19)
The exponent can be rewritten by completing the square in the following way

\[ ip_x R_x - p_x^2 \zeta \tau = - \left( p_x \sqrt{\zeta \tau} - \frac{iR_x}{2 \sqrt{\zeta \tau}} \right)^2 - \frac{R_x^2}{4 \zeta \tau} = -\zeta \tau \xi^2 - \frac{R_x^2}{4 \zeta \tau} \]  

(5.20)

where \( \xi = p_x - iR_x/(2\zeta \tau) \). The integral in Eqn. 5.19 is now easily evaluated

\[ \int e^{ip_x R_x - \zeta p_x^2 \tau} dp_x = \int e^{-\zeta \tau \xi^2 - R_x^2/(4\zeta \tau)} dp_x = e^{-R_x^2/(4\zeta \tau)} \sqrt{\pi \zeta \tau} \]  

(5.21)

which gives for the Green’s function

\[ g(R, \tau) = \frac{1}{2\sqrt{\pi} (\zeta \tau)^{3/2}} e^{-R^2/(4\zeta \tau)} u(\tau) \]  

(5.22)

It is interesting to note the units on this Green’s function, \([1/\text{length}^3]\), are different from the units of the Green’s function derived in Morse and Feshbach, \([1/(\text{length} \cdot \text{time})]\). The reason for this is the different form of the heat equation used in their text, \( \nabla^2 T - a^2 \partial T/\partial t = -4\pi q \). This places the coefficient, \( a^2 \), in front of the time derivative, giving \( a^2 \) units of \([\text{time}/\text{length}^2]\). Thus, the source term for that equation has units of \([\text{temperature}/\text{length}^2]\), whereas the heat equation I presented in Eqn. 5.7 has a source term has units of \([\text{temperature}/\text{time}]\). The difference in units of the Green’s function derived here and that from Morse and Feshbach are therefore consistent with the solution given in Eqn. 5.9.

Integrating over the angular dependence of \( R^2 \) Eqn. 5.22 gives the radially symmetric form of the Green’s Function corresponding to Eqn. 5.1. The integration is simplified by choosing \( \mathbf{r} \) to point along the \( z \)-axis, with \( r \) defining the observation point. This is possible to do because our system is radially symmetric (therefore, the direction of the \( z \)-axis is arbitrary). The vector,
\[ r_0, \text{ indicating the location of the source, is therefore inclined from } r \text{ by an angle, } \theta_0 \text{ giving} \]

\[ R^2 = (r - r_0) \cdot (r - r_0) = r^2 + r_0^2 - 2r \cdot r_0 = r^2 + r_0^2 - 2rr_0 \cos \theta_0 \quad (5.23) \]

Thus, the selection of \( \vec{r} \) to point along the z-axis eliminated the dependance of \( R^2 \) on the azimuthal angle, \( \varphi_0 \), as well as the polar and azimuthal angles of \( \mathbf{r} \). The Green’s function for the radially symmetric heat equation is therefore

\[
g_r(r, t| r_0, t_0) = \int_0^{2\pi} d\varphi_0 \int_{-1}^1 d(\cos \theta_0) \frac{r_0^2 g(R, \tau)}{r^2} \]

\[ = 2\pi r_0^2 \int_{-1}^1 d(\cos \theta_0) \left[ \frac{1}{2\sqrt{\pi}(\zeta \tau)^{3/2}} e^{-(R^2)/(4\zeta \tau)} u(\tau) \right] \]

\[ = \frac{r_0^2}{r^2} u(\tau) \int_{-1}^1 d(\cos \theta_0) e^{-(r^2 + r_0^2 - 2r_0 \cos \theta_0)/(4\zeta \tau)} \]

\[ = \frac{r_0^2}{r^2} \frac{2\sqrt{\pi}}{(\zeta \tau)^{3/2}} u(\tau) \int_{-1}^1 d(\cos \theta_0) \left[ e^{(2r_0)/(4\zeta \tau)} - e^{(-2r_0)/(4\zeta \tau)} \right] \]

\[ = \frac{2r_0 \sqrt{\pi}}{r^2 \zeta \tau} u(\tau) \left[ e^{(r-r_0)^2/(4\zeta \tau)} - e^{(r+r_0)^2/(4\zeta \tau)} \right] \quad (5.24) \]

So, the Green’s function for the radially symmetric heat equation of Eqn. 5.1 takes the final form

\[
g_r(r, t| r_0, t_0) = \frac{2r_0}{r} \sqrt{\frac{\pi}{\zeta(t-t_0)}} \left[ e^{(r-r_0)^2/(4\zeta(t-t_0))} - e^{(r+r_0)^2/(4\zeta(t-t_0))} \right] u(t - t_0) \quad (5.25) \]

which has units of \([1/\text{length}]\). Physically, this Green’s function gives the response of the system to an impulsive source with the shape of a spherical shell with radius \( r_0 \).

Figs. 5.1 and 5.2 plot \( g_r(r, t| r_0, t_0) \) due to a source located at the pore radius, \( r_0 = r_p \), at time \( t_0 = 0 \). The plot of \( g_r \) as a function of time, Fig. 5.1, indicates two key features of the physical
response of the system. Firstly, the short time scale for heating is evident from the rapid rise of the value of $g_r$ even for the values of $r = 0.1r_p$ and $r = 1.5r_p$. This corresponds to the fast characteristic time scale of the system, and also impacts the rapid fall of the peak temperature with time. Secondly, the long tails in the temperature distribution as a function of time indicate that the system is slow to return to its unperturbed temperature.

![Plot of $g_r$ as a function of $t$ at different values of $r$](image)

Figure 5.1: Plot of the radial Greens function, $g_r$, as a function of time at different locations, $r$, due to an impulse introduced at $r_0 = r_p$ and time $t_0 = 0$. When $r$ is very close to the location of the source the temperature becomes very high very quickly, as in the case of $r = 0.9r_p$ and $r = 1.1r_p$.

The plot of $g_r$ as a function of distance, Fig. 5.2, clearly shows the effect of radial symmetry of the system. The impulse at $r_p = 53.5$nm is a delta function which is a spherical shell with that radius. At small times close to $t_0$, for example $t = 0.1$ ns, the distribution will look like a symmetric Gaussian localized at $r = r_0$. However, at larger times, the distribution becomes asymmetric around $r = 0$ because of diffusion symmetrically inward toward the center of the
system elevating the temperature there. Ultimately the diffusion symmetrically outward from \( r_0 \) will win out and the temperature at \( r = 0 \) will decrease.

![Plot of \( g_r \) as a function of \( r \) for at different times](image)

**Figure 5.2:** Plot of the radial Greens function, \( g_r \), as a function of radius for different times \( t \). Note that at the small time, \( t = 0.1 \text{ns} \), the distribution appears like a Gaussian focused at \( r = r_0 \). At large times, as seen at \( t = 5 \text{ns} \), the distribution appears as a Gaussian centered at \( r = 0 \).

The total solution to the radially symmetric problem of Eqn. 5.1 is given by performing the integration in Eqn. 5.9. Since the initial condition is zero, the last term of Eqn. 5.9 disappears, and since the domain is infinite, the surface integrals also disappear. This leaves the integral over the radius, \( r_0 \), where the source is non-zero.

\[
T(r, t) = \int^t_0 \int_0 r_0 q(r_0) g_r(r, t | r_0, t_0) \, dr_0 \, dt_0
\]

(5.26)
The heat source, $Q$, is only nonzero for $0 < r_0 < r_p$. Thus

$$
q(r_0) = \begin{cases} 
\frac{Q}{4\pi \rho C_p} & r \leq r_p \\
0 & r > r_p 
\end{cases}
$$

(5.27)

and

$$
T(r, t) = \frac{Q}{4\pi \rho C_p} \int_0^r \int_0^{r_p} dr_0 \int_0^{r_0} dr_0 g(r, t | r_0, t_0)
$$

(5.28)

This gives the temperature as a function of $r$ and $t$. The units on this equation can also be seen to be correct since $Q$ has dimension of $[\text{energy} / (\text{volume} \cdot \text{time})]$. The result, $T(r, t)$, is plotted in Fig. 5.3 as a function of $r$ at different times.† The source term is shown in the inset as a constant between 0 to $r_p$.

![Plot of Source Term](image)

**Figure 5.3:** Plot of the temperature distribution, $T(r, t)$, obtained using the Green’s function method as a function of $r$ for different times. The inset plots the heat source $q$ from Eqn. 5.27.

†This result is graphically equivalent to the series solution of Eqn. C.26 derived in Appendix C.
5.3 Comparison of Analytical Solution with Numerical Results

In this section, I compare the analytical solutions presented in the previous section with the numerical results of the FEM model presented in Chapter 4. This comparison shows consistent behavior between the analytical model and the FEM model, building confidence in the FEM model results. However, there are also important differences in the analytical and FEM results which highlight the importance of including the temperature dependent properties of the electrolyte and the complex geometry of the system. These simplifications were required for the analytical solution. In contrast, the FEM model did not require these simplifying assumptions, thereby overcoming the fundamental limitation of the analytical approach.

![Figure 5.4: Plot of the temperature distribution, \( T(r, t) \), in blue obtained using the Green’s function method along with a plot of \( T(r, t) \) in red obtained using the FEM model. Temperature is plotted as a function of \( r \) at times \( t = 1 \mu s \) in both cases.](image)

The solution for the temperature distribution from the analytical model and the FEM model are shown as functions of \( r \) in Fig. 5.4 at time \( t = 1 \mu s \). Both distributions are shown to be highly peaked at the center of the nanopore, dropping quickly with increasing \( r \). However, the
temperature distribution calculated by the analytical model is more sharply peaked than that calculated by the FEM model. The broader temperature distribution of the FEM model results from the fact that the source term is not limited to $r < r_p$. In the FEM model, the current density is non-zero in the electrolyte for $r > r_p$, contributing to heating there.

Fig. 5.5 plots the maximum temperature in the pore center calculated for both models as a function of time. The rate at which the temperature increases is seen to be much faster for the analytical model than for the FEM model, the former of which rises in accordance with the characteristic time scale of the system, $r_p^2/\zeta = 13.3$ ns.

![Figure 5.5: Plot of the maximum temperature as a function of time for the analytical model in blue and the FEM model in red.](image)

The longer characteristic heating time of the FEM model in comparison to the analytical model is a consequence of the temperature dependent material properties and the geometrical features of the nanopore included in the FEM model. In particular, the assumption of spherical symmetry in the analytical model is a poor approximation for the Joule heating source term. The initial assumption of spherical symmetry was applied because the diffusion of heat will
be nearly isotropic, due to the fact that the membrane is very thin. This leads to the nearly spherically symmetric temperature distributions calculated by the FEM model, shown in Fig. 4.3. However, the Joule heating source, $\mathbf{J} \cdot \mathbf{E}$, term is not spherically symmetric and is in fact strongest close to the edge of the pore. This is shown in the contour plot of the source term in Fig. 5.6 calculated by the FEM model. Focusing of the source term to the pore edge is the result of the access resistance of the nanopore\textsuperscript{11,63} leading to a higher density of field lines at the edge of the pore.

![Magnitude of Joule Heating Source Term](image)

*Figure 5.6: Contour plot of the Joule heating source term, $\mathbf{J} \cdot \mathbf{E}$, as calculated by the FEM model upon application of an 8.22 V pulse at $t = 0$. Due to the temperature dependence of the electrical conductivity, the source term is dependent on time, changing with the increasing temperature as the solution heats.*

5.4 Remarks in Summary

The complicated FEM model build in COMSOL can appear to be a black box approach due to the complexity of its numerical implementation. The relationships connecting the input parameters and geometry to the output temperature is complicated and not necessarily clear from
studying the FEM model alone. As such it is important to study the analytical behavior of the
governing equations in order to independently assess whether the results from an FEM model are
reasonable. In this chapter I have shown that the predictions of the FEM model correspond well
to the behavior of the governing equations treated analytically. The simplifying assumptions
necessary to develop an analytical model can be seen to account for the differences between the
FEM model results and the analytical solution.
The most simple case of a system with a surface of discontinuity is that of two coexistent phases separated by a spherical surface, the outer mass being of indefinite extent. When the interior mass and the surface of discontinuity are formed entirely of substances which are components of the surrounding mass, the equilibrium is always unstable.

J. W. Gibbs

6

Kinetics of Bubble Nucleation in the Nanopore

All thermodynamic systems are subject to microscopic fluctuations that result from the system visiting any of the ensemble of microstates corresponding to the macroscopic state of the system. In the previous four chapters, I focused on determining the macroscopic state of the liquid in the nanopore by calculating the temperature distribution that arises as a result of Joule heating. I showed that the liquid in the nanopore can be strongly superheated to well above its boiling point. This treatment did not consider the possibility that the extensive thermodynamic variables can fluctuate at a given temperature. However, in actuality, the extensive variables of the system are
constantly fluctuating. It is these fluctuations which ultimately drive the change of phase from liquid to vapor in the form of nucleation of a bubble in the nanopore.

In this chapter, I focus on the nature of these fluctuations and how they precipitate the nucleation of a vapor bubble in the nanopore. The first half of the chapter presents the theoretical foundation for nucleation kinetics. This includes defining the surface tension induced barrier to the formation of the vapor phase, characterizing the fluctuations that drive change of phase, determining the size distribution function of fluctuations, and finally deriving the kinetics for this distribution giving the probability of a nucleation event of critical size occurring in the system leading the growth of a vapor phase. My treatment follows the theory as developed and discussed by Zeldovich, Becker and Döring, Volmer and Weber, and others.

In the second half of this chapter, I apply nucleation theory to the case of the superheated electrolyte in the nanopore. By determining the temperature dependent nucleation rate, I show that homogeneous nucleation of a single vapor bubble occurs within the pore as a result of the sharply peaked temperature distribution in the pore. Subsequently, I show that the probability for heterogeneous nucleation of the bubble occurring on the edge of the pore is insignificant in comparison to the probability of a homogeneous nucleation event occurring at the center. This chapter concludes with a discussion of the experimental results which confirm homogeneous nucleation of a vapor bubble does indeed occur at the center of the nanopore.

6.1 Surface Tension and the Size of the Critical Nucleus

The metastable nature of the superheated liquid state was described in the introductory chapter. It was discussed that the superheated liquid does not automatically convert to vapor under conditions where the vapor phase is lower in energy than the liquid phase. This is due to an energetic barrier associated with formation of the new vapor phase. This energetic barrier is the positive work that the system must do to create an interface between the liquid and vapor phases.
This section derives an expression for the work required to create a vapor bubble in a superheated liquid. It will be shown that the superheated liquid is unstable with respect to the formation of a vapor bubble; i.e., vapor bubbles below a critical size will collapse in the superheated liquid, and those above a critical size will grow. The size of this critical bubble, called the critical nucleus will be important in determining the kinetics governing the eventual transformation of phase.

The treatment of interfaces in the thermodynamic context was pioneered by J.W. Gibbs. He considered the contributions to the energy of a two phase system to consist of three parts: the two phases and the interface of separation between them. Thus, the total differential of internal energy of a system consisting of a vapor bubble in a liquid is given by

\[
dU_l = T_l dS_l - P_l dV_l + \mu_l dN_l
\]

\[
dU_v = T_v dS_v - P_v dV_v + \mu_v dN_v
\]

\[
dU_s = \gamma dA
\]

(6.1)

where the subscripts \(l\), \(v\), and \(s\) indicate the liquid, vapor, and interface, respectively. \(A\) is the area of the liquid-vapor interface, and \(\gamma\) is the surface tension, with units of energy per area (or force per length). The total volume of the closed system is \(V = V_l + V_v\), the total entropy is \(S = S_l + S_v\) and the total energy is \(U = U_l + U_v + U_s\). This gives

\[
dU = T dS - P_l d(V - V_v) - P_v dV_v + \mu_l dN_l + \mu_v dN_v + \gamma dA
\]

(6.2)

where it is implied that the temperatures of the liquid and vapor phases are equal. Any change in the number of vapor molecules must be balanced by an equal and opposite change in the number
of liquid molecules, thus $dN_v = -dN_l$. Therefore

$$dU = TdS - P_l d(V - V_v) - P_v dV_v + (\mu_v - \mu_l) dN_v + \gamma dA \quad (6.3)$$

The vapor bubble is assumed to be spherical: due to its small size, gravitational effects will not distort its shape.\textsuperscript{13,14} As such, $V_v = \frac{4}{3} \pi r^3$ and $A = 4 \pi r^2$ where $r$ is the radius of the bubble. Eqn. 6.3 therefore becomes

$$dU = TdS - P_l dV + (\mu_v - \mu_l) dN_v + \left[4 \pi r^2 (P_l - P_v) + 8 \pi r \gamma \right] dr \quad (6.4)$$

The system is assumed to be closed, held at constant energy, $dU = 0$, and constant volume, $dV = 0$. The radius of the bubble, $r$, and the number of molecules in the vapor phase, $N_v$, are an internal parameters of the system, not subject to outside manipulation.\textsuperscript{14} Therefore, the entropy must be a maximized with respect to them in order for the bubble to be at equilibrium. Stability of the bubble with respect to $r$ requires that the coefficient for $dr$ in Eqn. 6.4 must vanish. Thus,

$$P_v - P_l = \frac{2 \gamma}{r} \quad (6.5)$$

This is known as the Laplace Pressure Equation and gives the condition for mechanical equilibrium of the bubble. The critical radius for a stable bubble is therefore

$$r_{cr} = \frac{2 \gamma}{P_v - P_l} \quad (6.6)$$

Stability of the bubble with respect to $N_v$ requires

$$\mu_l(T, P_l) = \mu_v(T, P_v) = \mu_v \left( T, P_l + \frac{2 \gamma}{r_{cr}} \right) \quad (6.7)$$
where the Laplace pressure was used to define the pressure of the vapor. If the vapor is assumed to be ideal, $P_v V_v = N_v k_b T$, an expression for $\mu_v$ can be obtained by differentiating $G_v = \mu_v N_v$ with respect to $P_v$ such that $V_v = dG_v/dP_v = N_v d\mu_v/dP_v$ and integrating. This gives

$$\mu_v \left(T, P_l + \frac{2\gamma}{r_{cr}}\right) = k_b T \ln \left(P_l + \frac{2\gamma}{r_{cr}}\right) + f(T)$$  \hspace{1cm} (6.8)

where $f(T)$ is an integration factor. The requirement of Eqn. 6.7 for the stability of the bubble with respect to $N_v$ therefore reads

$$\mu_l(T, P_l) = \mu_v \left(T, P_l + \frac{2\gamma}{r_{cr}}\right) = k_b T \ln \left(P_l + \frac{2\gamma}{r_{cr}}\right) + f(T)$$  \hspace{1cm} (6.9)

Therefore, $r > r_{cr}$ will give $\mu_l > \mu_v$ and the vapor phase grows leading to expansion of the bubble; $r < r_{cr}$ will lead to $\mu_l < \mu_v$ and the liquid phase grows leading to collapse of the bubble.

![Figure 6.1: Plot of the surface tension of the liquid vapor interface of water as a function of temperature along the saturation curve.](image)

The size of the critical radius depends on the temperature of the superheated liquid. This results from the dependence of $r_{cr}$ in Eqn. 6.6 on surface tension and vapor pressure. Fig.
6.1 plots $\gamma(T)$ for water’s saturation curve. The figure shows that surface tension for a liquid-vapor interface of water decreases with increasing temperature. At the critical temperature, 647 K, and critical pressure 22.06 MPa, $\gamma(T)$ decreases to zero. Beyond this point the liquid and vapor phases are indistinguishable and surface tension characterizing an interface of separation between phases does not exist.

Fig. 6.2 plots the critical radius, $r_c(T)$, using the relationship for $\gamma(T)$ from Fig. 6.1 as well as the vapor pressure for water along the saturation curve. The value for the critical radius at 603 K is 1.2 nm. This is just over an order of magnitude larger than the 0.097 nm oxygen-hydrogen bond of a water molecule.

![Figure 6.2: Plot of the critical radius as a function of temperature, given by Eqn. 6.6](image)

This section has shown the critical radius to be an unstable equilibrium of the superheated liquid with respect to vapor bubble formation. The next section will consider the form of the energetic barrier to the formation of a new phase, building on the arguments presented here.
6.2 Fluctuations Driving Bubble Nucleation

Fluctuations in the density of the liquid will ultimately lead to the formation of a vapor bubble nucleus of critical size. The probability that such a nucleus will occur in the system is proportional to the exponential of the entropy of the system, \( \exp(S) \). This relationship was first applied to the study of fluctuations by Albert Einstein.\(^{13}\) It is consistent with the definition of entropy from statistical mechanics: entropy is the logarithm of the number of microstates consistent with the given macrostate of the system. The system will constantly fluctuate between the different microstates available to it.

The change in entropy for the system to go from one microstate to another, \( \Delta S \), can be shown to be equivalent to \( -W_{\text{min}}/k_b T \),\(^{13}\) where \( W_{\text{min}} \) is the minimum work needed to go between microstates. In the case of bubble nucleation, \( W_{\text{min}} \) is the minimum work needed to create a bubble as a result of a fluctuation in density. The probability, \( P \), that a bubble requiring \( W_{\text{min}} \) to form in the system is therefore proportional to

\[
P \propto \exp(\Delta S) = \exp\left( -\frac{W_{\text{min}}}{k_b T} \right) \tag{6.10} \]

\( W_{\text{min}} \) can be determined by considering the difference in internal energy of the system with and without the bubble. Before the bubble’s formation, the entire system is only in the liquid state with internal energy

\[
U_l^0 = TS - P_l V + \mu_l N \tag{6.11}
\]

where \( V = V_l + V_v \) and \( N = N_l + N_v \). After the formation of the bubble, the system is split into a region of vapor, the surrounding liquid region, and the liquid-vapor interface, with associated
energies

\[ U_l = TS_l - P_l V_l + \mu_l N_l \]
\[ U_v = TS_v - P_v V_v + \mu_v N_v \]  \hspace{1cm} (6.12)
\[ U_s = \gamma A \]

The minimum work is therefore

\[ W_{\text{min}} = U_l + U_v + U_s - U_l^0 \]
\[ = TS_l - P_l V_l + \mu_l N_l + TS_v - P_v V_v + \mu_v N_v + \gamma A - TS_l - P_v V_v + \mu_v N_v + \gamma A \]  \hspace{1cm} (6.13)
\[ = (\mu_v - \mu_l) N_v - (P_v - P_l) V_v + \gamma A \]

with \( S = S_v + S_l \). As discussed in the previous section, the chemical potentials of the liquid and vapor phases (equivalent to the Gibbs free energy per particle) are a functions of the pressure of each phase. For the formation of a nucleus of new phase, the pressures considered are those for which \( \mu_v(P_v) = \mu_l(P_l) \). This gives

\[ W_{\text{min}} = -(P_v - P_l) V_v + \gamma A \]  \hspace{1cm} (6.14)

Again, using \( V_v = \frac{4}{3} \pi r^3 \) and \( A = 4 \pi r^2 \) this gives

\[ W_{\text{min}} = -\frac{4}{3} (P_v - P_l) \pi r^3 + 4 \pi r^2 \gamma \]  \hspace{1cm} (6.15)

This relationship gives the minimum work required to create a bubble of size \( r \), and is plotted in Fig. 6.3(a). Using the critical radius of Eqn. 6.6 gives

\[ W_{\text{min}} = \frac{16}{3} \pi \frac{\gamma^3}{(P_v - P_l)^2} \]  \hspace{1cm} (6.16)
which is the minimum work required to create a bubble of critical size; this is plotted as a function of temperature in Fig. 6.3(b). As discussed in the previous section, a vapor bubble of radius \( r_{cr} \) in the superheated liquid is an unstable equilibrium. Thus, the maximum value for \( W_{\text{min}} \) in Fig. 6.3(a) occurs at \( r = r_{cr} \). A bubble of radius \( r < r_{cr} \) will collapse, thereby decreasing the energy of the system since \( W_{\text{min}} \) decreases. Likewise, a bubble of radius \( r > r_{cr} \) will grow since this will also decrease the energy of the system.\(^{18,68}\)

![Graph showing minimum work as a function of radius and temperature](image)

**Figure 6.3**: (a) The minimum work to create a bubble, Eqn. 6.15, as a function of the bubble’s radius, \( r \), at temperatures \( T = 600 \text{ K} \) and \( T = 590 \text{ K} \). The critical radius, \( r_{cr} \), for each temperature is indicated by a dashed line and corresponds to the maximum value of \( W_{\text{min}} \). (b) The minimum work to create a bubble with \( r = r_{cr} \), given in Eqn. 6.16, as a function of temperature.

The expression for minimum work to create a bubble of radius \( r \), Eqn. 6.15, can now be used
in Eqn. 6.10 to define the probability that a fluctuation of radius \( r \) occurs. This gives

\[
\mathcal{P} = \exp \left[ -\frac{1}{k_b T} \left( -\frac{4}{3} (P_v - P_l) \pi r^3 + 4 \gamma \pi r^2 \right) \right] \quad (6.17)
\]

This probability can be used to define \( f_0(r) \), which is the equilibrium distribution function for the number of nuclei of various sizes that exist in the liquid. The number of nuclei with radii within \( r \) and \( r + dr \) is \( f_0(r)dr \). Using \( (P_v - P_l) = 2 \gamma / r_{cr} \) this distribution is proportional to \( \mathcal{P} \) giving

\[
f_0(r) = C \exp \left[ -\frac{1}{k_b T} \left( -\frac{8 \gamma \pi r^3}{3 r_{cr}} + 4 \gamma \pi r^2 \right) \right] \quad (6.18)
\]

where \( C \) is the proportionality constant with units of number of nuclei per unit length to the fourth power. The maximum of \( W_{\text{min}} \), occurring at \( r_{cr} \), corresponds to an exponentially sharp minimum of the distribution \( f_0 \). Near to this maximum, \( W_{\text{min}} \) behaves as

\[
W_{\text{min}}(r) \approx \frac{4}{3} \pi \gamma r_{cr}^2 - 4 \pi \gamma (r - r_{cr})^2 \quad (6.19)
\]

which is the Taylor expansion of \( W_{\text{min}} \) around \( r = r_{cr} \) to the second-order term. The distribution function therefore becomes

\[
f_0(r) = C \times \exp \left[ -\frac{1}{k_b T} \left( \frac{4}{3} \pi \gamma r_{cr}^2 - 4 \pi \gamma (r - r_{cr})^2 \right) \right] \quad (6.20)
\]

where \( f_0(r_{cr}) = C \exp(-4 \pi \gamma r_{cr}^2 / 3k_b T) \).

It is important to note that size distribution of nuclei defined in Eqn. 6.20 applies only to the metastable state of the liquid before nucleation occurs. It was derived using a purely thermodynamic approach and therefore pertains only to systems in equilibrium. The metastable state
itself does not correspond to complete equilibrium and therefore the thermodynamic distribution only applies for times much less than the characteristic time for a critical nucleus to occur. The probability $P$ and the distribution, $f_0(r)$, are only strictly correct for $r < r_{cr}$ for that very reason: when a fluctuation of size greater than the critical radius occurs, a phase transition will take place taking the system out of equilibrium. Large fluctuations are therefore not among the set of microstates corresponding to the macrostate of the metastable, superheated liquid.

6.3 **The Kinetics of Phase Transformation**

Fluctuational development of nuclei larger than the critical size will cause a phase transition to occur. Information concerning the kinetics of this transformation from liquid to vapor cannot be provided by $f_0(r)$ in Eqn. 6.20 since this only applies to thermodynamic equilibrium. Instead, an analysis of the kinetics of the nucleation process is required. The theory presented by Zeldovich is discussed here.\(^{64}\)

Zeldovich defined a kinetic size distribution function for nuclei, $f(r,t)$. By considering the elementary process of addition or subtraction of individual molecules from the nucleus, thereby changing its size, he showed that the growth of nuclei is governed by the Fokker-Plank equation

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial r} J$$

(6.21)

where $J$ is the flux in size space of the nuclei, with units of number of nuclei per unit time per unit volume, given by

$$J = -B \frac{\partial f}{\partial r} + Af$$

(6.22)

where $B$ acts as a diffusion coefficient for the size of nuclei with units of length squared per unit
time. This flux will be zero for the equilibrium distribution, \( f_0 \). From Eqn. 6.10, this gives

\[
A = \frac{B}{f_0} \frac{\partial f_0}{\partial r} = -B \frac{W_{\text{min}}(r)}{k_bT} \quad (6.23)
\]

Eqn. 6.22 can be solved for the stationary solution wherein \( J \) is constant. This corresponds to a continuous or steady phase transition. Using Eqns. 6.23 and 6.10 in Eqn. 6.22 gives

\[
J = -B \frac{\partial f}{\partial r} + \frac{B}{f_0} \frac{\partial f_0}{\partial r} f = -B f_0 \frac{\partial}{\partial r} \left( \frac{f}{f_0} \right) \quad (6.24)
\]

Rearranging this and integrating gives

\[
\frac{f}{f_0} = -J \int_{r_c}^{\infty} \frac{dr}{Bf_0} + \text{constant} \quad (6.25)
\]

Both \( J \) and the integration constant can be determined by the boundary conditions on the size distributions at small and large values of \( r \). The probability, and therefore the size distribution, is very large for fluctuations of small size, and increases with decreasing \( r \). Small nuclei occur so frequently in the system even during a phase transition that they can be considered to have their equilibrium distribution. Therefore \( f/f_0 \rightarrow 1 \) as \( r \rightarrow 0 \). The boundary condition at large \( r \) can be determined by considering the fact that beyond the minimum at \( r = r_c \), \( f_0 \) will continue to increase without limit with increasing \( r \). Recall that the equilibrium distribution does not have physical meaning for \( r > r_c \) since this is the regime of a phase transition. In contrast, the physical distribution, \( f \), will remain finite. Therefore \( f/f_0 = 0 \) must be imposed at a radius greater than the critical, and can arbitrarily be set at \( r \rightarrow \infty \). Applying these two boundary conditions yields

\[
\frac{f}{f_0} = J \int_{r_c}^{\infty} \frac{dr}{Bf_0} \quad (6.26)
\]
with the flux determined by

$$\frac{1}{J} = \int_0^\infty \frac{dr}{Bf_0}$$

(6.27)

Because $f_0$ has a sharp minimum at $r = r_{cr}$, the integrand will have a sharp maximum there. Eqn. 6.20 can therefore be used for $f_0$ and the integration over $r - r_{cr}$ can then be extended from $-\infty$ to $\infty$ leading to the Gaussian integral

$$\frac{1}{J} = \frac{1}{f_0(r_{cr})B(r_{cr})} \int_\infty^{-\infty} \exp \left[ -\frac{4\pi\gamma(r - r_{cr})^2}{k_bT} \right] dr$$

(6.28)

which can be solved

$$J = 2 \sqrt{\frac{\gamma}{k_bT}} B(r_{cr}) f_0(r_{cr}) = 2C \sqrt{\frac{\gamma}{k_bT}} B(r_{cr}) \exp \left( -\frac{4\pi\gamma r_{cr}^2}{3k_bT} \right)$$

(6.29)

Using the Laplace pressure equation for the critical radius, Eqn. 6.6, this can be written as

$$J = 2C \sqrt{\frac{\gamma}{k_bT}} B(r_{cr}) \exp \left( -\frac{16\pi\gamma^3}{3k_bT(P_v - P_l)^2} \right)$$

(6.30)

This is the nucleation rate giving the number of viable nuclei passing through the critical value, $r_{cr}$, in size space, per unit time, per unit volume of the superheated liquid. These nuclei are viable from the perspective of precipitating the phase transition. Recall that $C$ has units of number per length to the fourth power and $B(r_{cr})$ has units of length squared per unit time. Thus, $J$ has units of number of nuclei per unit volume per unit time.

Determining the proper value for the preexponential factor of Eqn. 6.30 was an open question at the time Zeldovich presented his treatment of nucleation kinetics. Multiple approaches to determining this have subsequently been developed, although they are not all consistent due to different assumptions invoked in their derivation. However, the effect of the prefactor

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of the behavior of the nucleation rate is dominated by the exponential term, and is therefore of comparatively little significance.

Another difficulty that arises is determining the pressure in the vapor bubble. $P_v$ in Eqn. 6.30 is the vapor pressure of the liquid at a hydrostatic pressure equal to the ambient liquid pressure $P_l$ which here is atmospheric pressure in the case of the nanopore.\textsuperscript{18} However, the material data available is for the vapor pressure $P_v^0$ measured for a liquid under hydrostatic pressure along the saturation curve.\textsuperscript{70} Approximations for $P_v$ are therefore made to arrive at\textsuperscript{18}

$$J = \frac{\rho}{m} \sqrt{\frac{3\gamma}{\pi}} \exp \left[ -\frac{16\pi\gamma^2}{3k_BT(P_v^0 - P_l)^2\delta^2} \right]$$ \hspace{1cm} (6.31)

where $\gamma$ is the surface tension of the liquid-vapor interface, $\rho$ is the density of the liquid, $P_v^0$ is the equilibrium vapor pressure, $P_l$ is the ambient pressure of the liquid equal to 1 atm, and $m$ is the mass of a single water molecule. The factor $\delta$ is a correction factor required for using the equilibrium vapor pressure rather than the vapor pressure inside the bubble. This can be shown to be\textsuperscript{18,67,72,73}

$$\delta = 1 - \frac{\rho_V}{\rho} + \frac{1}{2} \left( \frac{\rho_V}{\rho} \right)^{1/2}$$ \hspace{1cm} (6.32)

where $\rho_V$ is the temperature-dependent density of the vapor in the bubble. The rate in Eqn. 6.31, including the prefactor, Eqn. 6.32, is widely used for bubble nucleation and I will likewise apply it to subsequent calculations concerning the nucleation rate in the superheated liquid in the nanopore.

A plot of $J$ as a function of temperature is shown in Fig. 6.4. The nucleation rate proves to be exquisitely sensitive to the temperature of the solution due to the strong temperature-dependence of the exponential factor in Eqn. 6.31. This dependence results from the decrease of $\gamma$ with increasing temperature, shown in the inset of Fig. 6.1, as well as the increase of $P_v^0$ with increasing temperature. Together, these cause the exponential of Eqn. 6.31 to grow as temperature rises.
At temperatures approaching the limit of superheat, J increases by as much as two orders of magnitude per degree kelvin increase.

![Graph showing nucleation rate vs. temperature](image)

**Figure 6.4: Plot of the nucleation rate in Eqn. 6.31 as a function of temperature.**

It is important to note that the dissolution of a strong electrolyte in water increases the surface tension.\(^7\)\(^4\)\(^7\)\(^5\) This will in turn decrease \(J\) because it increases the minimum work required to form a bubble of critical size. As a result, the kinetic limit of superheat of the 3 M NaCl solution is elevated from that of pure water.

### 6.4 Homogeneous Nucleation of the Vapor Bubble in the Nanopore

The magnitude of the localized temperature maximum calculated within the pore drastically increases the probability that a vapor bubble will nucleate homogeneously there. Experimentally, this nucleation event is observed as the rapid drop in the pore current as the nucleated bubble grows to block the ionic current through the pore.\(^1\) This was seen in the 8.22 V conductance
data plotted in Fig. 1.2, reproduced in Fig. 6.5(a), with an initial nucleation event occurring at 10.4 $\mu$s as shown by the drop in conductance in Fig. 1.3, reproduced in Fig. 6.5(b). Subsequent nucleation events occur quasi-periodically thereafter. The nucleation of a vapor bubble at a given time and location requires the extremely high temperatures calculated to be attained within the nanopore. Contour plots showing the temperature distribution for each applied voltage were shown in Fig. 4.3 and the calculated maximum temperatures attained for each were shown in Fig. 4.4.

![Figure 6.5: The conductance of a 53.5 nm radius, 71 nm thick nanopore at 4, 5, 6, 7, and 8.22 volts. Reproduced from Fig. 1.2. (b) Continuation of the 8.22 V conductance data after 10 $\mu$s. The data are filtered at 200 MHz; the faded line in the background is the unfiltered measured conductance data. Reproduced from Fig. 1.3.](image)

In order to quantify the likelihood of an initial nucleation event occurring at the pore center for 8.22 V applied, I use Eqn. 6.31 to calculate the nucleation rate $J$, as a function of distance from the center of the nanopore. Using the computed temperature distribution $T(r,t)$ in Eqn. 6.31 gives the nucleation rate as a function of the distance from the center of the nanopore shown in Fig.6.6, for times 8 $\mu$s, 9 $\mu$s, 10 $\mu$s, and 10.4 $\mu$s.

The exquisite sensitivity of the nucleation rate to temperature results in extreme focusing of
the nucleation rate at the center of the pore where the solution is hottest, and occurs rapidly over only a few microseconds. The inset of Fig. 6.6 shows this explicitly by plotting the maximum nucleation rate at the center of the pore as a function of time for 8.22 V, calculated from the curve in Fig. 4.4. The dependence $J(T)$ from Eqn. 6.31 indicating that the nucleation rate is negligible for the cases with applied voltage smaller than 8.22 V. The nucleation rate is only non-negligible after 8 $\mu$s and is localized to within 10 nm of the pore center, verifying the experimental observation that homogeneous nucleation occurs there.\(^1\)

The size of the critical radius at this temperature is also on the order of a few nanometers, therefore, given the localization of the peak in $J$ evidenced in Fig. 6.6 it is likely that only one
bubble nucleates at the pore center.

6.5 Heterogeneous Nucleation

The use of silicon nitride, Si$_3$N$_4$, as the membrane material reduces the likelihood that a bubble will nucleate heterogeneously at the edge of the pore. This is because Si$_3$N$_4$ is highly wettable and has a higher thermal conductivity than the electrolyte. Its hydrophilic nature reduces the energetically favorable probability of a solid-vapor interface which leads to heterogeneous nucleation, and its higher thermal conductivity serves to cool the electrolyte close to the edge of the nanopore. This is in contrast experiments where hydrophobic, thermally insulating membrane materials used to study heating in micron-sized pores where heterogeneous nucleation was reported to occur. $^76$

6.6 Experimental Confirmation of Homogeneous Nucleation

The calculation of the nucleation rate inside the nanopore that I have presented conclusively predicts that homogeneous nucleation of a single vapor bubble occurs at the center of the nanopore. This bubble accounts for the rapid drop in conductance observed to occur in Fig. 1.2. Once nucleated, the bubble grows to exclude the electrolyte from the nanopore, thereby obstructing the ionic current.

The theoretical and modeling results are therefore consistent with the experimental data to this point: given the extreme superheating of the electrolyte in the nanopore, homogeneous nucleation of a bubble will occur in the pore. However, we sought additional confirmation from the experiments that homogeneous nucleation was indeed occurring. Direct observation of the bubble nucleating was not possible, so we turned to an alternative method for optical detection of the bubble.
Figure 6.7 shows a second experimental setup, using a larger 1.9 μm radius, 2.5 μm thick pore, designed for optically probing the onset and location of the bubble nucleation in the pore. (Larger pores exhibit similar quasiperiodic bubble nucleation to that observed in the 53.5 nm radius pore albeit with lower frequencies at comparable voltage bias). Optical transmission of a focused 514 nm, 0.5 mW, cw laser through the pore is measured during the nucleation process. A 60× water immersion objective lens brings the laser to a beam waist diameter of 350 nm. The transmitted optical beam was captured and brought to a focus with f = 0.62 optics onto a 1 ns response time silicon photodiode (Thorlabs DET10A). The photodiode current was monitored simultaneously with the time-dependent electrical signal from the ionic current passing through the pore. For this experiment, the response time for the ionic current measurement was determined by the capacitance of the pore membrane. The lateral x-y position of the beam waist
could be accurately moved to different positions across the pore with beam steering optics.

Figure 6.8: Electrical conductance and photodiode current at the onset of a nucleation event with the focused laser at (a) the center and (b) the periphery of the pore.

Figure 6.8(a) shows both the electrical conductance and photodiode current falling rapidly at the onset of a nucleation event, stimulated by the application of an 18 V, 22 μs pulse. At this voltage, the nucleation events consistently occur 14 μs after the pulse is applied. For these data, the laser beam waist was positioned near the pore center. We define an event onset time for both the optical and ionic current signal to be the intercept of the prebubble current level with the extrapolated linear region of the current drop. These are labeled in the figure as \( t_i \) and \( t_p \) for the
ionic and photodiode current, respectively. Details of the optical signal beyond its initial rapid drop are not currently well understood but are unimportant for the current discussion.

When the laser beam waist is moved to the periphery of the pore, there is a clear increase in the delay in $t_p$ with respect to $t_i$ as seen in Fig. 6.8(b). This suggests that the bubble was formed at the center of the pore, and as a result of its finite growth velocity there is a delay until it scatters the incident laser beam at the pore periphery.

Figure 6.9: Plot of $\Delta t = t_p - t_i$ as a function of the laser position for x- and y-axis scan. Each point contains ten measurements; the error bars show the standard deviations from the mean. The measurements from the data shown in Figs. 6.8(a) and 6.8(b) were used in the points labeled (a) and (b). Linear fitting is performed for the scans across each axis.

Figure 6.9 confirms this view. It shows the offset $\Delta t = t_p - t_i$ as a function of the laser position across the pore in two perpendicular directions. The points corresponding to the data in Figs. 6.8(a) and 6.8(b) are indicated. The symmetry of the data around the pore center confirms that the bubble nucleation events are homogeneous and occur at the center of the pore. The bubble radius growth velocity obtained from the slope of the data in the figure is $52.1 \pm 1.6$ m/s
for the y-axis scan and 49.2 ± 1.7 m/s for the x-axis scan.

A straightforward interpretation of the data presented above involves rapid Joule heating of the electrolyte in and near the nanopore that ultimately results in nucleation of a vapor bubble at the pore center. The vapor bubble expands, cutting off the Joule heating when it reaches the pore periphery. It continues to grow due to fluid inertia and thermal energy stored in the superheated liquid. The bubble ultimately reaches a maximum size and then collapses after the vapor pressure in the bubble decreases below ambient pressure in the liquid sufficiently to overcome the inertial forces of liquid expansion.
In an ideal fluid, the momentum flux represents a completely reversible transfer of momentum, due simply to the mechanical transport of the different particle of fluid from place to place and to the pressure forces acting in the fluid. A viscous fluid has in addition the viscosity, due to another, irreversible, transfer of momentum from points where the velocity is large to those where it is small.

Lev Landau & Evgeny Lifshitz

7

Temperature and Bubble Dynamics in the Nanopore After Nucleation

Nucleation of a bubble of critical size or larger will cause the superheated liquid within the nanopore to convert to the vapor phase. This chapter concerns the temperature dynamics and hydrodynamics that result once a bubble has nucleated and begins to grow. The presence of the bubble is observed experimentally as the rapid drop of the nanopore conductance, shown in Fig. 1.3. This data is reproduced in Fig. 7.1 for the reader’s convenience.

Two distinctive features of the conductance data from Fig. 7.1 are the finite lifetime of each blockage event and the quasiperiodic repetition of blockage events subsequent to the initial event.
Figure 7.1: Reproduction of Fig. 1.3 showing blockage events in the nanopore conductance data.

The former is the result of the finite lifetime of the vapor bubble that nucleates at the center of the pore. The latter behavior, that of a relaxation oscillator, is the consequence of the temperature dynamics of the nanopore system. In this chapter, I will focus on elucidating both of these features.

The temperature dynamics that govern the behavior of the relaxation oscillation subsequent to the initial nucleation event will be addressed first. The data from Fig. 7.1 show that the periodicity of each nucleation event is about 120 ns. I will show that this frequency of about 8.3 MHz can be accurately predicted using the FEM model in COMSOL developed in Chapter 3. This allows for the conclusion that, with the exception of the bubble lifetime, the periodicity of the relaxation oscillator is governed entirely by the temperature dynamics of the system.

The lifetime of the bubble is subsequently treated. This is a very complex hydrodynamic, two-phase flow problem which must account for the dynamics of the vapor phase, the liquid phase, and the moving boundary conditions at the interface between phases. In addition, thermal
dissipation and mass transfer due to vaporization and condensation at the phase interface must be considered. I will begin by introducing the equations governing this two phase flow problem and discussing the relevant physics. This problem can be partition into two parts: first, the initial growth of the bubble; second, the bubble’s subsequent dynamics. I show that the former of these can be reasonably approximated by reducing the full hydrodynamical equations to Rayleigh-Plesset dynamics. The latter problem is beyond the scope of this thesis. However, I will conclude by discussing the appropriate numerical techniques needed to solve for the full bubble dynamics.

7.1 Dynamics of Heating and Relaxation Oscillation

The conductance trace in Fig. 7.1 shows that nucleation events occur quasiperiodically after the initial bubble nucleates. This behavior is that of a relaxation oscillator with a periodicity that can be understood from the finite element calculation of the heating dynamics.\(^7\)

![Figure 7.2: The maximum temperature calculated within the nanopore as a function of time for an applied pulse of 8.22 V. At \(t = 10.4 \mu s\), the applied voltage is turned off resulting in a drop in peak temperature. After 16 ns, representing the lifetime of the bubble, the pulse is turned back on, and the maximum temperature is seen to quickly return to its original value before the pulse was turned off.](image)
A plot of the maximum temperature as a function of time is shown in Fig. 7.2. For this calculation, an applied voltage of 8.22 V is turned on at $t = 0$, shut off for 16 ns at $t = 10.4 \mu s$, and then switched back on at $t = 10.416 \mu s$. The 16 ns over which the voltage is switched off approximates the 16 ns lifetime of the bubble measured experimentally. During this time, the maximum temperature drops by 180 K, plotted in Fig. 7.2. This rapid fall can be understood by the extreme temperature gradient driving thermal diffusion cooling.

Figure 7.3: The spatial distribution of temperature is plotted along the central axis for different times after the pulse is turned off.

Figure 7.3 shows a plot of the temperature distribution at different times along the central axis of the nanopore. At 10.4 $\mu s$ the temperature is extremely peaked, and is seen to drop rapidly for each increment of 4 ns. At 10.416 $\mu s$, the temperature at the pore center is still largely superheated, but the strong peak has dissipated. The amount of thermal energy that remains at 10.416 $\mu s$ explains why reheating can occur so rapidly. As seen in Fig. 7.2, once the voltage is turned back on, the maximum temperature is largely recovered within approximately 100 ns. The total blockage time and reheating time correspond well to the experimentally measured time to the
second bubble of 117 ns labeled in Fig. 7.1.

7.2 The Equations Governing Bubble Dynamics

The previous section demonstrated that the relaxation oscillation behavior, exhibited by quasiperiodic nucleation events, results from the temperature dynamics of the nanopore system. However, this does not explain the growth and lifetime of the bubble. In this section, I introduce the physics governing the bubble dynamics in the superheated liquid within the nanopore. This system, consisting of the vapor phase within the bubble, the liquid phase surrounding, and the separating interface belong to a class of fluid dynamics problems called multiphase flow. I will begin this discussion by deriving the Navier-Stokes equation for fluid flow and then show how it is applied to a multiphase system. I will also introduce the coupling of the system to the heat equation as is necessitated by the condition of superheat of the liquid electrolyte in the nanopore.

Multiphase flow is characterized by the presence of two or more fluid phases present in the system. The presence of interfaces between the different phases (that are often moving or deforming) is a central characteristic of multiphase flow and is responsible for the notorious complexity in modeling these systems.

Fluid flow of both the liquid and vapor phases is governed by equations of global conservation laws that are reduced to local partial differential equations. These equations express local balance of mass, linear momentum, angular momentum, total energy, and entropy that are derived in Appendix B. Conservation of linear momentum for both liquid and vapor is given by

---

*These could be a liquid and its vapor, immiscible liquids, or even a fluid and solid. In this context therefore, phase refers to the thermodynamic or compositional character of the system’s material constituents.

†Note that the two-phase flow literature consists of another class of problems, concerning the dynamics of many such units of fluid domains and their separating interfaces. This is also sometimes referred to as complex fluid flow, an example of which would be bubbly flow of many gas bubbles in a liquid.

‡Entropy balance is discussed in Ch. 2. Conservation of angular momentum of a fluid is not treated in Appendix B, but can be found in other sources.
Eqn. B.34

\[ \frac{d\rho_{v,l}}{dt} = -\rho_{v,l} \nabla \cdot \mathbf{v}_{v,l} \]  \hspace{1cm} (7.1)

where \( \rho \) is the density of either fluid and \( \mathbf{v} \) is its the velocity. The subscripts \( v \) and \( l \) refer to vapor and liquid respectively (previously no subscript was used for the liquid phase, but I use it here for clarity). The derivative \( d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla \) is the material derivative discussed in Appendix B and can be used to rewrite Eqn. 7.1 as

\[ \frac{\partial \rho_{v,l}}{\partial t} = -\nabla \cdot (\rho_{v,l} \mathbf{v}_{v,l}) \]  \hspace{1cm} (7.2)

which is a common form for the conservation of mass equation. Note that an incompressible fluid will have \( \nabla \cdot \mathbf{v} = 0 \).

The conservation of momentum for both liquid and vapor is expressed by the Cauchy equation of Eqn. B.36,

\[ \rho_{v,l} \frac{d\mathbf{v}_{v,l}}{dt} = \rho_{v,l} \mathbf{F} + \nabla \cdot \overline{T}_{v,l} \]  \hspace{1cm} (7.3)

where \( \overline{T}_{v,l} \) is the stress tensor for the vapor and the liquid, and \( \mathbf{F} \) is any external force acting on the fluid. For the fluids in the nanopore, \( \mathbf{F} = 0 \). Gravitational effects are negligibly small for the length scale of the fluid, and the fluid is effectively charge neutral so the applied electric field has no effect. The Cauchy equation is the precursor of the Navier-Stokes equation, which assumes a form for the stress tensor that describing a Newtonian fluid. Deriving the full form of \( \overline{T} \) requires establishing the constitutive relation between the stress and the deformation rate of strain tensor, \( \overline{\varepsilon} \). This latter tensor is the symmetric part of the velocity gradient tensor, \( \nabla \mathbf{v} \)

\[ \nabla \mathbf{v} = \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T) + \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T) = \overline{\varepsilon} + \overline{\Omega} \]  \hspace{1cm} (7.4)
therefore
\[
\vec{E} = \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T), \quad \vec{\Omega} = \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T)
\] (7.5)

The antisymmetric tensor, \( \vec{\Omega} \), is called spin or vorticity and does not contribute to deformation. The diagonal elements of \( \vec{E} \) contribute to dilation and the off-diagonal elements contribute to shear. Both dilation and shear are deformations. The relation between \( \vec{T} \) and \( \vec{E} \) is presented without derivation\(^8\)

\[
\vec{T}_{v,l} = -\left[ P_{v,l} - \zeta_{v,l} (\nabla \cdot \mathbf{v}_{v,l}) \right] I + 2 \mu_{v,l} \left[ \vec{E}_{v,l} - \frac{1}{3} (\nabla \cdot \mathbf{v}_{v,l}) I \right]
\] (7.6)

where \( P_{v,l} \) is the vapor pressure in the vapor and liquid, \( I \) is the identity matrix, \( \zeta_{v,l} \) and \( \mu_{v,l} \) are the coefficients of viscosity for the vapor and liquid, referred to as bulk viscosity and shear or dynamic viscosity, respectively. These properties of the fluid depend on the temperature and pressure. Due to the presence of strong temperature gradients for the superheated electrolyte in the nanopore, they cannot be assumed constant. The first term of \( \vec{T}_{v,l} \) contains the diagonal elements which correspond to isotropic, direct stresses. The second term are the off diagonal elements corresponding to shear stresses.

Thus, the momentum equations for the superheated liquid electrolyte and the vapor in the bubble are

\[
\rho_{v,l} \frac{d\mathbf{v}_{v,l}}{dt} = \nabla \cdot \vec{T}_{v,l}
\] (7.7)

with \( \vec{T}_{v,l} \) given by Eqn. 7.6. Using the material derivative, this can be rewritten as

\[
\rho_{v,l} \left( \frac{\partial \mathbf{v}_{v,l}}{\partial t} + (\mathbf{v}_{v,l} \cdot \nabla) \mathbf{v}_{v,l} \right) = \nabla \cdot \vec{T}_{v,l}
\] (7.8)

This equation is almost in the form of the Navier-Stokes equation which describes the motion of

\(^8\)Derivation can be found in the book by R. Aris.\(^{81}\)
a Newtonian, incompressible fluid, $\nabla \cdot \mathbf{v} = 0$, with constant coefficients of viscosity. The only assumptions in this equation were those required to establish the constitutive relation between stress and strain rate in Eqn. 7.6.\(^8\)

Consideration of heat transport in the liquid is the last required equation for describing the growth of a bubble in the superheated liquid in the nanopore. This follows the derivation of the heat equation that I presented in Ch. 2. Beginning with Eqn. 2.34 for entropy balance\(^\text{9}\)

$$\rho_l \frac{d s_l}{d t} = -\nabla \cdot \left( \mathbf{J}_q \right) + \mathbf{J}_q \cdot \nabla \left( \frac{1}{T_l} \right) - \frac{1}{T_l} \sum_k \mathbf{J}_k \cdot \nabla (\mu_k + \varphi_k) + \frac{1}{T_l} \overline{D}_l : \nabla \mathbf{v}_l \quad (7.9)$$

where $\overline{T}_l = -P_l \overline{I} + \overline{D}_l$, where $\overline{D}$ is the deviatoric stress tensor, defined in Appendix B. The third term on the right hand side gives rise to the Joule heating source term, $\mathbf{J} \cdot \mathbf{E}$, as was shown at the end of Ch. 2 and beginning of Ch. 3. Using the heat flux, $\mathbf{J}_q = -\kappa_l \nabla T_l$, from Eqn. 2.46, and the definition of $d s / d t$ from Eqn. 2.50 in Eqn. 7.9 gives

$$\rho_l C_{p,l} \frac{dT_l}{dt} = \nabla \cdot \left( \kappa_l \nabla T_l \right) + \overline{D}_l : \nabla \mathbf{v}_l + \mathbf{J} \cdot \mathbf{E} \quad (7.10)$$

which with the material derivative, Eqn. 2.25 becomes

$$\rho_l C_{p,l} \left( \frac{\partial T_l}{\partial t} + \mathbf{v}_l \cdot \nabla T_l \right) = \nabla \cdot \left( \kappa_l \nabla \cdot T_l \right) + \overline{D}_l : \nabla \mathbf{v}_l + \mathbf{J} \cdot \mathbf{E} \quad (7.11)$$

The term containing the deviatoric stress tensor, $\overline{D}$, is dominated by viscous forces and is often dropped in the context of studying bubble growth in a liquid.\(^8^2-8^4\) Therefore the heat equation for the liquid is

$$\rho_l C_{p,l} \left( \frac{\partial T_l}{\partial t} + \mathbf{v}_l \cdot \nabla T_l \right) = \nabla \cdot \left( \kappa_l \nabla \cdot T_l \right) + \mathbf{J} \cdot \mathbf{E} \quad (7.12)$$

\(^\text{9}\)The term concerning the chemical potential of different species has been excluded since the fluids are assumed to be single component in the context of bubble growth dynamics.
The heat equation for the vapor does not include the Joule heating source term and is therefore

\[ \rho_v C_{p,v} \left( \frac{\partial T_v}{\partial t} + \mathbf{v}_v \cdot \nabla T_v \right) = \nabla \cdot (\kappa_v \nabla \cdot T_v) \quad (7.13) \]

Note that the second term on the right hand side of Eqns. 7.12 and 7.13 accounts for the convective transfer of heat due to the motion of the fluid.

This completes the set of equations governing the growth of a vapor bubble in a superheated liquid. These are summarized in Table 7.1 and are in total ten equations: five for the liquid phase and five for the vapor phase. Each phase has an equation for conservation of mass, three equations for momentum balance in three dimensions, and one equation for heat transfer. An equation of state is also required for both the liquid and the vapor phases, thereby increasing the number of equations to twelve.

<table>
<thead>
<tr>
<th>System of Differential Equations for Vapor Bubble Dynamics in a Superheated Liquid</th>
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<tbody>
<tr>
<td>( \frac{\partial \rho_{v,l}}{\partial t} = -\nabla \cdot (\rho_{v,l}\mathbf{v}_{v,l}) )</td>
</tr>
<tr>
<td>( \rho_{v,l} \left( \frac{\partial \mathbf{v}<em>{v,l}}{\partial t} + (\mathbf{v}</em>{v,l} \cdot \nabla) \mathbf{v}<em>{v,l} \right) = \nabla \cdot \mathbf{T}</em>{v,l} )</td>
</tr>
<tr>
<td>( \rho_{l} C_{p,l} \left( \frac{\partial T_l}{\partial t} + \mathbf{v}_l \cdot \nabla T_l \right) = \nabla \cdot (\kappa_l \nabla \cdot T_l) + \mathbf{J} \cdot \mathbf{E} )</td>
</tr>
<tr>
<td>( \rho_v C_{p,v} \left( \frac{\partial T_v}{\partial t} + \mathbf{v}_v \cdot \nabla T_v \right) = \nabla \cdot (\kappa_v \nabla \cdot T_v) )</td>
</tr>
</tbody>
</table>

Table 7.1: This table summarizes the system of equations governing the vapor bubble dynamics in a superheated liquid in the nanopore. Eqn. 7.6 gives the stress tensor for the liquid and vapor phases, \( \mathbf{T}_{v,l} \), needed for the momentum equation. Equations of state for the liquid and vapor phase are needed along with initial and boundary conditions. The boundary conditions also require specification of the jump conditions at the liquid vapor interface.

Finally, the initial and boundary conditions of the system must be specified. The system
also contains the liquid-vapor interface of the bubble which is often represented as surface of discontinuity separating two fluidic phases.\(^1\) Thus, specifying the boundary conditions requires expressing the local conservation laws of Table 7.1 in terms of jump conditions across the liquid-vapor interface thereby relating the values of the conserved quantities across the interface. This has been done in several works and is not repeated here.\(^78,79,86,87\) The jump conditions account for mass transfer (evaporation and condensation), momentum transfer, and heat transfer at the liquid vapor interface.

### 7.3 Approximating the Initial Growth of the Bubble

The bubble blockage time of 16ns can only be understood by full hydrodynamic modeling of the bubble dynamics presented in the previous section. In total, these consist of twelve equations, along with initial, boundary, and jump conditions, which makes obtaining a solution quite challenging. However, it is possible to understand the conductance fall time of 1 ns from the Rayleigh-Plesset theory for the growth of a spherical bubble in superheated liquid.\(^82,84,88-92\)

The equation describing the time-dependent, radial growth \(R(t)\) of a spherical bubble with initial radius \(R_0\) and internal pressure \(P_v\) is

\[
R(t)\ddot{R}(t) + \frac{3}{2} \dot{R}(t)^2 = \frac{P_v - P_l}{\rho_l} - 4\nu_l \frac{\dot{R}(t)}{R(t)} - \frac{2\gamma}{\rho_l R(t)} \tag{7.14}
\]

where \(P_l\) is the pressure of the liquid equal to 1 atm and \(\nu_l = \mu_l/\rho_l\) is the kinematic viscosity of the superheated liquid. In Appendix C, I show that this equation can be derived directly from the momentum equation, Eqn. 7.8, by assuming radial symmetry and only considering the motion of the liquid with a moving boundary that is the bubble wall. For simplicity, I assume constant

---

\(^1\)This approach means that the interface is idealized as a mathematically thin discontinuity analogous to a step function. In reality, the interface will have a finite thickness.\(^85\)
material properties in the Rayleigh-Plesset equation, assigning values of $P_v = 1.3 \times 10^7$ Pa, 
$\rho_l = 640 \text{ kg/m}^3$, $\nu_l = 1.2 \times 10^{-7} \text{ m}^2/\text{s}$, and $\gamma = 0.008 \text{ N/m}$ corresponding to liquid-vapor saturation of water at 603 K. $^70$ $R_0$ is assumed to be slightly larger than the critical bubble radius at 603 K. The critical radius, $r_{cr}$, given by the Laplace pressure in Eqn. 6.6, is equal to 1.2 nm at 603 K. This is the condition for unstable mechanical equilibrium of the bubble, which means the initial radius required for a nucleated bubble to grow is slightly larger. I therefore assume $R_0 = r_{cr} + \epsilon_R$ where $\epsilon_R$ is a small perturbation factor equal to 0.1 nm. The resulting time dependence of $R(t)$ is plotted in Fig. 7.4, showing the bubble radius reaching the pore wall in 0.6 ns with an average velocity over this time of 90 m/s. This corresponds well with the measured 50 m/s bubble growth velocity calculated from the optical experiment data in Fig. 6.9.

Figure 7.4: Bubble radius and velocity as a function of time, calculated using Rayleigh-Plesset dynamics. The bubble is calculated to reach the nanopore radius in 0.62 ns. This compares well with the 1-ns fall time seen in the experimental conductance data presented in Fig. 7.1.
7.4 Exploring the Complete Bubble Dynamics

Rayleigh-Plesset dynamics proved to be sufficient for modeling the growth of the bubble in the nanopore. However, this accounts for only the beginning stage of the bubble blockage event that is measured experimentally. The complete dynamics of the bubble over the remainder of its lifetime remains unknown and indeed the question of what occurs to the bubble is unanswered. In this section I will describe why studying the full bubble dynamics is complicated, both experimentally and theoretically, and include a summary of work I have done on this problem.

A natural way to study the bubble dynamics experimentally is using optics. Preliminary experiments were conducted using the optical setup in shown in Fig. 6.7. In those experiments, optical transmission of a laser through the pore was measured over the entire bubble lifetime. The optics is very sensitive to the details of the bubble. As such, significant and complex light scattering was observed to accompany the drop in ionic current. Interpreting these data proved to be very challenging. I have done initial work of Mie scattering theory to the results. However, experimental determination of what occurs to the bubble after initial growth remains unanswered due to the complexity of the optical transmission data.

In addition to this experimental work, we pursued modeling of the complete bubble dynamics. The full hydrodynamical equations governing the behavior of the bubble were summarized in Table 7.1. It is evident that solving these equations is a highly nontrivial problem. This is due to the large number of equations and the fact that the size of the domains over which the equations must be solved is changing as a result of the changing bubble size. In addition, as already mentioned, it is necessary to include mass transfer and heat transport at the moving boundary of the liquid vapor interface. Further, the temperature dependence of the material properties of the liquid and vapor must be included.

Sophisticated numerical approaches have been developed to address these problems associ-
ated with two phase flow. There are two general approaches to two-phase flow modeling that COMSOL can implement. The first is a two-fluid approach, which consists of specifying two sets of field equations, one for each fluid, and the jump conditions at the fluid-fluid interface. The set of governing equations summarized in Table 7.1 follows this method. The second is a one-fluid approach, whereby only one set of field equations are needed along with an equation tracking the convection of the fluid-fluid interface defined by a marker function. The two most common one-fluid approaches are called phase-field method and level set method, which differ in the way the marker function is defined.

We focused on developing FEM model for bubble dynamics using COMSOL Multiphysics implementing one of these methods. COMSOL’s built-in physics modules include all three methods: the two-fluid approach using a moving mesh to track the motion of the fluid interface, and the level-set and phase-field methods using an auxiliary function to track the motion of the interface over a fixed mesh. Of these, the two-fluid approach with moving mesh was most suitable to bubble growth since only two fluid domains need to be considered and defining an auxiliary or marker function is not necessary. The only disadvantage to the moving mesh method is that it cannot account for topological changes, for example if the bubble were to break apart. However, we were not concerned with that specific possibility since no experimental evidence exists to indicate that this occurs. Initial results from modeling simple bubble dynamics indicated that an FEM model could successfully reproduce Rayleigh-Plesset dynamics. However, COMSOL’s built-in two phase flow module does not include all boundary conditions needed for the full bubble dynamics. Inclusion of these boundary conditions requires input of weak-form boundary conditions, which is complicated by the possibility that numerical errors may occur and must be rigorously checked. Therefore, the development of a model solving for the full bubble dynamics remains a work in progress.
The only merit of which I personally am conscious was that of having pleased myself by my studies, and any results that may be due to my researches were owing to the fact that it has been a pleasure for me to become a physicist. [On receiving the Order of Merit, 1902]

Lord Rayleigh

Conclusion

We have discovered that Joule heating in nanopores is a unique experimental platform to investigate extreme superheating and homogeneous vapor bubble nucleation. In this thesis, I have presented the theory and calculations that I have implemented which have succeeded in elucidating this phenomenon. The most important result of this work was the calculated spatial and temporal temperature distribution in the electrolyte within the nanopore. The temperatures of the electrolyte that are achieved in the nanopore are remarkably high, far beyond our expectations at the onset of this project, and approach the limit of superheat of the liquid.

The extreme, highly localized temperature distribution that results in the nanopore leads to several interesting results. These include the possibility of nonzero local charge density, the kinetics of homogeneous single-bubble nucleation, and the quasiperiodic nature of nucleation
events in the nanopore. We believe this work contributes to understanding of controlled super-
heating and bubble nucleation in nanopores, opening the possibility for developing applications
of this system in chemistry\textsuperscript{99–101} and microfluidics.\textsuperscript{102–104}

8.1 Summary of Results Presented in this Thesis

The following are the main results and conclusions that I have presented in the context of this
thesis. Reference to the chapter or section of this thesis for each concluding point is provided.

• A Finite Element Model was developed (Ch. 3) and used to calculate the spatial and time
resolved temperature distribution (Sec. 4.2). The temperature is calculated to be strongly
localized within the pore with extremely high peak values indicating superheating of the elec-
trolyte occurs.

• Fitting of experimental data was accomplished to calculate the electrical conductivity of su-
perheated 3 M NaCl solution (Sec. 4.1). Knowledge of this electrical conductivity was needed
for the calculation of the temperature distribution.

• Analytical approaches to the problem of Joule heating (Ch. 5) were shown to support the
results from the FEM model.

• The kinetics of bubble nucleation were successfully calculated (Sec. 6.4) using the com-
puted temperature, and indicate that nucleation of a vapor bubble within the nanopore occurs
homogeneously. This conclusion supports experimental results demonstrating homogeneous
nucleation occurs (Sec. 6.6).

• Quasiperiodic nucleation of vapor bubbles that is observed to occur experimentally was shown
to result from temperature dynamics of the nanopore system (Sec. 7.1).
• The initial growth of the bubble in the pore was modeled with Rayleigh-Plesset dynamics (Sec. 7.2), indicating that this growth is dominated by inertial effects.

• The lifetime of the bubble was investigated (Sec. 7.4) but because of the complexity of this problem, full modeling of the dynamics remains a work in progress.

8.2 The Future for Joule Heating in Nanopores

Our knowledge of the physics of nanopore heating as presented in this thesis, enables us to push the experiments to new limits. Calculations also indicate that high frequency relaxation oscillation is achievable. At smaller pore sizes, the bubble lifetime, as well as the reheating time will be much smaller due to the the smaller volume of fluid in the nanopore.

The Joule heating experiments also provide a unique platform to study nucleation theory due to the highly controlled, and reproducible, homogeneous bubble nucleation that is achieved. Studying the kinetics of phase change is therefore possible. An experiment can be designed to apply a voltage large enough to superheat the liquid, but too low to allow phase change to occur on reasonable time scales. As the voltage is increased beyond this threshold, a collection of time points at which bubble nucleation first occurs can be accumulated. This first-time to passage data could then be used to calculate the nucleation rate using

\[ J_{\text{exp}} = \frac{1}{V_{\text{pore}} \langle \tau \rangle} \]  

(8.1)

where \( V_{\text{pore}} \) is the volume of the nanopore and \( \langle \tau \rangle \) is the average first time to bubble. This experimentally determined nucleation rate could then be compared with the theoretical nucleation rate determined by Eqn. 6.31.

It would be interesting to conduct the nanopore Joule heating experiments using electrolytic solutions of different salinities and with different salts. This would determine the effects that
ionic concentration and possibly ionic species have on the nucleation experiments. These experiments can be guided by predictions made with the theory and modeling presented in this work. Such experiments would enable exploration of the limit of increasing dilution for which the theories of Debye, Hückel, and Onsager apply. However, increasingly dilute solutions will require much higher applied voltages to induce sufficiently strong Joule heating for superheating to occur. It is possible that temperatures would not rise to high enough levels for bubble nucleation to occur.

Further work is also needed to understand the dynamics that determine the lifetime of the bubble. In this thesis, I have laid out the theoretical framework for this problem. Efforts at coupling experiment and theory should be used to guide these calculations. Specifically, the experimental optical transmission data should be explored further. The impact on bubble lifetime from variation of experimental parameters such as size of the pore and applied voltage should also be studied, enabling further validity to future work on modeling the bubble dynamics.
Debye and Hückel developed a successful approach to solving the many body problem of an equilibrium ionic solution by imposing a reasonable assumption to express the distribution of ions in terms of the potential. This is used in the Poisson equation to solve for the potential in a self-consistent manner. They applied the reasoning that ions in solution will interact with each other by means of the Coulomb force. As such, an individual ion at a given location in the solution will effect the spatial distribution of the ions in its vicinity. For example, a single positive ion will attract negative ions and repel other positive ions, leading to a negative charge density in its direct surroundings. As discussed in Ch. 2, this is referred to as the ionic atmosphere of
the positive ion, and is assumed to be spherically symmetric about the positive ion. In the same way, a negative ion will have a spherically symmetric ionic atmosphere consisting of a local positive charge density.

In equilibrium, the mutual dependence of the forces and ion distributions is expressed by the Poisson equation

$$\nabla^2 \phi = -\frac{q}{\epsilon}$$ (A.1)

where $\phi$ is the electrical potential, $\epsilon$ is the electrical permittivity of the solution, and $q$ is the charge density of positive and negative ions in solution. Spherical symmetry allows the potential due to the $j$th ion and its atmosphere to be written $\phi_j(r)$, where the origin of has been taken to be the location of the $j$th ion. The Poisson equation for this potential is

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \phi_j(r) = -\frac{q_j(r)}{\epsilon}$$ (A.2)

where $q_j(r)$ is the spherically symmetric charge density consisting of the $j$th ion and its ionic atmosphere. The $j$th ion has valance of $z_j$, positive for a cation and negative for an anion; therefore, it has a total charge of $z_j e$. Correspondingly, its ionic atmosphere must have a total charge equal to $-z_j e$ if charge neutrality of the solution is to be maintained.

The assumption is now made that each ion, $j$, has an effective radius, $r_j^0$ which is defined as the lower limit beyond which no other ion can approach. As such, $q_j(r)$ can be written as $q_j^0(r) + q_j^*(r)$ where $q_j^0(r)$ is the charge density of the ion $j$ alone, distributed in some manner for $r < r_j^0$. For example, a point charge $z_j e$ at the origin gives $q_j(r) = z_j e \delta(r) + q_j^*(r)$ for the charge

---

*This is the symmetry of the time-averaged distribution of ions in the vicinity of the ion under consideration.

†It is understood that the Poisson equation is applied to time-averaged charge distributions in this instance, ameliorating any difficulties with using Eqn. A.1 for non-static ionic charge distributions. Strictly speaking, the Poisson equation is valid for only a static distribution of charges, and not for charges in motion as in the case of ions in solution.
density of the ion and its ionic atmosphere. The total charge density, \( q_j(r) \), must integrate to

\[
\int_{r_j^0}^{\infty} 4\pi r^2 \rho_j dr = -z_j e
\]  

(A.3)

in order for charge neutrality to hold. This statement is equivalent to integrating \( \rho_j^*(r) \) from \( r_j^0 \) to \( \infty \) since the ion \( j \) is located entirely within \( r < r_j^0 \). Note that the use of \( r_j^0 \) assumes that all ions are spherically symmetric in solution, which is not necessarily the case. The value of \( r_j^0 \) will also be different for different ionic species.

A form for \( q_j(r) \) can be found by defining \( n_{j,i}(r) \) as the concentration of \( i \) ions at a distance \( r \) from the origin due to an ion \( j \) located at the origin. The units of \( n_{j,i}(r) \) are number of ions per unit volume. The total charge density can be written as a sum over the all \( s \) ionic species

\[
q_j(r) = \sum_{i=1}^{s} z_i e n_{j,i}(r)
\]  

(A.4)

It is reasonable to assume that \( n_{j,i}(r) \) will be proportional to \( n_i \), the bulk concentration of \( i \) ions, as well as dependent on the potential energy of finding \( i \) a distance \( r \) from \( j \). This latter dependence was assumed by Debye and Hückel to take the form of the the Maxwell Boltzmann distribution, giving

\[
n_{j,i}(r) = n_i \exp \left( -\frac{z_i e \varphi_j(r)}{k_b T} \right)
\]  

(A.5)

where \( k_b \) is Boltzmann’s constant, \( T \) is temperature, and \( z_i e \varphi_j(r) \) is the potential energy of the \( i \)th ion a distance \( r \) from the \( j \)th ion due to the electrical potential \( \varphi_j(r) \) from \( j \) and its ionic atmosphere. The charge density is therefore

\[
q_j(r) = \sum_{i=1}^{s} z_i e n_i \exp \left( -\frac{z_i e \varphi_j(r)}{k_b T} \right)
\]  

(A.6)
This is the desired result: an expression for the charge density in terms of the potential that can be used in the Poisson equation to solve for the potential. However, Eqn. A.6 does not obey the principle of linear superposition of electrostatics requiring that the electrical potentials resulting from multiple different charge densities can simply be added. For example, doubling the charge density in a region doubles the potential. This is not true in Eqn. A.6 since $\varrho_j$ depends exponentially on $\varphi_j$. This is somewhat remedied by taking the Taylor expansion of the exponential

$$q_j(r) = \sum_{i=1}^{s} z_i e n_i \left( 1 - \frac{z_i e \varphi_j(r)}{k_b T} + \frac{1}{2!} \left( \frac{z_i e \varphi_j(r)}{k_b T} \right)^2 - \frac{1}{3!} \left( \frac{z_i e \varphi_j(r)}{k_b T} \right)^3 + \ldots \right) \quad (A.7)$$

Overall charge neutrality of the electrolyte requires the first term $\sum_{i=1}^{s} z_i e n_i$ to equal zero. Further, assuming that $z_i e \varphi_j \ll k_b T$, yields

$$q_j(r) = - \sum_{i=1}^{s} \frac{n_i(z_i e)^2}{k_b T} \varphi_j(r) \quad (A.8)$$

which restores linearity between the charge density and the potential as required by the principle of superposition. However, this is only valid for when the potential of the $i$th ion, $z_i e \varphi_j$ is much less than the thermal energy $k_b T$. This is not necessarily the case for highly concentrated solutions when the $i$th ion may be in close proximity to the $j$th ion, and deviations from the idealized behavior of Eqn. A.8 are observed to occur. The approximation also does not hold for electrolytes with high valency or low dielectric constance since $z_i e \varphi_j$ will be comparably large in either case.

For 1:1 electrolytes such as NaCl, the approximation in Eqn. A.8 is much more reasonable for the simple fact that all of the odd terms on the right hand side Eqn. A.7 cancel. In this case, the number of ionic species is $s = 2$, and the valances of the ions are $z_+ = 1$ for sodium and
For chloride, giving for Eqn. A.7

$$
\varrho_j(r) = e(n_+-n_-)-(n_++n_-)\frac{e^2 \varphi_j(r)}{k_b T} + \frac{e(n_+-n_-)}{2!} \left( \frac{e \varphi_j(r)}{k_b T} \right)^2 - \frac{e(n_++n_-)}{3!} \left( \frac{e \varphi_j(r)}{k_b T} \right)^3 + \ldots
$$

The concentrations \(n_+\) and \(n_-\) must be equal to each other due to the stoichiometric balance between sodium ion and chloride ions in solution required for overall charge neutrality. Thus all odd terms cancel giving

$$
\varrho_j(r) = -(n_++n_-)\frac{e^2 \varphi_j(r)}{k_b T} - \frac{e(n_++n_-)}{3!} \left( \frac{e \varphi_j(r)}{k_b T} \right)^3 + \ldots \quad (A.9)
$$

This automatic cancelation of the third term of Eqn. A.7 makes the approximation of Eqn. A.8 much more reasonable for 1:1 electrolytes.

Using the expression for charge density, Eqn. A.8, in Eqn. A.2, the Poisson equation, gives

$$
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \varphi_j(r) \right) = \frac{1}{\varepsilon} \sum_{i=1}^{s} n_i (z_i e)^2 \frac{e \varphi_j(r)}{k_b T} \quad (A.10)
$$

This expression can be simplified by introducing the constant

$$
\kappa_D^2 = \frac{e^2}{\varepsilon k_b T} \sum_{i=1}^{s} n_i z_i^2 \quad (A.11)
$$

with the unit of \(\kappa_D\) being reciprocal length. This gives the form for the differential equation

$$
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \varphi_j(r) \right) = \kappa_D^2 \varphi_j(r) \quad (A.12)
$$

which with the substitution, \(u_j(r) = r \varphi_j(r)\), is reduced to

$$
\frac{d^2}{dr^2} u_j(r) = \kappa_D^2 u_j(r) \quad (A.13)
$$

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This equation has the general solution

\[ u_j(r) = Ae^{\kappa_D r} + Be^{-\kappa_D r} \]  \hspace{1cm} (A.14)

giving for the potential

\[ \varphi_j(r) = \frac{A}{r}e^{\kappa_D r} + \frac{B}{r}e^{-\kappa_D r} \]  \hspace{1cm} (A.15)

The constant \( A \) must be equal to zero since the potential has to remain finite at \( r \to 0 \). Thus,

\[ \varphi_j(r) = \frac{B}{r}e^{-\kappa_D r} \]  \hspace{1cm} (A.16)

This equation gives the combined potential resulting from the \( j \)th ion and its atmosphere. This potential can be expressed as the sum of the contribution from the \( j \)th ion and the contribution from its atmosphere

\[ \varphi_j(r) = \frac{z_j e}{4\pi\varepsilon r} + \varphi_j^* (r) \]  \hspace{1cm} (A.17)

The first term on the right hand side is the potential due to the \( j \)th ion corresponding to a point charge \( z_j e \) at the origin, and \( \varphi_j^* (r) \) is the potential due to the ionic atmosphere, equal to

\[ \varphi_j^* (r) = \frac{B}{r}e^{-\kappa_D r} - \frac{z_j e}{4\pi\varepsilon r} \]  \hspace{1cm} (A.18)

The constant \( B \) can be solved for using the fact that the electric field at \( r = r_j^0 \), is the field resulting from the \( j \)th ion alone. This is true by Gauss’s law since the only charge within \( r < r_j^0 \) is the \( j \)th ion; recall \( r_j^0 \) is the closest distance that any other ion can approach ion \( j \). Therefore the electric
field from the ionic atmosphere must be zero at \( r = r_j^0 \). This is expressed as

\[
\frac{d\varphi^*_{ij}(r)}{dr} \bigg|_{r=r_j^0} = \left( \frac{B}{(r_j^0)^2} + \frac{\kappa_D B}{r_j^0} \right) e^{-\kappa_D r_j^0} - \frac{z_j e}{4\pi \epsilon (r_j^0)^2} = 0
\]  

(A.19)

Solving for \( B \) gives

\[
B = \frac{z_j e}{4\pi \epsilon} \left( \frac{e^{\rho_j \kappa_D}}{r_j^0 \kappa_D + 1} \right)
\]  

(A.20)

Consequently, the total potential is

\[
\varphi_{ij}(r) = \frac{z_j e}{4\pi \epsilon} \left( \frac{e^{\rho_j \kappa_D}}{r_j^0 \kappa_D + 1} \right) \frac{1}{r} e^{-\kappa_D r}
\]  

(A.21)

and the potential due to the ionic atmosphere alone is

\[
\varphi^*_{ij}(r) = \frac{z_j e}{4\pi \epsilon r} \left[ \left( \frac{e^{\rho_j \kappa_D}}{r_j^0 \kappa_D + 1} \right) e^{-\kappa_D r} - 1 \right]
\]  

(A.22)

This potential is the result derived by Debye and Hückel. This can be shown to be consistent with the requirement of charge neutrality defined in the integral of Eqn. A.3. The total charge distribution, \( \varrho_{ij}(r) \), of the ion \( j \) and its atmosphere can be defined using the total potential of Eqn. A.21 in Eqn. A.8. The resulting expression for \( \varrho_{ij}(r) \) gives the desired result for charge neutrality when integrated in Eqn. A.3. Note that Eqn. A.8 holds only for defining the total charge distribution \( \varrho_{ij}(r) \) in terms of the total potential \( \varphi_{ij}(r) \); it cannot be used with \( \varphi^*_{ij}(r) \) to determine \( \varrho^*_{ij}(r) \).

The theory of Debye and Hückel thus presented, provides a physical picture of an electrolyte under equilibrium conditions. Every ion in solution is understood to be a hard sphere in a dielectric continuum surrounded by an excess of ions of opposite sign, called the ionic atmosphere. This ionic atmosphere is assumed to be a spherically symmetric, time-averaged distribution of
ions extending a characteristic distance of $1/\kappa_D$ around the $j$th ion. This length scale, called the
Debye screening length, appears in the exponential argument of Eqn. A.21 and is equal to

$$\Lambda_D = \frac{1}{\kappa_D} = \sqrt{\frac{e^2}{e^2 \sum_{i=1}^{s} n_i z_i^2}}$$ (A.23)

This quantity determines the extent of the electric field due to the $j$th ion such that for $r > \Lambda_D$, the field resulting from ion $j$ is largely screened out by its ionic atmosphere. The Debye length varies inversely with the square root of the ionic concentrations $n_i$: as concentration increases, more ions are available in close proximity to a given ion $j$ to screen out its field over a decreasing distance. Physically, the screening length cannot become smaller than the inter-atomic distances of the ions characterized by $r_j^0$. Empirically, the theory extends well up to when applied to concentrations of 0.01 M for 1:1 electrolytes in water\textsuperscript{21,23} and therefore does not apply well to the 3 M NaCl solution used for the Joule heating experiments. However, the physical picture provided by the ionic atmosphere is a powerful foundation from which electrolytic solutions can be understood. Complications of extending the theory to higher concentrations include invalidation of the assumptions that ameliorate mathematical complications such as the restoration of linearity by truncation of the Taylor expansion given in Eqn. A.8, as well as more complex physical effects that manifest. These latter considerations include the breakdown of spherical symmetry assumed by the Maxwell-Boltzmann distribution Eqn. A.6, and the hard sphere radius of closest approach, possible electrostriction of the solution, polarization of the electron clouds of both ionic species and the solvent, partial screening leading to long-range action, and the breakdown of symmetry of the net field acting in the neighborhood of the ion.\textsuperscript{23} Possible association of ions also comes into play. Attempts have been made to model at least some of these effects, but developing a comprehensive theory to capture the behavior of concentrated solutions remains exceptionally difficult.\textsuperscript{21,23}
Equations of Continuity and Conservation

This appendix will show the derivations of the conservation laws of mass, momentum, and energy in their local form. These conservation laws are central to the theoretical frameworks of irreversible thermodynamics and hydrodynamics. Both theories describe macroscopic phenomena and therefore treat the medium or fluid under consideration as a continuous system. The state parameters of these theories are consequently treated as field variables, continuous

*Irreversible thermodynamics is primarily concerned with the local change of energy and entropy in a system; hydrodynamics is primarily concerned with the local change of momentum in a system. However, since mass, momentum, energy, and entropy can all change locally, these two theories are inextricably linked and require local conservation laws for all quantities.
functions of space and time, and the conservation equations therefore contain quantities referring to only a single point in space and time. These are called the local form of the equations, or continuity equations. These equations are used in Chapter 2 of this thesis along with entropy balance to derive the heat equation, as well as in Chapter 7 to derive the Navier-Stokes equation.

**State Parameters of a Continuous Fluid**

The scope of this thesis concerns only fluid systems: those of the aqueous electrolyte and ultimately the vapor bubble. Note that the principles of irreversible thermodynamics apply to solids as well. The treatment of a fluid as a continuous medium requires that any infinitely small volume element of the fluid – as considered within the theoretical framework – contains a great many molecules of the fluid. Such a fluid element is large compared to intermolecular distances despite being physically small in comparison to the bulk.†

The mathematical and thermodynamic state of a moving fluid is described by functions giving the distribution of the fluid velocity \( v(x, y, z, t) \) and any two thermodynamic quantities, for example, \( P(x, y, z, t) \) and \( \rho(x, y, z, t) \).† Knowledge of these latter two quantities along with an equation of state fully specify the thermodynamic state of the fluid if it is single component, since all thermodynamic quantities can thenceforth be derived.

The state of a multicomponent fluid, consisting of \( k \) different chemical and/or colloidal components, also requires a description of the spatially and temporally dependant concentrations of each component. These can be expressed as mass fractions: \( c_k(x, y, z, t) = \frac{\rho_k(x, y, z, t)}{\rho(x, y, z, t)} \), where \( \rho_k \) is the density of component \( k \). Additional knowledge such as equations of state, are also required for multicomponent fluids (one additional equation of state for each additional component).†

†It is important to note that these quantities are functions defined at a given point in space, \( (x, y, z) \), at a given time, \( t \). I.e, they refer to a fixed point in space and time not to a fixed particle in the fluid.
**Conservation of Mass**

The first fundamental equation of irreversible thermodynamics and fluid mechanics expresses the conservation of matter. Consider a multicomponent fluid. The rate of change of the mass of component \( k \) within a volume is

\[
\frac{d}{dt} \int \rho_k \, dV
\]

This must be equal to the amount of mass of component \( k \) flowing into or out the bounding surface of the volume. If \( k \) has a velocity \( \mathbf{v}_k \), then this is equal to

\[
\frac{d}{dt} \int \rho_k \, dV = - \int \rho_k \mathbf{v}_k \cdot d\mathbf{A}
\]

The magnitude of \( d\mathbf{A} \) is the area of the surface element and its direction is along the outward normal. Therefore, \( \rho_k \mathbf{v}_k \cdot d\mathbf{A} \) is positive if the fluid is flowing out of the volume and negative if fluid is flowing into the volume. The negative sign is therefore required since in the former case, the total mass inside the volume decreases and in the latter case it increases.

Since the volume considered does not change with time, the derivative with respect to time can be pulled into the volume integral (as per the Reynold’s Transport Theorem for a stationary volume). Applying divergence theorem to the surface integral and rearranging the equation gives

\[
\int \left[ \frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v}_k) \right] \, dV = 0
\]

The integrand must vanish since this equation is true for any arbitrary volume; therefore

\[
\frac{\partial \rho_k}{\partial t} = - \nabla \cdot (\rho_k \mathbf{v}_k) \tag{B.1}
\]

This is the equation for continuity of mass without the possibility of chemical reactions occurring.
in the fluid. Chemical reactions would require a source term\textsuperscript{35} for component \(k\) being produced by a reaction inside the volume considered.\textsuperscript{4}

Summing over all \(k\) components of the fluid gives the well known equation expressing conservation of mass

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})
\]  

(B.2)

where \(\rho = \sum_k \rho_k\) is the total density, and \(\mathbf{v} = \sum_k (\rho_k \mathbf{v}_k)/\rho\) is the center of mass (barycentric) velocity. For an incompressible fluid, the continuity equation simplifies to \(\nabla \cdot \mathbf{v} = 0\) because the density does not change with time.

It is conventional to rewrite Eqn. B.1 in a different form using the barycentric substantial derivative \textsuperscript{§}

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla
\]  

(B.3)

which along with Eqn. B.2 this gives the following property

\[
\frac{d\mathbf{x}}{\rho dt} = \frac{\partial (x\rho)}{\partial t} + \nabla \cdot (x\rho \mathbf{v})
\]  

(B.4)

\textsuperscript{4}Note that Eqn. B.1 has the form of a balance equation: the local change of a quantity on the left hand side equals the negative divergence of the flux of the quantity, plus any source term which is zero in this case.

\textsuperscript{§}The derivative \(d\mathbf{x}/dr\) denotes the rate of change of the vector quantity \(\mathbf{x}\) of a given fluid particle as it moves about in space; it \textit{does not} denote the change of \(\mathbf{x}\) at a fixed point in space. To express this derivative in terms of quantities fixed in space, we recognize that the change, \(d\mathbf{x}\), of the vector \(\mathbf{x}\) of a fluid particle in time \(dr\) is composed of two parts. The first is the change in \(\mathbf{x}\) at a fixed point in space during time \(dr\). The second is the difference in \(\mathbf{x}\) at a given instant between two different locations \(dr\) apart, where \(dr\) equals the distance moved by the fluid particle during time \(dr\). Mathematically, this is written as

\[
d\mathbf{x} = \frac{\partial \mathbf{x}}{\partial t} dt + d\mathbf{x} + dy \frac{\partial \mathbf{x}}{\partial y} + dz \frac{\partial \mathbf{x}}{\partial z} = \frac{\partial \mathbf{x}}{\partial t} dt + (dr \cdot \nabla)\mathbf{x}
\]

Dividing by \(dt\), and replacing \(dr/dt\) with \(\mathbf{v}\), we have

\[
\frac{d\mathbf{x}}{dt} = \frac{\partial \mathbf{x}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{x}
\]

which is the barycentric substantial time derivative.
true for any scalar or component of $\mathbf{x}$.

Employing the barycentric derivative of Eqn. B.3 in Eqn. B.1 gives

$$\frac{d\rho_k}{dt} = -\nabla \cdot (\rho_k (\mathbf{v}_k - \mathbf{v})) - \rho_k \nabla \cdot \mathbf{v}$$  \hfill (B.5)$$

and in Eqn. B.2 gives

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}$$  \hfill (B.6)$$

Using Eqn. B.6 in Eqn. B.5 yields

$$\frac{d\rho_k}{dt} - \frac{\rho_k}{\rho} \frac{d\rho}{dt} = -\nabla \cdot (\rho_k (\mathbf{v}_k - \mathbf{v}))$$  \hfill (B.7)$$

The left hand side is rewritten

$$\frac{d\rho_k}{dt} - \frac{\rho_k}{\rho} \frac{d\rho}{dt} = \rho \frac{d}{dt} \left( \frac{\rho_k}{\rho} \right)$$

and Eqn. B.7 becomes

$$\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k$$  \hfill (B.8)$$

where $c_k = \rho_k/\rho$ are the mass fractions of each component, and $\mathbf{J}_k = \rho_k (\mathbf{v}_k - \mathbf{v})$ is the diffusive flow of each component relative to the center of mass velocity, $\mathbf{v}$.

**Conservation of Momentum: Euler’s Equation**

The momentum equation is Newton’s second law: the rate of change of momentum per unit time of a fluid particle is equal to the total force acting on a fluid particle. The force exerted on a surface element, $dA$, is equal to $P \, dA$, where $P$ is the pressure acting on the element $dA$. Therefore, the total force acting on a fluid particle is equal to the integral over its bounding
Recall that the negative is required since the force is acting inward on the surface bounding the fluid particle, opposite to the defined positive outward direction of the $dA$.

The surface integral can be transformed into a volume integral (this identity is derived from the divergence theorem)

$$-\oint P \, dA = -\int \nabla P \, dV$$

indicating that the fluid surrounding the volume element $dV$ exerts a force $-\nabla P$ on that element; i.e., a force of $-\nabla P$ acts on unit volume of the fluid.

The equation of motion of a volume element within the fluid can therefore be written by equating the force acting on the particle with the rate of change of momentum per unit time

$$\rho \frac{dv}{dt} = -\nabla p \quad \text{(B.9)}$$

As noted in the previous section, $dv/dt$ denotes the rate of change of the velocity of a given fluid particle as it moves about in space subject to the force from the surrounding fluid; it does not denote the change of velocity of the fluid at a fixed point in space. Thus, although the density can change with time at a given point in space, it does not change for a given fluid particle moving through space; $\rho$ is therefore outside the barycentric time derivative (analogous to the rocket fuel problem). Eqn. B.9 can be expressed in terms of quantities fixed in space using Eqn. B.3

$$\frac{dv}{dt} = \frac{\partial v}{\partial t} + (v \cdot \nabla)v$$
giving

\[
\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\nabla P}{\rho}
\]  

(B.10)

This form of the equation of motion is called Euler’s equation and applies to an ideal fluid (non-viscous, incompressible) in the absence of external forces. It is important to realize that in deriving Eqn. B.10, no account was taken of processes leading to energy dissipation in the fluid; specifically, internal friction (viscosity) and heat exchange. The next section derives the more general equation of motion, accounting for internal friction as well as external forces acting on the fluid particle.

**Conservation of Momentum: Cauchy’s Equation**

In order to derive a more general equation of motion, all forces acting on a fluid particle must be considered. These consist of external or body forces such as gravity or electromagnetic force that act throughout the volume of a fluid particle as well as internal or contact forces that act only on the surface of the fluid particle. These latter forces are those exerted by the medium surrounding the fluid particle of which pressure is an example.

Consider a small surface element with area \(dA\) and unit direction, \(\mathbf{n}\), of a small particle of fluid \((dA = \mathbf{n} \, dA)\). The contact force per unit area acting on this surface element is \(\mathbf{t}_{(n)}\). This is a vector quantity whose magnitude and direction depend not only on the position and time, but also on the direction \(\mathbf{n}\) of the surface element on which it acts. The total contact force exerted by the surrounding material on the particle of fluid through its bounding surface is

\[
\int \mathbf{t}_{(n)} \, dA
\]

The vector \(\mathbf{t}_{(n)}\) is also referred to as the stress or traction vector.\(^8\) The parenthesis in the subscript are to indicate that \(\mathbf{n}\) is a direction, not an index. Also, note that \(\mathbf{t}_{(n)}\) and \(\mathbf{n}\) are not necessarily in
the same direction. From the derivation of Euler's equation, it is obvious that the stress vector had the simple form \( t_{(n)} = -Pn \).

We also define \( F_k \) as the external force per unit mass acting on the component \( k \) of the fluid, giving a total external force of

\[
\sum_k \int \rho_k F_k \, dV
\]

acting on the fluid particle, (integration is over the total volume of the fluid particle).

In accordance with Newton’s second law, the rate of change of momentum of the fluid particle is equal to the sum of the body and contact forces acting on the particle

\[
\int \rho \frac{dv}{dt} \, dV = \sum_k \int \rho_k F_k \, dV + \oint t_{(n)} \, dA \quad (B.11)
\]

To proceed, consider \( \delta \) to be the characteristic length of the fluid particle such that its volume is \( \sim \delta^3 \) and its surface area is \( \sim \delta^2 \). If the fluid element is shrunk down to infinitesimal size \( \delta \to 0 \), then the volume integrals of Eqn. B.11 will decrease as \( \delta^3 \) whereas the surface integral will decrease as \( \delta^2 \). Dividing both sides of the equation by \( \delta^2 \) and taking the limit of \( \delta \to 0 \) gives

\[
\lim_{\delta \to 0} \frac{1}{\delta^2} \oint t_{(n)} \, dA = 0 \quad (B.12)
\]

Therefore, the stresses are locally in equilibrium.\(^{81}\)

The nature of the stresses on a point in the fluid are elucidated by considering a (vanishingly small) tetrahedron with three sides parallel to the coordinate planes with outward normals \( -e_{(i)} \) and the fourth slanted face with normal \( n \). If the fourth side has area \( dA \), the area of the three sides is given by \( dA_i = n_i dA \) (the projection of the area of the slanted face on the coordinate planes). The stress vector acting on the first three faces is \( -t_{(i)} \) (\( t_{(i)} \) denotes the stress vector when the outward normal is \( e_{(i)} \)), and on the fourth face is \( t_{(n)} \).
Applying the principle of local equilibrium of stresses on our system from Eqn. B.12, we have

\[ t(n)dA - t(1)dA_1 - t(2)dA_2 - t(3)dA_3 = (t(n) - t(1)n_1 - t(2)n_2 - t(3)n_3)dA = 0 \]

giving

\[ t(n) = t(1)n_1 + t(2)n_2 + t(3)n_3 \quad (B.13) \]

Now let \( T_{ji} \) be the \( j \)th component of the vector \( t(i) \), then Eqn. B.13 can be written

\[ t(n)_i = T_{ji}n_j \rightarrow t(n) = n \cdot \overline{T} \quad (B.14) \]

\( \overline{T} \) is called the stress tensor. As such, “the system of stresses in a fluid is not so complicated as to require a whole table of functions \( t(n)(x,n) \) at any given instant, but that it depends on \( n \) rather simply through the nine quantities \( T_{ji}(x) \).”

Using Eqn. B.14 in the surface integral of Eqn. B.11 and applying Green’s theorem converts it to a volume integral

\[
\int \rho \frac{dV}{dt} dV = \sum_k \int \rho_k F_k dV + \oint t(n) dA
\]

\[
= \sum_k \int \rho_k F_k dV + \int \overline{T} \cdot n dA = \int \left( \sum_k \rho_k F_k + \nabla \cdot \overline{T} \right) dV
\]

Since the volume over which the integral is taken is arbitrary, the integrands must relate as follows

\[
\rho \frac{dV}{dt} = \sum_k \rho_k F_k + \nabla \cdot \overline{T} \quad (B.15)
\]

This is called Cauchy’s equation of motion. The second rank stress tensor, \( \overline{T} \) is often decomp-
posed into two parts: \( \overline{T} = -P\overline{I} + \overline{D} \). The first term is the hydrostatic pressure with \( \overline{I} \) being the identity matrix; this was the pressure encountered in Euler’s equation, Eqn. B.9. The second term of the stress tensor, \( \overline{D} \), is called the deviatoric or viscous stress tensor and has both diagonal and off diagonal elements. Deriving the full form of \( \overline{T} \) requires establishing the constitutive relation between the stress and the deformation rate of strain tensor, \( \overline{E} \). This will be done in Ch. 7 for the derivation of the Navier-Stokes equation.

Eqn. B.15 can be written in the form of a balance equation for linear momentum by using Eqn. B.4

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} - \overline{T}) + \sum_k \rho_k \mathbf{F}_k \tag{B.16}
\]

where \( \mathbf{v} \mathbf{v} \) is an ordered (dyadic) product. It is evident that \( \rho \mathbf{v} \mathbf{v} - \overline{T} \) can be interpreted as a momentum flux density and \( \sum_k \rho_k \mathbf{F}_k \) as a momentum source. Due to the fact that momentum is a vector quantity, it is not surprising that its flux density should be a tensor and its source should be a vector. Scalar quantities, such as mass and energy, will have vector flux densities and scalar sources.

**Conservation of Energy**

The law of conservation of energy states that the total energy must be conserved, it cannot be created or destroyed. However, this is not necessarily true for kinetic energy, potential energy, and internal energy considered in isolation of each other. This section derives the balance equations for kinetic, potential, and internal energy in the context of treating conservation of total energy.

Kinetic energy and potential energy are both familiar from studies of mechanics and force fields such as electromagnetism and gravity. However, internal energy is arises uniquely in the

\(^7\overline{E} \) is not equivalent to \( \overline{D} \), but the relationship \( \overline{T}(\overline{E}) \) can be written in the form \( \overline{T}(\overline{E}) = -P\overline{I} + \overline{D} \).
fields of thermodynamics and statistical mechanics as a result of the treatment of large systems, for example, $> 10^{23}$ molecules. Internal energy refers to the energy contained in atomic or molecular modes of the system that are not macroscopically realized, these include thermal motion of molecules and intermolecular interactions. Macroscopically, it is defined from subtracting the kinetic and potential energy contributions from the total energy. As such, the continuity of kinetic energy and potential energy is initially considered which together with conservation of total energy, yields continuity of potential energy.

**Balance Equation for Kinetic Energy**

Eqn. B.15 can also be used to derive a balance equation for kinetic energy. Multiplying both sides by $\mathbf{v}$ and simplifying (carefully due to tensor products) gives

$$\rho \frac{d}{dt} \left( \frac{1}{2} \mathbf{v}^2 \right) = \sum_k \rho_k \mathbf{F}_k \cdot \mathbf{v} + \nabla \cdot (\overline{\mathbf{T}} \cdot \mathbf{v}) - \overline{\mathbf{T}} : \nabla \mathbf{v}$$

which can be rewritten as a balance equation using Eqn. B.4

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{v}^2 \right) = -\nabla \cdot \left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \overline{\mathbf{T}} \cdot \mathbf{v} \right) + \overline{\mathbf{T}} : \nabla \mathbf{v} + \sum_k \rho_k \mathbf{F}_k \cdot \mathbf{v}$$

(B.18)

Here we see the flux density for kinetic energy is equal to $\left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \overline{\mathbf{T}} \cdot \mathbf{v} \right)$. More physical intuition can be gained with rewriting this using $\overline{\mathbf{T}} = -\rho \mathbf{I} + \mathbf{D}$

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{v}^2 \right) = -\nabla \cdot \left( \frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \overline{\mathbf{D}} \cdot \mathbf{v} \right) + \overline{\mathbf{D}} : \nabla \mathbf{v} + \sum_k \rho_k \mathbf{F}_k \cdot \mathbf{v}$$

(B.19)

where again, $\overline{\mathbf{D}}$, is the deviatoric or viscous stress tensor. The expression in the square brackets is the flux density of kinetic energy of the fluid. The term $\left( \frac{1}{2} \rho \mathbf{v}^2 - P \right)$ is the energy flux due to
the actual transfer of fluid mass. The second term in the brackets, $\overline{D} \cdot \mathbf{v}$, is the energy flux due to processes of internal friction. This results from the fact that with any transfer of momentum, a transfer of energy will also take place given by a flux density equalling the product of the momentum flux with the velocity. The term $\overline{J} : \nabla \mathbf{v}$ is the energy dissipated per unit time per unit volume; thus kinetic energy is not conserved.

**Balance Equation for Potential Energy**

This treatment will only concern conservative body forces acting on the liquid, of the form

$$\mathbf{F}_k = -\nabla \psi_k$$

(B.20)

where $\psi_k$ is the scalar potential of the force acting on a particle of component $k$. The total potential energy per unit volume of the liquid is therefore $\rho \psi = \sum_k \rho_k \psi_k$. Multiplying the mass continuity equation of a single component, Eqn. B.1, by $\psi_k$ gives

$$\psi_k \frac{\partial \rho_k}{\partial t} = -\psi_k \nabla \cdot (\rho_k \mathbf{v}_k)$$

(B.21)

assuming $\partial \psi_k / \partial t = 0$ and recalling $\mathbf{J}_k = \rho_k (\mathbf{v}_k - \mathbf{v})$ allows

$$\frac{\partial (\rho_k \psi_k)}{\partial t} = -\nabla \cdot (\psi_k \rho_k \mathbf{v}_k) + \nabla \psi_k \cdot \rho_k \mathbf{v}_k$$

$$= -\nabla \cdot (\psi_k [\mathbf{J}_k + \rho_k \mathbf{V}]) + \nabla \psi_k \cdot [\mathbf{J}_k + \rho_k \mathbf{V}]$$

$$= -\nabla \cdot (\psi_k \mathbf{J}_k) - \nabla \cdot (\psi_k \rho_k \mathbf{v}) + \nabla \psi_k \cdot \mathbf{J}_k + \nabla \psi_k \cdot (\rho_k \mathbf{v})$$

$$= -\nabla \cdot (\psi_k \mathbf{J}_k) - \nabla \cdot (\psi_k \rho_k \mathbf{v}) - \mathbf{F}_k \cdot \mathbf{J}_k - \rho_k \mathbf{v} \cdot \mathbf{F}_k$$

(B.22)
Summing over all \( k \) components gives

\[
\frac{\partial (\rho \psi)}{\partial t} = -\nabla \cdot \left( \psi \rho \mathbf{v} + \sum_k \psi_k \mathbf{J}_k \right) - \sum_k \mathbf{F}_k \cdot \mathbf{J}_k - \sum_k \rho_k \mathbf{v} \cdot \mathbf{F}_k \quad \text{(B.23)}
\]

which is the balance equation for potential energy with the flux density of potential energy equalling \((\psi \rho \mathbf{v} + \sum_k \psi_k \mathbf{J}_k)\). The presence of source terms show that potential energy is also not conserved.

**Balance Equation for Kinetic and Potential Energies**

The sum of kinetic energy, Eqn. B.18, and potential energy, Eqn. B.23, is

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \mathbf{v}^2 + \rho \psi \right) = -\nabla \cdot \left[ \rho \left( \frac{1}{2} \mathbf{v}^2 + \psi \right) \mathbf{v} + \bar{T} \cdot \mathbf{v} + \sum_k \psi_k \mathbf{J}_k \right] + \bar{T} : \nabla \mathbf{v} - \sum_k \mathbf{F}_k \cdot \mathbf{J}_k \quad \text{(B.24)}
\]

Again, the presence of source terms on the right hand side indicates that the combined kinetic and potential energies are not conserved.

**Conservation of Total Energy**

It must be true that the total energy is conserved; ie, there can be no sources or sinks of energy. Therefore, the balance equation for total energy per unit mass, \( E \), must be

\[
\frac{\partial (\rho E)}{\partial t} = -\nabla \cdot \mathbf{J}_E \quad \text{(B.25)}
\]

where \( \mathbf{J}_E \) is the flux density of total energy per unit time per unit area. The total energy per unit volume of an element of fluid consists of its kinetic energy, potential energy, and internal energy

\[
E = \frac{1}{2} \mathbf{v}^2 + \psi + u \quad \text{(B.26)}
\]
where \( u \) is the internal energy per unit mass. Eqn. B.26 can be taken to be the definition of internal energy; however, from a microscopic perspective, the internal energy is the energy associated with thermal agitation and intermolecular interactions\(^{35} \). These modes of atomic or molecular motion are not macroscopically measurable, but they are just as capable of transferring energy as mechanical modes (mechanical work) or modes associated with body forces such as electric or gravitational fields (electrical work and gravitational work respectively)\(^{12} \). An energy transfer to the hidden atomic or molecular modes is called heat.

It can therefore be reasoned that the total energy flux density consists of the following contributions:\(^{35,105} \) internal friction and mechanical work done on the system \( \overrightarrow{T} \cdot \mathbf{v} \), convection \( \rho \mathbf{E} \mathbf{v} \), flux of potential energy due to diffusion of material components in a potential field \( \sum J_k \psi_k \) and due to chemical potential \( \sum J_k \mu_k \), and heat flux \( J_q \). Together these four contributions give

\[
\mathbf{J}_E = \overrightarrow{T} \cdot \mathbf{v} + \rho \mathbf{E} \mathbf{v} \sum \psi_k \mathbf{J}_k \sum \mu_k \mathbf{J}_k + \mathbf{J}_q \tag{B.27}
\]

This equation can also be viewed as the definition of \( \mathbf{J}_q \). It should be noted that\(^ {35} \) does not include the term \( \sum \mu_k \mathbf{J}_k \) in expressing the flux density of total energy. However, it is required since motion of particles occurs due to gradients in both a potential field as well as chemical potential.

**Balance Equation for Internal Energy**

Subtracting Eqn. B.24, the balance equation for kinetic and potential energy, from Eqn. B.25, the balance equation for total energy yields a balance equation for internal energy as follows

\[
\tau \frac{\partial}{\partial t} \left( \rho E - \frac{1}{2} \rho \mathbf{v}^2 - \rho \psi \right) = - \nabla \cdot \left[ \mathbf{J}_E - \rho \left( \frac{1}{2} \mathbf{v}^2 + \psi \right) \mathbf{v} - \overrightarrow{T} \cdot \mathbf{v} - \sum \psi_k \mathbf{J}_k \right] - \overrightarrow{T} : \nabla \mathbf{v} + \sum \mathbf{F}_k \cdot \mathbf{J}_k \tag{B.28}
\]
Using the definition of $u$ in Eqn. B.26 and the definition of $\mathbf{J}_E$ in Eqn. B.27, this can be rewritten

$$
\frac{\partial (\rho u)}{\partial t} = -\nabla \cdot \left( \rho \mathbf{u} + \sum_k \mu_k \mathbf{J}_k + \mathbf{J}_q \right) + \mathbf{T} : \nabla \mathbf{v} + \sum_k \mathbf{F}_k \cdot \mathbf{J}_k 
$$

(B.29)

It is again evident that the internal energy is not conserved due to the presence of source terms. However, these source terms are equal and opposite to those in Eqn. B.24, consistent with conservation of total energy. Using $\mathbf{T} = -P \mathbf{I} + D$ this can be written

$$
\frac{\rho}{\rho} \frac{du}{dt} = -\nabla \cdot \left( \mathbf{J}_q + \sum_k \mu_k \mathbf{J}_k \right) - P \nabla \cdot \mathbf{v} + \mathbf{T} : \nabla \mathbf{v} + \sum_k \mathbf{F}_k \cdot \mathbf{J}_k 
$$

(B.30)

where $\mathbf{T} : \nabla \mathbf{v} = \nabla \cdot \mathbf{v}$ and Eqn. B.4 have been used. This can be written in the form of the first law of thermodynamics by introducing the specific volume $v = \rho^{-1}$. By conservation of mass in Eqn. B.6

$$
\nabla \cdot \mathbf{v} = -\frac{1}{\rho} \frac{d\rho}{dt} = \rho \frac{dv}{dt} 
$$

(B.31)

which in Eqn. B.30 gives

$$
\frac{\rho}{\rho} \frac{du}{dt} = -\nabla \cdot \left( \mathbf{J}_q + \sum_k \mu_k \mathbf{J}_k \right) - P \frac{dv}{dt} + \mathbf{T} : \nabla \mathbf{v} + \sum_k \mathbf{F}_k \cdot \mathbf{J}_k 
$$

(B.32)

Expanding the term $\nabla \cdot \left( \sum_k \mu_k \mathbf{J}_k \right) = \sum (\nabla \mu_k \cdot \mathbf{J}_k + \mu_k \nabla \cdot \mathbf{J}_k)$ and substituting Eqn. B.8, $\rho (dc_k/dt) = -\nabla \cdot \mathbf{J}_k$, and $\rho (dq/dt) = -\nabla \cdot \mathbf{J}_q$, where $dq$ is the heat per unit mass, gives

$$
\frac{du}{dt} = \frac{dq}{dt} - P \frac{dv}{dt} + \sum_k \mu_k \frac{dc_k}{dt} + v \mathbf{T} : \nabla \mathbf{v} + v \sum_k \nabla \mu_k \cdot \mathbf{J}_k + v \sum_k \mathbf{F}_k \cdot \mathbf{J}_k 
$$

(B.33)

which is a form for time rate of change of the first law of thermodynamics. Note that thermodynamics is formulated on the assumption of equilibrium and does not consider dynamical behavior of systems approaching equilibrium. Therefore, this last equation has additional terms.
in comparison to the standard form of the first law (expressing \( du \)) related to the time dependent behavior.

**SUMMARY OF EQUATIONS**

The continuity equations derived in this section that are cited in the main text of this thesis are summarized here for ease of reference. For mass, Eqn. B.6

\[
\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}
\]  

(B.34)

or Eqn. B.8 for multicomponent systems

\[
\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k
\]  

(B.35)

for momentum, Eqn. B.15

\[
\rho \frac{d\mathbf{v}}{dt} = \sum_k \rho_k \mathbf{F}_k + \nabla \cdot \mathbf{T}
\]  

(B.36)

and for internal energy, Eqn. B.32

\[
\rho \frac{du}{dt} = -\nabla \cdot \left( \mathbf{J}_q + \sum_k \mu_k \mathbf{J}_k \right) - \rho P \frac{dv}{dt} + \nabla \cdot \mathbf{v} + \sum_k \mathbf{F}_k \cdot \mathbf{J}_k
\]  

(B.37)

These are all given in terms of the barycentric or material derivative and can be converted to local coordinate derivatives using Eqn. B.4. All quantities appearing in these equations are defined in the context of this appendix.
Solution of Joule Heating with Separation of Variables

This appendix uses the method of separation of variables to derive the solution to the analytical problem for Joule heating presented in Ch. 5. The result is equivalent to the Green’s function solution presented in the main text.

The method of separation of variables can easily be applied the case of the homogeneous heat equation, when the the source term is missing. This solution is then extended in order to solve the inhomogeneous heat equation of Eqn. 5.5. In the case of the homogeneous equation
in spherical polar coordinates

\[ \frac{\partial}{\partial t} T(r, \theta, \phi, t) = \nabla^2 T(r, \theta, \phi, t) \]  

(C.1)

and the assumed form of the separable solution is

\[ T(r, \theta, \phi, t) = \Gamma(t) \Psi(r, \theta, \phi) = \Gamma(t) R(r) Y(\theta, \phi) \]  

(C.2)

giving

\[ \frac{1}{\Gamma(t)} \frac{\partial}{\partial t} \Gamma(t) = \frac{1}{\Psi(r, \theta, \phi)} \nabla^2 \Psi(r, \theta, \phi) = -\gamma \]  

(C.3)

Both sides of the equation are functionally dependent on different variables, but are nevertheless equal; therefore they must be equal to a constant value which we call \(-\gamma < 0\). The time dependent equation

\[ \frac{\partial}{\partial t} \Gamma(t) = -\gamma \Gamma(t) \]  

(C.4)

has the solution

\[ \Gamma(t) = C e^{-\gamma t} \]  

(C.5)

The negative separation constant therefore prevent the solution tending to infinity as \( t \to \infty \).

It is also evident that for the homogeneous case, having an initial condition of zero everywhere would yield a solution of zero everywhere for all time. This situation is avoided in the case of the inhomogeneous heat equation due to the presence of the source term.

This leaves the spatial eigenvalue problem of Eqn. C.3, called the Helmholtz equation

\[ \nabla^2 \Psi(r, \theta, \phi) = -\gamma \Psi(r, \theta, \phi) \]  

(C.6)
with boundary conditions $\Psi(\tilde{r}, \theta, \varphi) = 0$ and $\Psi(0, \theta, \varphi) = \text{finite}$. This is solved by separating variables again by writing $\Psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$ giving differential equations for $Y(\theta, \varphi)$ and $R(r)$. The equation for $Y$ can be shown to be

$$\frac{\partial^2 Y}{\partial \theta^2} + \cot \theta \frac{\partial Y}{\partial \theta} + \csc^2 \theta \frac{\partial^2 Y}{\partial \varphi^2} + \mu Y = 0 \quad \text{(C.7)}$$

where $\mu$ is the constant resulting from separation of variables. This equation has non-trivial solutions when $\mu = l(l + 1)$, with $l = 0, 1, 2, \ldots$. For each value of $\mu$, there are $2l + 1$ solutions. Specifically this equation is solved by the spherical harmonics $Y_l^m(\theta, \varphi)$ with $m = -l, -l + 1, \ldots, 0, \ldots, l - 1, l$. The equation for $R$ can be shown to be

$$r^2 R'' + 2R' + (\lambda^2 r^2 - l(l + 1))R = 0 \quad \text{(C.8)}$$

where $\gamma$ has been replaced by $\lambda^2$ and $\mu$ by $l(l + 1)$. This is the spherical Bessel equation, solved by a linear combination of the spherical Bessel functions of the first kind and the spherical Bessel functions of the second kind (the latter are also called Neumann functions). Spherical Bessel functions are not considered in this solution because they diverge in the limit $r \to 0$ whereas have $R(0) = 0$ according to Eqn. C.6. Therefore the solution to Eqn. C.8 is a linear combination of be spherical Bessel functions of the first kind, $j_l$

$$R_{l,n}(r) = j_l(\lambda_{l,n}r), \quad l = 0, 1, 2, \ldots, \quad n = 1, 2, \ldots \quad \text{(C.9)}$$

where the constant $\lambda$ is given by

$$\lambda = \lambda_{l,n} = \frac{\alpha_l + 1/2, n}{\tilde{r}_p} \quad \text{(C.10)}$$

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with \( \alpha_{l+1/2,n} \) denoting the \( n \)th positive zero of the Bessel function \( J_{l+1/2} \). The spherical Bessel functions of the first kind are in turn defined by

\[
j_l(r) = \left( \frac{\pi}{2r} \right)^{1/2} J_{l+1/2}(r)
\]

Therefore the eigenvalue problem of Eqn. C.6 has eigenvalues of \( \gamma = \lambda^2 \) where each \( \lambda = \lambda_{l,n} \) has \( 2l + 1 \) eigenfunctions

\[
\Psi_{n,l,m}(r, \theta, \varphi) = j_l(\lambda_{l,n}r)Y^m_l(\theta, \varphi)
\]

This gives the solution to the homogeneous heat equation from Eqn. C.2 as

\[
T(r, \theta, \varphi, t) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C e^{-\gamma t} j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi)
\]

Solutions of the form of Eqn. C.12 can now be used to solve the inhomogeneous heat equation of Eqn. 5.5. This is done by taking advantage of special properties resulting from the orthogonality of the Bessel functions and of the Spherical Harmonics. The orthogonality of the solutions of the Helmholtz equation is summarized as follows without proof for the case where \( (n, l, m) \neq (n', l', m') \). When these indices are equal

\[
\int_{0}^{\tilde{r}_p} \int_{0}^{2\pi} \int_{0}^{\pi} j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi) j_l(\lambda_{l',n'} r) Y^m_l(\theta, \varphi) r^2 \sin(\theta) d\theta d\varphi dr = 0
\]

for the case where \( (n, l, m) \neq (n', l', m') \). When these indices are equal

\[
\int_{0}^{\tilde{r}_p} \int_{0}^{2\pi} \int_{0}^{\pi} j_l^2(\lambda_{l,n} r) |Y^m_l(\theta, \varphi)|^2 r^2 \sin(\theta) d\theta d\varphi dr = \frac{\tilde{r}_p^3}{2} j_l^2(\alpha_{l+1/2,n})
\]
where again \(\alpha_{l+1/2,n}\) is the \(n\)th positive zero of \(J_{l+1/2}\). A consequence of this orthogonality is that any function, \(f(r, \theta, \varphi)\), defined in spherical coordinates of \(0 < r < \tilde{r}_p\), \(0 < \theta < \pi\), \(0 < \varphi < 2\pi\), can be expanded using the spherical Bessel functions and Spherical Harmonics. This expansion is as follows

\[
f(r, \theta, \varphi) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{nlm} j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi) \quad \text{(C.16)}
\]

where

\[
A_{nlm} = \frac{2}{\tilde{r}_p^3 j_{l+1}(\alpha_{l+1/2,n})} \int_0^{\tilde{r}_p} \int_0^{2\pi} \int_0^\pi f(r, \theta, \varphi) j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi) r^2 \sin(\theta) d\theta d\varphi dr \quad \text{(C.17)}
\]

Proof for this is based on the orthogonality property of these functions. This property can now be used to solve inhomogeneous heat equation, which including angular dependence is

\[
\frac{\partial}{\partial t} T(r, \theta, \varphi, t) = \nabla^2 T(r, \theta, \varphi, t) + \tilde{Q}(r, \theta, \varphi) \quad \text{(C.18)}
\]

with initial condition \(T(r, \theta, \varphi, 0) = f(r, \theta, \varphi)\) and boundary conditions \(T(\tilde{r}_d, \theta, \varphi, t) = 0\), \(T(0, \theta, \varphi, t) = \text{finite}\). Because separation of variables is not possible with the heat source term \(\tilde{Q}\), a form for the time dependence of the solution cannot be assumed. However, a solution for the spatial dependence of a form very similar to the solution of the homogeneous case given in Eqn. C.13 is assumed

\[
T(r, \theta, \varphi, t) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} B_{nlm}(t) j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi) \quad \text{(C.19)}
\]

In order to fully specify the solution, the time dependent coefficients, \(B_{nlm}\) need to be solved for. This is done by expanding the initial condition, \(f(r, \theta, \varphi)\) and the equation for the heat source,
\( \tilde{Q}(r, \theta, \varphi) \) in terms of the spherical Bessel functions and Spherical Harmonics. According to Eqn. C.16, this gives

\[
f(r, \theta, \varphi) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} f_{nlm} j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi)
\]

(C.20)

\[
\tilde{Q}(r, \theta, \varphi) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} q_{nlm} j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi)
\]

(C.21)

were the coefficients \( f_{nlm} \) and \( q_{nlm} \) are given by Eqn. C.17. To solve for \( B_{nlm}(r, \theta, \varphi) \), substitute Eqns. C.19, C.20, and C.21 into the differential equation of Eqn. C.18, giving

\[
\sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} B'_{nlm}(t) j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi) = \sum_{n=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left( -\lambda_{l,n}^2 B_{nlm}(t) + q_{nlm} \right) j_l(\lambda_{l,n} r) Y^m_l(\theta, \varphi)
\]

(C.22)

This gives a differential equation for \( B_{nlm}(t) \)

\[
B'_{nlm}(t) + \lambda_{l,n}^2 B_{nlm}(t) = q_{nlm}
\]

(C.23)

with initial condition \( B_{nlm}(0) = f_{nlm} \), which is solved by

\[
B_{nlm}(t) = e^{-\lambda_{l,n}^2 t} \left( f_{nlm} - \frac{q_{nlm}}{\lambda_{l,n}^2} \right) + \frac{q_{nlm}}{\lambda_{l,n}^2}
\]

(C.24)

Using this in Eqn. C.19 gives the solution to the general inhomogeneous problem in spherical coordinates.

This can be used to write down a solution for the radial heat equation of Eqn. 5.5 with the Joule heating source term that describes the nanopore heating. Since the differential equation is independent of angular coordinates, the only spherical harmonic in the solution must be that
which is independent of $\theta$ and $\varphi$
\[
Y_0^0(\theta, \varphi) = \frac{1}{2\sqrt{\pi}}
\] (C.25)

where $l$ and $m$ are equal to zero resulting in a single value of the separation constant $\mu = 0$.

Following Eqn. C.19, the solution to Eqn. 5.5 is
\[
T(r, t) = \sum_{n=1}^{\infty} B_n(t) j_0(\lambda_0,n r) Y_0^0(\theta, \varphi) = \frac{1}{2\sqrt{\pi}} \sum_{n=1}^{\infty} B_n(t) j_0(\lambda_0,n r)
\] (C.26)

where Eqn. C.10 gives
\[
\lambda_0,n = \frac{\alpha_{1/2,n}}{r_p}
\] (C.27)

with $\alpha_{1/2,n}$ denoting the nth positive zero of the Bessel function $J_{1/2}$. The time dependent coefficients, $B_n(t)$ are given by
\[
B_n(t) = \frac{q_n}{\lambda_0,n} \left(1 - e^{-\lambda_0,n t}\right)
\] (C.28)

Here, the coefficients $q_n$ come form expanding $\tilde{Q}(r)$ in terms of spherical Bessel functions as follows
\[
\tilde{Q}(r) = \sum_{n=1}^{\infty} q_n j_0(\lambda_0,n r) Y_0^0(\theta, \varphi) = \frac{1}{2\sqrt{\pi}} \sum_{n=1}^{\infty} q_n j_0(\lambda_0,n r)
\] (C.29)

with $q_n$ given by Eqn. C.17 as
\[
q_n = \frac{2}{r_p J_1^2(\alpha_{1/2,n})} \int_0^{r_p} \int_0^{2\pi} \int_0^{\pi} \tilde{Q}(r) j_0(\lambda_0,n r) Y_0^0(\theta, \varphi) r^2 \sin(\theta) d\theta d\phi dr
\] (C.30)

Integrating the angular variables and inserting the definition for $\tilde{Q}(r)$ gives
\[
q_n = \frac{4\sqrt{\pi}}{r_p J_1^2(\alpha_{1/2,n})} \left[ \int_1^{r_p} \tilde{Q}_0(\lambda_0,n r) r^2 dr + \int_1^{r_p} 0 r^2 dr \right]
\] (C.31)

where the limit of integration, $1 = r_d/r_d$, is the pore radius in natural coordinates. This integral
can be solved by using the definitions of the spherical Bessel functions

\[ j_0(s) = \frac{\sin(s)}{s}, \quad j_1(s) = \frac{\sin(s)}{s^2} - \frac{\cos(s)}{s} \]  

(C.32)

giving

\[ q_n = \frac{4\sqrt{\pi}Q}{r^2 j_1^2(\alpha_{1/2,n})} j_1(\lambda_{0,n} r) \]  

(C.33)

This equation, along with Eqns. C.27 and C.28 define the coefficients of \( T(r, t) \) in Eqn. C.26, completing the solution of the heat equation, Eqn. 5.5, for nanopore heating using the method of separation of variables. It should be noted that this method gives an infinite series solution which must be summed up numerically, thus, although Eqn. C.26 has been obtained without the use of a computer, any evaluation of the expression must be done numerically.

A plot of the temperature distribution, Eqn. C.26, as a function of radius is plotted for different times in Fig. C.1, using the parameters from Table 5.1. The value for the room temperature, \( T_0 = 293.15 \) K has been added to the solution correcting for the imposed Dirichlet boundary condition. The temperature is seen to rise rapidly into a strongly peaked distribution as \( t \) increases, reaching a maximum at just over 600 K.

This solution can be compared with the steady state solution solution in the limit of \( t \rightarrow \infty \) to verify whether it is correct. The steady state solution is analytically solvable in the sense that it does not contain infinite series. The solution is not time dependent so the time derivative is absent in the problem.

\[ 0 = \kappa \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) T(r) + Q(r) \]  

(C.34)

where again, \( Q(r) \) is given by Eqn. 5.2, and the boundary conditions are \( T(r_d) = 0 \) and \( T(0) = \text{finite} \). The step function for \( Q(r) \) allows for splitting the differential equation into an
inhomogeneous ODE for $r \leq r_p$ and a homogeneous ODE for $r > r_p$.

\[
\begin{align*}
0 &= \kappa \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) T(r) + Q & r \leq r_p \\
0 &= \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) T(r) & r > r_p
\end{align*}
\]  

(C.35)

Both solutions, $T_{\text{in}}(r)$ and $T_{\text{out}}(r)$ share the boundary conditions

\[
T_{\text{in}}(r_p) = T_{\text{out}}(r_p), \quad \frac{dT_{\text{in}}}{dr} \bigg|_{r=r_p} = \frac{dT_{\text{out}}}{dr} \bigg|_{r=r_p}
\]  

(C.36)

Note that although each solution has three boundary conditions which it must obey, this is not
an over-specification since two of those boundary conditions are shared by the two solutions. Therefore, with two solutions, each of which must solve a second order differential equation, there are four total boundary conditions. Physically, the condition that the temperature must be the same at \( r = r_p \) enforces the fact that the temperature distribution will not have any discontinuities across a boundary in a homogeneous system. The condition matching the first derivative at \( r = r_p \) physically corresponds to the fact that the heat flux into a boundary must be the same as the heat flux out of a boundary by conservation of energy.

Both differential equations in Eqn. C.35 can be solved by simple integration. The solution to the ODE inside the pore is

\[
T_{in}(r) = -\frac{Q}{6\kappa} r^2 - \frac{A}{r} + B \quad \rightarrow \quad T_{in}(r) = -\frac{Q}{6\kappa} r^2 + B
\]

where \( A \) and \( B \) are integration constants. The boundary condition at \( r = 0 \) requires that \( A = 0 \). The solution to the ODE outside the pore is

\[
T_{out}(r) = -\frac{C}{r} + D \quad \rightarrow \quad T_{out}(r) = \frac{C}{r_d} \left( 1 - \frac{r_d}{r} \right)
\]

where again, \( C \) and \( D \) are integration constants. The boundary condition at \( r = \tilde{r}_d \) requires that \( D = C/\tilde{r}_d \). Finally, applying the boundary conditions in Eqn. C.36, we arrive at the solution

\[
T(r) = \begin{cases} 
-\frac{Q}{6\kappa} r^2 + B & r \leq r_p \\
-\frac{Q r_p^3}{3\kappa r_d} \left( 1 - \frac{r_d}{r} \right) & r > r_p
\end{cases}
\]

with

\[
B = \frac{Q r_p^2}{3\kappa} \left[ \frac{1}{2} + \left( 1 - \frac{r_p}{r_d} \right) \right]
\]
This solution has been plotted as a dashed line in Fig. C.1 and overlaps with the plot of the time dependent solution Eqn. C.26, at large times. Note that $B$ gives the maximum possible temperature at the center of the pore, $r = 0$ which for the parameters in Table 5.1 is 601.24 K.
From Navier-Stokes to Rayleigh-Plesset

The full set of equations required to specify the dynamics of the bubble are summarized in Table 7.1. This appendix demonstrates how to derive the Rayleigh-Plesset equation from the Cauchy equation for momentum, Eqn. 7.8.

\( R(t) \) is used to denote the radius of the bubble at time \( t \). This is the relationship that the following calculation will derive which is applied to the problem of characterizing bubble growth in Ch. 7 of this thesis. In order to simplify the problem of bubble growth, all material properties of the fluid are assumed constant, and the superheated liquid is assumed to be incompressible, \( \nabla \cdot v_i = 0 \). These two simplifications, along with the stress tensor in Eqn. 7.6, reduce the Cauchy equation, Eqn. 7.8, to the Navier-Stokes equation which describes the dynamics of an
incompressible, Newtonian fluid

\[
\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\nabla p}{\rho} + \nu \nabla^2 \mathbf{v}
\]  \hspace{1cm} \text{(D.1)}

Spherical symmetry is assumed, and the velocity field of the fluid therefore has the form \( \mathbf{v} = v_r(r, t) \hat{r} + 0 \hat{\theta} + 0 \hat{\phi} \). Thus, Eqn. D.1 takes the form

\[
\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left[ \frac{\partial^2 v_r}{\partial r^2} + \frac{2}{r} \frac{\partial v_r}{\partial r} - \frac{2v_r}{r^2} \right]
\]  \hspace{1cm} \text{(D.2)}

The incompressible liquid is also described continuity equation, Eqn. 7.2, which in spherical coordinates becomes

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 v_r \right) = \frac{\partial v_r}{\partial r} + \frac{2 v_r}{r} = 0
\]  \hspace{1cm} \text{(D.3)}

Recall that incompressibility requires constant density, \( \partial \rho / \partial t = 0 \). Eqns. D.2 and D.3 form a system of two differential equations which must be solved. Integrating Eqn. D.3 gives the following form for the solution

\[
v_r(r, t) = \frac{F(t)}{r^2}
\]  \hspace{1cm} \text{(D.4)}

To determine the form of \( F(t) \), apply the boundary condition

\[
v_r(r, t) \big|_{r=R} = \frac{\partial R}{\partial t}
\]  \hspace{1cm} \text{(D.5)}

for the velocity at the bubble wall, giving

\[
v_r(r, t) = \frac{\dot{R} R^2}{r^2}
\]  \hspace{1cm} \text{(D.6)}

where dots indicate derivatives with respect to time. This is the velocity of the fluid outside of
the bubble in terms of the radius of the bubble and the velocity of the bubble wall. To find the equation for the bubble radius, $R(t)$, take the following derivatives

\[ \frac{\partial v_r}{\partial t} = \frac{\ddot{R}R^2 + 2R\dot{R}^2}{r^2} \]
\[ \frac{\partial v_r}{\partial r} = -\frac{2\dot{R}R^2}{r^3} \]
\[ \frac{\partial^2 v_r}{\partial r^2} = \frac{6\dot{R}R^2}{r^4} \]  \hspace{1cm} (D.7)

and insert them back into the Navier Stokes equation, Eqn. D.2, to arrive at

\[ \frac{1}{\rho} \frac{\partial p}{\partial r} = -\frac{R^2\ddot{R} + 2R\dot{R}^2}{r^2} + \frac{2\dot{R}^2R^4}{r^5} \]  \hspace{1cm} (D.8)

Note that the second term on the right hand side of Eqn. D.2 containing the viscosity coefficient, $\nu$, disappears. This should not be surprising since this term arises from shear (tangential) stress which is not present in the system. Integration of Eqn. D.8 with respect to $r$ yields

\[ \frac{p}{\rho} = \frac{R^2\ddot{R} + 2R\dot{R}^2}{r} - \frac{1}{2} \frac{\dot{R}^2R^4}{r^3} + C \]  \hspace{1cm} (D.9)

The integration constant, $C$, is found by noting a second boundary condition that $p \rightarrow p_\infty$ as $r \rightarrow \infty$. Thus, $C = p_\infty/\rho$, which is plugged into Eqn. D.9

\[ \frac{p(r,t) - p_\infty}{\rho} = \frac{R^2\ddot{R} + 2R\dot{R}^2}{r} - \frac{1}{2} \frac{\dot{R}^2R^4}{r^3} \]  \hspace{1cm} (D.10)

This equation can be used to find the bubble radius as a function of time, $R(t)$. This is done by inserting $r = R$, yielding

\[ \frac{p(R,t) - p_\infty}{\rho} = RR\dddot{R} + \frac{3}{2} \dot{R}^2 \]  \hspace{1cm} (D.11)

To find $p(R)$ a third boundary condition is applied: the normal stresses acting on the bubble must
be zero in the case of no mass transfer. This net force per unit area is

\[ \mathbf{n} \cdot (\mathbf{n} \cdot \mathbf{F}_{\text{outside}} - \mathbf{n} \cdot \mathbf{F}_{\text{inside}}) - \frac{2\sigma}{R} = 0 \quad (D.12) \]

where \( \sigma \) is the surface tension. This final surface tension term is required by Laplace’s equation for mechanical equilibrium of the bubble. The definition of the stress tensor was given in Eqn. 7.6

\[ \mathbf{\bar{T}} = -[P - \zeta(\nabla \cdot \mathbf{v})] \mathbf{I} + 2\mu \left[ \mathbf{\varepsilon} - \frac{1}{3}(\nabla \cdot \mathbf{v}) \mathbf{I} \right] \]

in the case of an incompressible fluid is simplified to

\[ \mathbf{\bar{T}} = -p\mathbf{I} + 2\mu\mathbf{\varepsilon} \]

The normal stress on the surface is given by

\[ \mathbf{n} \cdot \mathbf{\bar{T}} = \mathbf{T}_{rr} = -p + 2\mu \frac{\partial v_r}{\partial r} \]

Using the fluid velocity field, Eqn. D.6, gives

\[ \mathbf{n} \cdot \mathbf{\bar{T}}_{\text{outside}} = -p(R, t) + 2\mu \frac{\partial}{\partial r} \left( \frac{\dot{R}^2 R^2}{r^2} \right) \bigg|_{r=R} = -p(R, t) - \frac{4\mu \dot{R}}{R} \quad (D.13) \]

\[ \mathbf{n} \cdot \mathbf{\bar{T}}_{\text{inside}} = -p_v \quad (D.14) \]

Substituting Eqns. D.13 and D.14 in Eqn. D.12 gives the following

\[ p(R, t) = p_v - 4\mu \frac{\dot{R}}{R} - \frac{2\sigma}{R} \quad (D.15) \]
Applying this result to Eqn. D.10 giving the Rayleigh Plesset equation for the dynamics of bubble growth

\[
\frac{p_v - p_\infty}{\rho} = R\ddot{R} + \frac{3}{2}R^2 + 4\frac{\dot{R}}{R} + \frac{2\sigma}{\rho R}
\]

(D.16)

This equation reduces to the condition for static equilibrium of the bubble (Laplace pressure equation for spherical interfaces) when both the first and second derivatives are zero.

**Inertial Growth**

The simple case of inertially driven growth considers the dynamics of the bubble in response to the difference in pressure within the vapor bubble and the ambient pressure manifest to simulate growth. This neglects heat transport, surface tension and viscosity. Eqn. D.16 reduces to

\[
R\ddot{R} + \frac{3}{2}R^2 = \frac{p_v - p_\infty}{\rho}
\]

(D.17)

The initial condition for the bubble radius \(R(t = 0) = R_0\), with \(R_0 = r_{cr} + \epsilon_R\) being the critical radius plus a perturbation factor, and the initial bubble velocity is assumed to be zero, \(\dot{R}(t = 0) = 0\). Temperature is assumed to be constant everywhere and equal to \(T_\infty\) and the vapor pressure inside the bubble, \(p_v\), is assumed to be constant. Of course, this latter assumption is very limited since as the bubble grows, the vapor pressure must decrease if the number of molecules in gaseous phase remains the same. In assuming that the vapor pressure does not change, an implicit assumption is made that more molecules are entering the bubble either as gas or as vapor.

Eqn. D.17 can be solved by multiplying both sides by \(F(t) = \dot{R}R^2\) from Eqns. D.4 and D.6

\[
R^3\dddot{R} + \frac{3}{2}R^2\ddot{R}^3 = \frac{p_v - p_\infty}{\rho}R^2\dot{R}
\]
which can be rewritten

$$\frac{1}{2} \frac{d}{dt} \left( R^3 \dot{R}^2 \right) = \left( \frac{P_v - P_\infty}{\rho} \right) \frac{1}{3} \frac{d}{dt} (R^3)$$

Integrating both sides with respect to $t$

$$\frac{1}{2} \int \frac{d}{dt} (R^3 \dot{R}^2) \, dt = \int \left( \frac{P_v - P_\infty}{3\rho} \right) \frac{d}{dt} (R^3) \, dt$$

giving

$$\frac{1}{2} R^3 \dot{R}^2 = \frac{P_v - P_\infty}{3\rho} R^3 + C$$

The integration constant is determined by using the initial conditions, $R(t = 0) = R_0$ and $\dot{R}(t = 0) = 0$

$$C = -\frac{P_v - P_\infty}{3\rho} R_0^3$$

giving

$$\dot{R} = \sqrt{\frac{2(P_v - P_\infty)}{3\rho} \left( 1 - \left( \frac{R_0}{R} \right)^3 \right)^{1/2}}$$

(D.18)

This gives the integral equation

$$\sqrt{\frac{2(P_v - P_\infty)}{3\rho}} \int dt = \int \left( 1 - \left( \frac{R_0}{R} \right)^3 \right)^{-1/2} dR$$

The integral on the right hand side can be computed numerically. However, even without doing this integral, it is evident that $R$ grows approximately linearly with $t$ from Eqn. D.18. This results from neglecting the second term $(R_0/R)^3$ as being negligible due to the small size of $R_0$ and the increasing size of $R$. Indeed, this term is only significant at the onset of inertial growth when $t$
is still small. With this approximation

\[ \dot{R} \approx \sqrt{\frac{2(P_v - P_\infty)}{3\rho}} \]

which integrating and using the initial condition \( R_0 = R \) gives

\[ R(t) \approx \sqrt{\frac{2(P_v - P_\infty)}{3\rho}} t + R_0 \]  \hspace{1cm} (D.19)

This is an analytical form for the solution to inertial bubble growth showing the bubble growing linearly with time. The initial growth problem is only one aspect of the very complicated problem of bubble dynamics discussed in Ch. 7 of this thesis.
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