MODELING OF HYDROGEN-BASED PLASMAS IN MICROWAVE PLASMA-ASSISTED CHEMICAL VAPOR DEPOSITION REACTORS AT MODERATE PRESSURES

By

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ABSTRACT

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Microwave Plasma-Assisted Chemical Vapor Deposition (PACVD) systems are used in the deposition of high quality diamond films. These systems have traditionally been operated at less than 20% atmospheric pressure (atm), resulting in growth rates up to 5 μ m/hr. Under such conditions, the system operation and plasma behavior are well-understood and have been successfully modeled. Recent experiments at pressures approaching 40% atm have demonstrated faster growth rates and better quality samples. At these increased pressures, the system operation and plasma behavior are not completely understood, with unusual plasm abehavior sometimes observed. Experimental measurements within these systems can be difficult, making numerical models attractive for aiding in understanding this behavior. This thesis presents a multiphysics numerical model of Microwave PACVD systems, which is accurate under these operating conditions. Electromagnetic field propagation, chemical reactions, species diffusion, thermal processes, energy transfer, and convective flows are all included in the multiphysics model. The model is verified against canonical problems and validated against experimental data. Extensive numerical results are provided for different operating conditions and system configurations. Copyright by COLLIN STEPHEN MEIERBACHTOL 2013 For Krista.

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KEY TO SYMBOLS

SYMBOL	DESCRIPTION	UNITS
ā	Acceleration vector	m/s^2
α	Plasma chemical species designation	
\vec{B}	Magnetic flux density	Wb/m^2
с	Speed of light in vacuum	m/s
c_S	Molar concentration of species s	mol/m^3
c_{tot}	Total molar concentration	mol/m^3
C_p	Specific heat capacity	J/kg~K
$ec{D}$	Electric flux density	C/m^2
Da	Ambipolar diffusion coefficient	m^2/s
D_S	Diffusion coefficient for species s	m^2/s
D_{sr}	Binary diffusion coefficient between species s and r	m^2/s
$\Delta_{s,r}^{(1)}$	Modified collision integral of the first kind	$m \ s$
$\Delta_{s,r}^{(2)}$	Modified ollision integral of the second kind	m-s
∇	Gradient operator	1/m
$ abla \cdot$	Divergence operator	1/m
abla imes	Curl operator	1/m
$ec{E}$	Electric field intensity	V/m
E_a	Chemical reaction activation energy	J
E_{r}	Radial electric field component	V/m
E_t	Tangential electric field component	V/m
E_z	Vertical electric field component	V/m
EEDF	Electron Energy Distribution Function	abbr.
$\hat{\epsilon}$	Complex electromagnetic permittivity	F/m
ϵ_0	Free space electromagnetic permittivity	F/m

ϵ_r	Relative electromagnetic permittivity	
$\epsilon_{v,s}$	Vibrational mode energy of species s	J
$\epsilon_{v,s}^{(1)}$	Vibrational mode electron equilibrium energy of species s	J
$\epsilon_{v,s}^{(2)}$	Vibrational mode neutral equilibrium energy of species s	J
f	Electromagnetic wave frequency	Hz
\vec{f}	Plasma distribution function	
\vec{g}	Gravitational acceleration	m/s^2
h_S	Enthalpy of chemical species s	J
\vec{H}	Magnetic field intensity	H/m
\mathcal{Z}	Imaginary component operator	
j	Imaginary unit	
J_0	Zeroeth order bessel function of first kind	
\vec{J}_e	Electric current density	A/m^2
\vec{J}_m	Magnetic current density	V/m^2
k	Electromagnetic wavenumber magnitude	1/m
\vec{k}	Electromagnetic wavenumber	1/m
k _b	Boltzmann's Constant	J/K
k_r	Radial electromagnetic wavenumber mangitude	1/m
$k_{r,s}$	Chemical reaction rate constant for r and s	
k_z	Vertical electromagnetic wavenumber mangitude	1/m
λ	Electromagnetic wavelength	m
λ_0	Free space electromagnetic wavelength	m
λ_D	deBye length of plasma	m
λ_e	Electron thermal conductivity coefficient	W/m - K
λg	Neutral species thermal conductivity coefficient	W/m - K
λ_r	Rotational modes thermal conductivity coefficient	W/m - K
λ_t	Translational modes thermal conductivity coefficient	W/m - K

λ_{tr}	Summation of $\lambda_t + \lambda_r$	W/m - K
$\lambda_{\mathcal{V}}$	Vibrational modes thermal conductivity coefficient	W/m - K
log	Natural logarithm function	
\log_{10}	Base-10 logarithm function	
m	Mass	kg
m_e	Electron rest mass	kg
m_S	Mass of species s	kg
М	Plasma molar mass	kg/mol
\bar{M}	Average molar mass of gas mixture	kg/mol
M_S	Molar mass of species s	kg/mol
n	Volumetric number density	$1/m^{3}$
n _e	Electron volumetric number density	$1/m^{3}$
$^{\mathrm{n}}H$	Atomic hydrogen volumetric number density	$1/m^{3}$
Nav	Avagadro constant	1/mol
N_S	Number of individual chemical species in gas mixture	
η_1	Stoichiometric coefficient prior to chemical reaction	
η_2	Stoichiometric coefficient following chemical reaction	
$\pi \bar{\Omega}_{s,r}^{(1,1)}$	Collision integral between s and r of first kind	m^2
$\pi \bar{\Omega}_{s,r}^{(2,2)}$	Collision integral between s and r of second kind	m^2
р	Pressure	Pa
$ec{p_e}$	Electron momentum	kg - m/s
$P\alpha$	Pressure of species α	Pa
pe	Electron pressure	Pa
p_0	Standard atmospheric pressure	Pa
PACVD	Plasma-Assisted Chemical Vapor Deposition	abbr.
PEC	Perfect Electric Conductor	abbr.
$ar{\mathcal{P}}$	Time-averaged absorbed microwave power density	W/m^3

\mathcal{P}_{abs}	Steady absorbed microwave power density	W/m^3
\mathcal{P}_{tot}	Total absorbed microwave power density	W
π	pi	
$\hat{\phi}$	Azimuthal direction unit vector	
q	Electron charge	C
\vec{q}_{lpha}	Vector heat flux	W/m^2
\mathbf{q}_{S}	Charge on species s	C
Q	Quality factor	
Q_{et}	\mathbf{Q}_{ij} from electrons to Hydrogen translational modes	W/m^3
Q_{ev}	\mathbf{Q}_{ij} from electrons to Hydrogen vibrational modes	W/m^3
\mathbf{Q}_{f}	Volumetric flow rate	sccm
\mathbf{Q}_{H}	Heat flux	W/m^2
Q_{ij}	Volumetric power transfer density from i to j	W/m^3
Q_{rad}	Volumetric power loss due to radiation	W/m^3
Q_{tv}	\mathbf{Q}_{ij} from Hydrogen translational to vibrational modes	W/m^3
\hat{r}	Radial direction unit vector	
\vec{r}	Generic spatial vector	m
R	Gas constant	J/K - mol
R_e	Reynolds number	
ρ	Volumetric mass density	kg/m^3
ρ_S	Volumetric mass density of species s	kg/m^3
$ ho_e$	Electron volumetric mass density	kg/m^3
R	Real component operator	
\vec{S}	Electromagnetic Poynting vector	W/m^2
sccm	Standard cubic centimeter-per-minute (see $Q_{f})$	abbr.
SOR	Successive Overrelaxation	abbr.
$\hat{\sigma}_{e}$	Complex electric conductivity	S/m

$\sigma \chi$	Collision cross section between electrons and neutrals	m^2
T_e	Electron temperature	K
T_g	Neutral and ion species temperature	K
$T_{\mathcal{V}}$	Hydrogen vibrational modes temperature	K
t	Instantaneous time	s
τ	Time constant	s
$\hat{\tau}$	Kinematic viscosity tensor	Pa
$\theta_{v,s}$	Characteristic vibration temperature of species s	K
\hat{U}	Internal thermal energy per unit mass	J/kg
μ	Kinematic viscosity of gas mixture	kg/m-s
μ_0	Permeability of free space	H/m
μ_{T}	Relative permeability	
\vec{v}	Average vector gas velocity	m/s
v_r	Radial component of average vector gas flow	m/s
v_{th}	Electron thermal velocity	m/s
$v_{\mathcal{Z}}$	Vertical component of average vector gas flow	m/s
ν_{eff}	Effective collision rate between electrons and H	Hz
ν_S	Rate of chemical production of species s	Hz
W_S	Net molar production rate of chemical species s	$mol/m^3 - s$
$\mathbf{W}_{surf,s}$	Net surface molar production rate of chemical species s	$mol/m^2 - s$
ω	Angular electromagnetic wave frequency	rad/s
x_{S}	Molar fraction of species s	
\hat{z}	Vertical direction unit vector	
\mathcal{Z}^+	Set of all positive integers	

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CHAPTER 1

INTRODUCTION

1.1 Diamond

1.1.1 History

Diamond is a unique material. It is just one of several stable forms of carbon. It is chemically inert with pure samples appearing transparent and colorless in the optical wavelengths. Diamond has long been of interest to mankind. It was used as an abrasive for many thousands of years. It is revered for its brilliance and relative scarcity, and is sometimes used for monetary trade. To this day, diamond remains a precious gem in common circulation.

1.1.2 Applications

Diamond is also known for its uncommon mechanical hardness and inherent physical properties. This led to various industrial applications over the last half century including industrial coatings such as saw blades and cutting tools, and applications to hard surfaces and materials.

The optical and thermal properties of diamond have more recently been utilized for various scientific and technological purposes. Diamond lenses and lens coatings have been developed for use in high power lasers and systems. Their use is required under such conditions where material degradation under normal operating conditions is a concern.

Diamond is also known to exhibit semiconducting properties under the right conditions with a relatively wide bandgap. Therefore, the fact that it is considered a semiconductor allows for applications as transistors and electrical devices. In fact, diamond has been utilized in the production and research of diodes. Taking advantage of its unique thermal properties, such devices are able to operate at much higher power densities without degradation compared to similar silicon or III-V semiconductor materials. Thus, they could have significant impacts in the high power transistor industry.

1.2 Synthetic Diamond

Historically, diamond was only obtainable naturally. However, with the increased cost of mining and other economic and ethical factors, natural diamond is becoming more expensive and difficult to find and produce in large quantities. An alternative to natural diamond discovery is to produce diamond via synthetic methods. These diamond samples are known as *synthetic diamond*. Synthetic diamond is becoming a viable option, due in part to its increasing quality and predictable rate of production. However, several considerable hurdles stand in its way of replacing the need for natural diamond mining. The current bottleneck in this process lies in producing large quantities of high quality synthetic diamond at an acceptable rate. This requires improvements in both the quality and production rate for the diamond synthesis process, meaning the underlying physical processes in such systems much be better understood. By developing accurate simulations, this understanding can be greatly advanced at lower costs. Thus, the drive for more efficient, accurate, and powerful simulations is underway.

In order to provide suitable context for the present work, a brief history of synthetic diamond and related modeling research is required. Michigan State University (MSU) has

played a major role in the development of Microwave Plasma-Assisted Chemical Vapor Deposition (MPACVD) reactors for diamond film growth [1–5]. A good review of the history of MPACVD, and synthetic diamond growth itself, is given in [3] and is paraphrased in the following paragraphs. A history of related numerical modeling will also be given.

1.2.1 High Pressure Production

Synthetic diamond growth is divided into two categories: high pressure (HPHT) and low pressure deposition. Here, *high* pressure growth (via high pressure, high-temperature or HPHT) represents pressures exceeding several thousand times greater than standard atmospheric pressure. The basics of both are discussed in the following paragraphs.

The objective of the HPHT process is to mimic conditions necessary for natural diamond growth. During natural growth, carbon in the earth's mantle is heated and pressurized to extreme conditions. This causes the atoms in the carbon to align at the atomic level, resulting in a highly ordered crystal structure. Only under these extreme conditions is diamond produced naturally.

In order to recreate these conditions in HPHT growth, a quantity of graphite is used as a seed. This graphite is then pressurized under the weight of a diamond-tipped anvil and heated in a furnace. Pressures produced during HPHT growth often exceed several GPa, with temperatures reaching several thousand Kelvin. These pressures and temperatures roughly mimic those produced in the earth's mantle during natural growth. After a length of time, the graphite has been aligned on the atomic level, and transforms to diamond. The HPHT method results in small, volumetric, and pure diamond samples. Large synthetic diamonds are difficult to produce via HPHT due to the difficulties associated with applying an extreme pressure uniformly over a brittle substance. Moreover, the diamonds produced are similar to those mined naturally resulting in polyhedral shapes. HPHT often results in very pure synthetic diamond. Of course, this is dependent on the purity of the initial graphite sample and the cleanliness of the system during growth.

1.2.2 Low Pressure Production

Low pressure synthetic diamond production is often achieved via some application of the Chemical Vapor Deposition (CVD) process. The CVD method has been used in the production of numerous materials, and is not limited to diamond. For example, CVD is popular in the semiconductor industry, where it is often used to produce aluminum or arsenide-based compounds for use in transistors. Its advantages include growth within a relatively controlled environment, and the capability of large-area deposition.

The fundamental physical process for material deposition and production in CVD is the chemical reactions of gas species at the growth surface. During the CVD process, one or a mixture of gases flow into a chamber containing the growth surface and a chemical precursor. The chamber is typically under vacuum, with operating pressures of μ Torr to atmospheric pressure. This gas flows into the chamber, and chemical reactions take place between gases and the precursor at the substrate. The newly-produced chemical species then migrate toward the growth surface and attach, forming a new material layer. At the same time, more chemical reactions are taking place with more species migrating toward the surface. This process is indefinitely repeatable, only ceasing once the gas flow is stopped or new species no longer move to the surface.

In the case of diamond production, the feed gas is typically a mixture comprising of predominantly hydrogen with a small percentage (<10%) methane [1, 2, 4, 5]. The methane contributes the carbon necessary for diamond production, while the hydrogen is used as a chemical reaction precursor for the production of various other species. These are complex reactions that are not completely understood. However, a significant amount of research has been conducted in this area, and generally well-known approximations to empirical data are often made. For example, it is known the standard CVD production method does not supply the energy necessary for some of the important precursor chemical reactions required for diamond growth at the substrate surface. A plasma is thus utilized to transfer energy to

those species requiring activation during chemical reactions. The result is diamond deposition via *plasma-enhanced* or *plasma-assisted* CVD (PACVD).

Even in the PACVD process, there are many well-known and studied deposition methods. These include hot filament, direct current, and Microwave PACVD (MPACVD). In all of these systems, the basic principle of the plasma capturing and transferring energy to the necessary chemical reactions remains. The basic principle of MPACVD systems is that energy is transfered to the much less massive electrons via their high frequency oscillations induced by the microwave electric fields. The energy is then transferred to the other heavy species via chemical reactions, allowing for carbon, and therefore diamond, deposition at the growth surface. A much more detailed description of this process is provided in Chapter 2. MPACVD will be exclusively considered as the primary diamond film growth method from hereon.

1.3 MPACVD Systems

1.3.1 History

In order to provide context for MPACVD modeling, a brief history related to the development of synthetic diamond and MPACVD systems is provided in the following paragraphs. After many unsuccessful attempts in the first half of the twentieth century, Bundy, *et. al.* were the first to report the successful synthetic production of diamond in 1955 [6], using a HPHT process involving pressurizing a molten carbon sample toward the thermodynamic diamond transition. This ushered in the era of HPHT diamond growth, which is still used today.

In low pressure diamond deposition, carbon is atomically deposited at the growth surface. Thus, the goal is to produce free carbon atoms in a stable manner. The first report of low pressure diamond growth can be traced to Eversole, who patented the growth mechanism in 1962 [7,8]. Hydrocarbon gas was passed over a diamond seed at very low pressures (<1 Torr) and moderate temperatures (600-1000 C). This resulted in diamond depositions of several milligrams, and signaled the first successful synthesis of diamond at low pressures [8].

Several years later, Angus *et. al.* reported the first successful synthetic diamond growth specifically via Chemical Vapor Deposition (CVD) [9]. Pure methane gas, along with mixtures of methane and hydrogen gases, were heated to approximately 1300 K. Pressures ranging from roughly <1% to almost 60% atmosphere were used in experimental runs of several hours. This resulted in diamond deposition in upwards of several milligrams.

The rate of diamond deposition was greatly increased when Spitsyn *et. al.* and Matsumoto *et. al.* reported their findings around 1980 of several μ m/hr [10–12]. Their contributions include the selection of a methane-to-hydrogen ratio around 1:100, which is still used today.

The following year, the Matsumoto group was the first to report high frequency plasma enhanced deposition of diamond [13]. Growth on non-diamond surfaces including silicon were reported for a methane fraction of 1-3%. Absorbed powers ranged from 300-700 Watts at relatively low temperatures (<1000 C). Pressures were restricted to <60 Torr. This resulted in a maximum growth rate of 3 μ m/hr; comparable to their previous works.

MPACVD has become a prominent growth technique for diamond deposition since then. Several distinct reactor designs have been developed [2, 3, 14–16]. Various additional gases and mixing ratios have been reported, leading to improved deposition rates [17–19].

In the mid 2000s, work began on investigating growth at higher pressures [4, 5, 20]. It was realized that such conditions increase the deposition rate and diamond quality [4, 5]. Thus, the MSU MPACVD reactor operating at higher pressures (>20% atmosphere) will be used as the example reactor for the numerical simulations from hereon.

1.3.2 Advantages of MPACVD Diamond Growth

MPACVD systems have many advantages over similar PACVD diamond deposition methods. High deposition rates extending into the tens of microns per hour have been reported [5, 21]. This is comparable, if not higher, than similar PACVD systems mentioned previously.
Moreover, the system geometry is often tunable, allowing for efficient and maximized growth over the characteristic lengthy experimental run time [5]. Finally, their behavior at lower pressure conditions is relatively well understood with several decades of data to draw from [4, 5, 21, 22]. This allows for improved overall efficiency and deposition rates.

1.3.3 Higher Pressure Experiments

MPACVD systems have traditionally operated at pressures not exceeding roughly 150 Torr. This resulted in stable plasma behavior for long time periods. Growth rates of up to 5 μ m/hr have been reported when operating with up to 3 kW of microwave power. The rather lengthy period of constant operation led to many improvements in the reactor design and tuning, ultimately improving the diamond quality and growth rate. At the same time, numerical models were developed to aid in the understanding of their operation. These models have been successful in predicting MPACVD system behavior at these pressures. These have also been employed to aid in the design of new reactor designs meant to run at the same pressures.

Recent experiments conducted at higher pressures (approaching 300 Torr) have been performed in the last several years with the majority of this work being carried out at Michigan State University [5, 21]. While maintaining several kilowatts of power, the operating pressure often reaches between 200 and 300 Torr [5, 21]. Experimental results have confirmed higher growth rates at such conditions [5]. The sample quality at these pressures is also higher than similar diamond samples grown at lower pressure conditions. This suggests that simply increasing the pressure during diamond deposition may lead to improved deposition rates and sample quality.

However, the plasma behavior and properties at these operating conditions are not completely understood. For example, during higher pressure MPACVD operation, the plasma has been observed to *lift off* the substrate apparently influenced by some buoyant force [5]. It has also been known to move around the plasma region, even forming below and outside of the substrate pedestal toward the reactor floor. These observations have led to the hypothesis that the gas flow may be the cause of such adverse effects. The hydrogen and hydrocarbon gas mixture flows throughout the plasma region regardless of pressure. At a constant calibrated flow rate, its inlet flow speed is expected to decrease with increasing operating pressure. At the same time, the overall flow speed within the plasma is expected to increase with increasing pressure due to increased gas temperature gradients. This is important to the overall plasma behavior and properties, and may influence the plasma position. However, it is nearly impossible to empirically measure such effects during system operation due to the high temperatures present, and the fact that such a measurement would likely influence the plasma properties itself. Thus, numerical models would provide the necessary insight into these important processes and quantify their effects. Unfortunately, unlike the standard lower pressure conditions, no numerical models currently exist that accurately describe the plasma behavior under these operating conditions.

1.4 Multiphysics Plasma Models

1.4.1 Motivation

Although the end result in the MPACVD process is the atomic deposition of carbon over a surface, understanding the complex processes occurring in the plasma above the surface is of significant importance. For example, characterizing its chemical behavior can lead to estimations of the rate of atomic carbon production and its constituents. The localized density of various species may also be determined. Thus, the behavior of the plasma and its related processes will remain the primary focus from here on.

1.4.2 History

The development of numerical simulations of PACVD systems allowed for the first time the prediction of these systems before they were physically built. This resulted in the ability to predict growth mechanisms in terms of geometries and system conditions before any hard-ware was developed. Recognizing these possibilities, numerical models and their accurate development have received much attention. A brief background on their development will now be presented.

High frequency induction plasmas were some of the first systems to be numerically modeled, with the first reported in the late 1960s. One of the first multiphysics models coupling both electromagnetic fields with high frequency plasmas was introduced by Armstrong and Ranz in 1968 [23]. Analytic derivations were used to model the fields within a radio frequency induction coupled plasma. Constant temperature profiles were assumed. Power loss through both radiative and convective processes were included.

Improving upon the constant temperature profile assumption, Miller and Ayen proposed a similar two-dimensional model for a similar system the next year [24]. This was a finitedifference numerical model, but did not couple with the imposed electromagnetic fields. Temperature and current distributions were plot against various geometry parameters, and compared to experimental agreement. Boulos *et. al.* later developed a coupled, multiphysics numerical model that accurately coupled both electromagnetic fields, temperature profiles, and flows [25, 26].

In the mid-1980s, Mostaghimi *et. al.* introduced multiphysics, fully two-dimensional models [27, 28]. Charge, momentum, and energy were all explicitly conserved in the plasma flow module. Two years later, Mostaghimi *et. al.* introduced a second temperature specifically governing the electrons [29]. This was developed for argon plasmas in a radio frequency inductively coupled plasma torch. These became the first instances of a two-dimensional multiphysics model for high frequency coupled plasmas.

One of the first plasma models describing the CVD process was introduced by Pfender et. al. in the mid 1990s [30]. This work described the reactive flows for a supersonic plasma jet nozzle. About the same time, this group also introduced the Thermal Plasma CVD simulation [31]. This model described the chemical and thermal properties of methanehydrogen gas mixtures for supersonic and high speed CVD reactors for diamond growth.

In the mid-1990s, Hassouni *et al.* reported on their development of a one-dimensional MPACVD reactor model [32]. In 1999, Hassouni *et. al.* reported a two-dimensional, coupled multiphysics numerical model specifically designed for hydrogen-based low pressure MPACVD reactors [16]. A finite-difference time domain (FDTD) model was used to update the electromagnetic fields, from which the absorbed power density was calculated. This was then fed to the plasma module, where the two temperature model used by Mostaghimi was again employed. Eight different hydrogen species, and electron distributions were solved via a Gauss-Seidel line relaxation method. This model was only valid at lower pressures (<20% atmosphere), where convective and viscous forces were assumed to be negligible and thus neglected.

The work by Hassouni *et. al.* has been recently improved upon by including a onedimensional hydrocarbon module [33] and temporal response [34]. However, these models remain valid only within the lower pressure regime. This is one of the significant limitations of the current simulation capabilities. Thus, a primary objective of this work is to develop a model capable of simulating systems at higher pressures.

Previous MPACVD models have been developed which include convective flows and forces [35–39]. Some of these models have reported results extending above the lower pressure limit of 150 Torr [36, 38, 39]. Time-dependent convective flow models were used to treat the non-linear convection terms. Vector flow fields were provided in several of these works [35–37]. The only fully coupled, multiphysics MPACVD simulation was that of Koldanov *et al.* [35]. However, the reported pressures remained below 100 Torr.

1.4.3 Current State of MPACVD Modeling

As stated previously, current MPACVD models omitting or ignoring convective flows and momentum conservation remain limited to lower pressures (< 150 Torr) [16, 33, 34]. Those that do include convective flows either do not include electromagnetic fields in a coupled manner [36–38], or do not extend to the higher pressures where convective flows are expected to influence the plasma properties [35]. No known reports of a fully coupled, multiphysics MPACVD model capable of simulating plasma behavior at pressures exceeding 150 Torr while also including convective flows is known to exist. The primary thrust of the current work is to develop a fully coupled, multiphysics model which includes momentum conservation in the plasma modeling scheme.

1.5 Contributions

The objectives of this thesis are related to the development of a plasma simulation that can operate at higher pressures (up to 300 Torr). Specifically, these objectives will include the following, listed in order of importance:

- 1. Including convective flow forces via the momentum transport equation (average gas flow, convective and buoyant forces, local pressure gradients, etc.)
- 2. Developing an internal substrate temperature model
- 3. Developing a more stable and numerically efficient simulation

These objectives are discussed in more detail in the following chapters.

CHAPTER 2

PROBLEM STATEMENT

The basic operation, various configurations of, and important characteristics pertaining to MPACVD reactors are now discussed. Since the beginning of their development several decades ago, MPACVD reactors have been studied extensively with the goal of improving both the diamond deposition rate and sample quality. This resulted in a number of different approaches. The following section details the principal MPACVD designs that have been reported. Extending from these designs is a seemingly endless stream of systems with numerous configurations, operating modes, and intricacies, each with their own advantages and disadvantages. An overview of these systems is now presented.

2.1 Introduction to MPACVD Systems

2.1.1 MPACVD System Configurations

Several different MPACVD system configurations have been developed and reported over the last several decades. Many of these MPACVD systems are presented elsewhere in the literature including detailed descriptions of their operation and performance [4, 5, 16, 21, 22, 33, 34, 40–44]. For reasons of operation familiarity and easy access to geometric and experimental data, the class of Michigan State University MPACVD reactors are chosen as the primary systems of choice from hereon. These will be described in the following paragraphs.

The Michigan State University MPACVD reactor is based upon a main cylindrical cavity with a substrate pedestal at its base. A schematic of the MSU MPACVD system is provided in Fig. 2.1.

In the MSU reactor, the microwave energy is fed into the system via a coaxial waveguide located at the top of the main chamber. This configuration is designed to support a TM₁₀₃ like dominant mode in the microwave frequency range. The reactor height is thus chosen to be roughly $3\lambda_0/2$, with λ_0 being the free space electromagnetic wavelength at the excitation frequency [4]. With an input microwave power frequency of 2.45 GHz, this corresponds to a reactor height on the order of 20 cm. This ensures reasonable power matching across the feed-cavity interface, leading to efficient power absorption by the plasma.

The diamond sample and growth surface is located at the top edge of the pedestal. As will be noticed from the proceeding configurations, this growth surface is often raised from the bottom of the main reactor chamber. This serves to improve the coupling between the plasma and the incident microwave power by effectively positioning the plasma within the electromagnetic mode structure [4, 5].

Other research groups have been known to use this reactor configuration outside of Michigan State University. For example, experimental data measured from, and simulation results based upon, a similar MPACVD reactor have been reported by Koldanov, *et al.* [35]. Similarities can also be found between the MSU MPACVD reactor and those developed by other research groups. For example, a similar reactor configuration was developed by the CVD Diamond group at the University of Paris LIMHP. Many common characteristics are observed, including a cylindrical main cavity, a microwave coaxial feed at the top of the main reactor chamber, a raised deposition surface pedestal, and a main chamber height dependent on half-integer free space wavelengths [16, 34].



Figure 2.1: Saggital view of the MSU MPACVD system. [4]

2.1.2 MSU MPACVD System Overview

What follows is a description of the main components and their purpose during nominal system operation. Those geometry components labeled in Fig. 2.1, along with the important omitted components during labeling, are described.

Microwave power is generated external to the system via a magnetron source. This power is delivered to the PACVD chamber via a waveguide structure. The microwave power is then introduced into the main cavity via the coaxial waveguide located at the top the of reactor chamber as denoted by the thatched arrow pointing along $-\hat{z}$. The coaxial waveguide dimensions are chosen to provide the maximum power transfer between it and the main reactor chamber at the designed microwave operating frequency of 2.45 GHz. The excitation probe located at the center of the coaxial waveguide forms the center conductor, is adjustable, and is used to tune the reflected (and ultimately absorbed) power during operation. Minimizing the reflected power necessarily improves the power absorption by the plasma and decreases the power lost to the reactor walls via resistive loading.

The main reactor cavity height is also adjustable. Like the antenna probe, the cavity height tunes the amount of power absorbed by the plasma by altering the electromagnetic field intensity and mode formation within the main cavity. Electromagnetic fields in the cavity form a standing wave pattern. This pattern depends heavily on the reactor configuration, its various geometry parameters, and the microwave discharge properties.

The growth surface and substrate rest on a raised cooling stage. This cooling stage acts to regulate the substrate temperature during deposition via an internal closed water loop. Its surface temperature can exceed 1500 K due to power deposited via species collisions and thermal conduction from the much hotter plasma. Its position is also tunable through the adjustment of shims located at its base. However, these cannot be changed during the deposition process. Instead, it must be adjusted between experiment runs. Similar to the main cavity height and probe positions, the vertical position of the substrate greatly affects the plasma properties and position.

Another main component in the MSU MPACVD reactors is the silica bell jar. This bell jar (sometimes referred to as the *quartz dome*) acts to contain the hydrogen-hydrocarbon gas mixture separated from the rest of the reactor cavity, which is at atmospheric pressure. It also serves to confine the plasma and its available formation region to the volume in the immediate vicinity of the substrate. In an electromagnetic sense, the bell jar is translucent to the electromagnetic fields, with a (essentially) purely real component of permittivity. Losses across this material during electromagnetic power transfer and scattering within the reactor are negligible. However, it does affect the electromagnetic field patterns, and so its position remains fixed.

To the immediate outside of the cooling stage outer radius is a small vacuum gap where the excess hydrocarbon feed gas exits the plasma region. This is depicted in Fig. 2.1 by the downward arrows labeled *Processing Gas Exit* on either side of the cooling stage structure. It allows the hydrocarbon gas to escape the chamber to avoid accumulation during deposition. The physical system pressure is measured downwind from this outlet, which is an important measurement used to characterize the system during deposition. Plasma is not expected to form in this region, and would be undesirable.

Forming the outer boundary of the processing gas exit region is the substrate silica wall. This is labeled as the *Fused Silica Tube* in Fig. 2.1. Its main purpose is to form the outer wall of the gas exit region with minimal effect on the electromagnetic field pattern. This is achieved by using the same silica or quartz material as in the bell jar and keeping its thickness to a minimum. Its thickness and inner radius with respect to the outer pedestal wall is fixed. However, it always joins with outer substrate lip at its top edge.

With the feed gas exit point detailed, the feed gas *entry* point must be described. Experimentally, the hydrocarbon gas flows through several small holes distributed azimuthally toward the base of the reactor. This is labeled as the *Feedgas Input* in Fig. 2.1 at its bottom left corner.

The last of the primary components to describe in the MSU MPACVD reactor are the outer baseplates. These baseplates are locate at either side of Fig. 2.1 below the substrate vertical position. They partition the reactor into two separate electromagnetic regions: the main reactor where the TM_{103} mode is supported, and the lower region below the substrate where TEM modes are known to be supported [5,21]. With the adjustable cavity height setting its upper boundary, the top surface of the baseplate sets its lower electromagnetic boundary. These also affect the field formation below the substrate, which in turn affects the plasma properties via power efficiency and coupling.

2.2 Basics of MPACVD operation

A detailed description of the important physical processes and their resulting effects on the typical MPACVD reactor and corresponding plasma is provided. This will include the important chemical reactions taking place both in the bulk plasma region, as well as a description of those important to the deposition process itself. The latter occur only at the growth surface and are important to both the successful and efficient deposition of diamond.

2.2.1 Detailed description of physical processes

The collisions between electrons and heavy species result in the production of new species via chemical reactions. Many of these chemical reactions either occur at very low rates or in relatively few numbers, and so are not discussed in detail. However, they will be necessary to track as they may represent precursor production paths for various important hydrogen and hydrocarbon species in the MPACVD plasma. These chemical reaction data are listed in several external sources for further reading [45].

The electron collisions with molecular hydrogen dominate MPACVD plasmas, and typically lead to the excitation of an excited vibrational mode [16, 45]. If it contains enough energy, the molecular hydrogen will dissociate into atomic hydrogen via the following chemical reaction

$$H_2 + e^- \to 2H + e^- \tag{2.1}$$

where H_2 , H, and e^- represent the molecular and atomic hydrogen, and electron chemical species, respectively. Eq. (2.1) represents one of the primary methods through which atomic hydrogen is produced in MPACVD systems. This statement holds true regardless of operating conditions such as pressure or absorbed power levels.

At higher operating pressures, three body recombination becomes important. It is also at these conditions, where the electrons and heavy species approach the same temperature, that energy is also transferred from the electrons to the hydrogen and hydrocarbon species directly via elastic collisions [45]. Furthermore, the reversible production and consumption of atomic hydrogen with other heavy species is also possible [45].

MPACVD plasmas are typically considered to be under local equilibrium conditions in the bulk region. Thus, the production of atomic hydrogen within the plasma must be balanced by its consumption either in the bulk plasma or at the reactor boundaries. The recombination of atomic hydrogen requires upwards of several seconds at typical MPACVD operating conditions [46]. This suggests its primary consumption or extraction takes place via recombination and attachment at the substrate and reactor walls.

In the presence of methane, the atomic hydrogen may also recombine to form molecular hydrogen and hydrocarbon species via the two reactions

$$H + CH_3 + M \to CH_4 + M \tag{2.2}$$

$$H + CH_4 \rightleftharpoons CH_3 + H_2 \tag{2.3}$$

where M represents a heavy molecule. However, due to the small percentage of methane typically present in the feed gas mixture within MPACVD systems, these reactions represent only a fraction of the total recombination of the atomic hydrogen.

As a result, the atomic hydrogen predominantly diffuses and is lost via recombination

at the diamond surface. This recombination rate is vital not only to the plasma properties in order to balance its concentration in the bulk region, but also in the diamond deposition process. As such, it has received much attention and has been measured by several groups [47–51]. The resulting recombination reaction

$$2H \to H_2$$
 (2.4)

is exothermic, depositing between 20 and 100 *kcal/mol* on the diamond surface, which may represent the primary substrate heating mechanism in many plasma-enhanced diamond deposition systems [45, 52].

The chemical reactions involving hydrocarbons is likewise complex and lengthy to fully describe. These species are similarly produced via collisions between heavy species, primarily atomic hydrogen which was described earlier to dominate the radicals within the gas mixture. Depending on operating conditions and physical location within the plasma, acetylene and the methyl radical CH_3 are known to be abundant in comparison to other hydrocarbon radicals [33, 34, 45]. Methane dominates even atomic hydrogen in mole fraction in the bulk plasma region at lower operating powers and pressures [45, 53, 54]. However, for the higher pressure operating conditions which are of particular interest here, the atomic hydrogen is known to dominate hydrocarbon radicals [45, 53, 54]. Thus, the hydrocarbon chemistry becomes rather complex with rates of production and consumption depending heavily on the operating conditions. Further insight and detail regarding these hydrocarbon processes in the bulk plasma region are provided elsewhere [45].

Of course, to this point the process of carbon transfer to the diamond surface has remained untouched. That is, the production of atomic hydrogen and its recombination at the surface, along with the production of carbon radicals in the bulk plasma have been discussed. However, the method by which carbon recombines at the growth surface ultimately resulting in diamond deposition has not been discussed. This would of course require a hydrocarbon molecule to diffuse to the diamond surface as the presence of at least one carbon atom is required for sustainable deposition. A series of experiments at Rice University in the early 1990s concluded that it is in fact the methyl radical CH_3 which is primarily responsible for the deposition of diamond [45, 55–57]. This result was independently confirmed by others, with further experiments suggesting other radicals may also contribute but ultimately result in slower growth with worse quality [45, 58, 59]. Likewise, atomic carbon may play a small role in the deposition process, but results have not been conclusive of this conjecture [45]. Thus, it appears both acetylene and the methyl radical CH_3 recombination at the diamond surface contribute to the deposition process.

At this point, the chemistry at the diamond surface must be addressed. Due to the high atomic hydrogen diffusion at the sample surface, the majority of this area is hydrogenated and nonreactive [45]. However, for the small fraction that remains reactive, the surface sites are governed by a balance between the following two reactions

$$C_d H + H \to C_d * + H_2 \tag{2.5}$$

$$C_d * + H \to C_d H \tag{2.6}$$

where $C_d H$ represents a hydrogen-terminated surface site and C_d^* is likewise a surface site without hydrogen terminated [45]. Goodwin *et al.* showed that Eq. (2.6) is the dominant hydrogen termination reaction at typical atomic hydrogen mole fraction levels [60]. Surface chemistry at these open sites is equally important and discussed elsewhere [45].

2.2.2 Role of plasma in MPACVD

From the above description, it is clear chemical reactions between species play an important role in the plasma dynamics within MPACVD reactors. Interactions between these physical processes are important not only for the correct operation of the system, but also for the successful deposition of diamond. Aside from chemical reactions, the transport of various physical quantities via several kinetic phenomena are equally important in MPACVD systems. These processes include the transport of mass, momentum, and energy throughout the gas flow region via convection, the diffusion of mass and conduction of heat, and energy lost via radiative processes. For example, species are transported throughout the plasma via diffusion and convection processes. This overall process results in a redistribution of mass according to the reactor geometry and energy distribution. Moreover, the average gas flow also affects the flow of species within the plasma, with the quantification of its exact distribution and significance being one of the primary objectives of this work. Similarly, energy is redistributed from hotter to cooler regions according to the laws of thermodynamics. Finally, both the de-excitation of excited electrons and their acceleration result in a net energy loss via radiation. Thus, several complex and important physical phenomena are present within MPACVD systems. These are all interacting on different time and length scales making their interdependence and properties difficult to predict. As a result, these processes must be treated carefully in order to accurately capture the total system behavior.

From the above descriptions, it is clear the role of the plasma in MPACVD systems is to produce and direct the important reactive species toward the diamond surface. Moreover, this plasma must create and maintain the correct physical conditions required for diamond deposition. At the same time, these plasma properties and environmental conditions must remain consistent throughout the duration of the deposition process in order to maximize the growth rate and maintain high quality. It is this combination of complex interrelated dependencies and conditions which make the deposition of diamond difficult.

2.3 Motivation for Numerical Model

The system described above represents an extremely complex and nonlinear set of interacting processes. While each individual process is typically well understood and characterized, the interactions between the dynamics within a complex material environment is not necessarily well understood. Moreover, the basic understanding or prediction of the system is not easy and often is unavailable using pen and paper calculations. Instead, a numerical approach is typically used to predict, or simulate, these MPACVD systems. This same approach is developed here, as it provides the most approachable and applicable method for predicting the system behavior under a variety of conditions. Unlike physical MPACVD systems, a simulation is easily adjusted in terms of several variables including geometry, operating conditions, and system makeup in order to evaluate future designs.

Aside from the numerous advantages associated with a numerical model of the MPACVD system, several concerns often arise. Many of these concerns are directly related to the particular system at hand, and are listed below. For example, one difficulty in the current simulation is capturing the inherently nonlinear behavior of the entire system in a numerically efficient manner. That is, the formation and stability of the plasma even during experiments is sometimes difficult to ensure. Coupling this need with reasonable numerical efficiency is also a difficult task. This nonlinearity of the system behavior is directly related to the interdependence of the many physical processes. For instance, the electromagnetic field propagation is heavily influenced by the plasma position and properties. Moreover, the power absorption, which is also dependent on the electromagnetic field structure, strongly influences the plasma properties and formation. These are just a few examples of this strong interdependence between physical processes resulting in nonlinear system behavior.

On top of predicting future reactor configurations and operating conditions, the numerical simulation of MPACVD reactors provides important insight into the behavior of the system not otherwise available from experiments. That is, the observation and analysis of diamond deposition in MPACVD reactors is often limited to qualitative data. Aside from substrate temperatures and optical images captured via optical cameras, the direct measurement of important plasma properties such as gas temperature and electron number density are difficult to achieve [40]. Moreover, it may also be difficult to single out important precursor species from others present in the plasma to take measurements. Numerical simulation of these systems provides a tool for accessing this information easily and efficiently. It also allows for the reevaluation of MPACVD system performance under a change of reactor configurations and operating conditions. What may take several days to even weeks to perform experimentally, numerical simulations can often predict in a matter of hours or even minutes. Improved efficiency in the evaluation of reactor performance is expected to result in many more reactor configurations and operating conditions, which in turn may lead to more efficient diamond deposition of higher quality.

The motivation behind the coupled, multiphysics numerical simulation of the MPACVD reactors has been discussed, with numerous advantages over experimentation listed. These include the further and ease of analysis of important physical properties, along with the ability to more quickly evaluate changes to reactor designs and configurations. As a first step in the simulation process, the mathematical framework must be derived. This includes the governing mathematical equations and applicable boundary conditions.

CHAPTER 3

MATHEMATICAL FORMALISMS

Many complex and interrelated physical processes are present in MPACVD reactors during standard operation. Physically, these processes are all ongoing simultaneously and dependent on one another. In order to mimic this interdependence between physical processes, the most accurate solution is to simulate these in a multiphysics framework. This necessitates the understanding of each individual process, as well as their interdependence, in order to accurately describe the entire system. The result is an accurate model of the entire system. The numerous equations governing the physical operation of the MPACVD system will be derived, with its theoretical foundation presented, in the following paragraphs.

3.1 Choice of Temporal Frame

The characteristic time scales of inherent plasma and electromagnetic processes within MPACVD systems can range from picoseconds to milliseconds or more. On the other hand, MPACVD systems typically operate for several hours, days, or even weeks in order to deposit appreciable amounts of diamond. Thus, it is the long-term, effectively steady behavior of the system that is important to capture in the current simulation. As a result, this steady behavior and thus time independence is applied across the entire simulation.

3.2 Electromagnetics

A derivation of the equations governing the electromagnetic fields and their propagation within the MPACVD system is now presented. As stated previously, these electromagnetic fields are assumed to be purely time-harmonic.

3.2.1 Maxwell's Equations

The frequency domain, point form of the four oft-referenced Maxwell's Equations govern the electromagnetic fields within the MPACVD reactor. These are

$$\nabla \cdot \vec{D} = \rho_e \tag{3.1a}$$

$$\nabla \cdot \vec{B} = 0 \tag{3.1b}$$

$$\nabla \times \vec{E} = -j\omega \vec{B} \tag{3.1c}$$

$$\nabla \times \vec{H} = \vec{J_e} + j\omega \vec{D} \tag{3.1d}$$

where \vec{D} and \vec{B} are the electric and magnetic flux densities, respectively, \vec{E} and \vec{H} are the electric and magnetic field intensities, respectively, ρ_e the volumetric electric charge density, $\vec{J_e}$ is the electric current density, j the imaginary unit, and ω the radial electromagnetic excitation frequency. Before manipulating and simplifying the above expressions given in Eq. (3.1), several assumptions and approximations are applied.

3.2.2 Physical Approximations and Assumptions

Charge accumulation is neglected within dielectrics, and all metal surfaces are assumed to behave as perfect electric conductors (PECs). The electromagnetic field solutions are assumed to be purely oscillatory in form, resulting in trivial solutions to both Eq. (3.1a) and Eq. (3.1b). The magnetic and electric flux densities are related to their corresponding field intensities by introducing the following material properties

$$\vec{D} = \epsilon_0 \epsilon_T \vec{E} \tag{3.2a}$$

$$\vec{B} = \mu_0 \mu_r \vec{H} \tag{3.2b}$$

where ϵ_0 and μ_0 are the permittivity and permeability of free space, and ϵ_r and μ_r are the relative permittivity and permeability, respectively.

All materials present within the MPACVD system are assumed to be non-magnetic, resulting in $\mu_r = 1$ applied everywhere. This reduces Eq. (3.1) to Eq. (3.3) below.

$$\nabla \times \vec{E} = -j\omega\mu_0 \vec{H} \tag{3.3a}$$

$$\nabla \times \vec{H} = \vec{J_e} + j\omega\epsilon_0\epsilon_r \vec{E} \tag{3.3b}$$

Ohm's Law relates the electric current density to the electric field intensity and the material dependence via Eq. (3.4)

$$\vec{J_e} = \hat{\sigma}_e \vec{E} \tag{3.4}$$

where $\hat{\sigma}_e$ is the complex electrical conductivity. This results in the final form of Ampere's Law as given below in Eq. (3.5).

$$\nabla \times \vec{H} = \left(\hat{\sigma}_e + j\omega\epsilon_0\epsilon_r\right)\vec{E} \tag{3.5}$$

Eq. (3.3a) and Eq. (3.5) represent a set of two coupled, linear equations that completely govern all electromagnetic field scattering, propagation, and absorption within the MPACVD system. They must be solved simultaneously for accurate electromagnetic field calculation.

3.2.3 Final Coupled Form

Eq. (3.3a) and Eq. (3.5) could thusly be solved in their present form via iterative procedures. Instead, Eq. (3.3a) and Eq. (3.5) may be solved simultaneously via one equation by back substituting one solution variable into its corresponding equation.

To begin this process, the electric field intensity is first solved from Eq. (3.5)

$$\vec{E} = \frac{1}{(\hat{\sigma}_e + j\omega\epsilon_0\epsilon_r)} \nabla \times \vec{H}$$
(3.6)

which is then operated upon by the curl operator

$$\nabla \times \vec{E} = \nabla \times \left[\frac{1}{(\hat{\sigma}_e + j\omega\epsilon_0\epsilon_r)} \nabla \times \vec{H} \right] = -j\omega\mu_0 \vec{H}$$
(3.7)

Eq. (3.7) may then be simplified and expressed in terms of the excitation frequency after multiplying through by $j\omega\epsilon_0$. The result is the final electromagnetic field intensity governing equation given in Eq. (3.8) below.

$$\left[\nabla \times \frac{1}{\left(\frac{-j\hat{\sigma}_e}{\omega\epsilon_0} + \epsilon_r\right)} \nabla \times - \left(\frac{\omega}{c}\right)^2\right] \vec{H} = 0$$
(3.8)

The electric field intensity is readily calculated from the magnetic field intensity solution to Eq. (3.8) via Eq. (3.6).

3.2.4 Plasma Influence

Note in Eq. (3.8) the electromagnetic fields are coupled to the plasma influence through the complex conductivity, $\hat{\sigma}_e$, inside the curl operator. This term is calculated from the plasma properties themselves. Also note the spatial dependence of this conductivity is correctly treated and remains inside the curl operator. This will remain important to the overall accuracy of the coupled solution.

3.2.5 Boundary Conditions

With the equations governing electromagnetic energy propagation inside the MPACVD reactor volume now derived, the conditions necessary to enforce at the reactor boundaries are discussed. The assumption of PECs at all outer reactor interfaces requires zero tangential electric fields at these surfaces. Moreover, the same tangential fields must be continuous across dielectric material interfaces. These accurately capture all necessary material boundary conditions applied to electromagnetic fields.

With the governing equations for the electromagnetic field propagation and scattering now stated, the equation used to calculate the absorbed power distribution may now be derived. This will depend on the electric field intensity as derived in the following section.

3.3 Absorbed Power

The electromagnetic absorbed power density is important to the behavior of the plasma discharge in MPACVD systems. Here, it is calculated via a transformation of the timeaveraged absorbed power over one wave cycle to the frequency domain as given in Eq. (3.9).

$$\mathcal{P}_{abs} = \frac{1}{2} \Re\{\sigma_e\} |E_0|^2 \tag{3.9}$$

where \mathcal{P}_{abs} is the absorbed microwave power density, $\Re\{\sigma_e\}$ denotes the real component of the complex electrical conductivity, and $|E_0|^2$ is the square of the complex electric field magnitude. This power density distribution is then passed to the plasma solution module. The total absorbed microwave power may be calculated via

$$\mathcal{P}_{tot} = \int \mathcal{P}_{abs} d^3 \vec{r} \tag{3.10}$$

where \mathcal{P}_{tot} represents the total absorbed power and $\int d^3 \vec{r}$ represents a volumetric integration over the entire plasma region.

3.4 Plasma Physics

The governing equations describing both the macroscopic behavior of the plasma in the presence of the microwave power density and average gas flow are derived in the following section.

3.4.1 Approximations

The approximations applied to the plasma solution module are now listed. These include the reasoning behind their application and an argument for their validity. Their anticipated impact on the overall solution process will also be discussed.

Arguably the most important approximation applied when typically modeling MPACVD plasmas is the assumption of a Maxwellian Electron Energy Distribution Function (EEDF). As electrons represent the primary species via which the majority of the microwave power is transferred to the plasma, their energy distribution function is important when characterizing these systems. By approximating this distribution with a well-known function, the distribution function may be stated analytically. This greatly reduces the number of required calculations at each solution step, in turn allowing for much faster overall computation run times. Thus, approximating the EEDF is advantageous to the overall success and numerical efficiency of the simulation.

For the plasmas supported in MPACVD reactors, it has been shown that the EEDF may be approximated via a Maxwellian distribution [32, 61]. That is, Hassouni, *et al.* developed a one-dimensional transport model located along the axis of symmetry for a MPACVD system [32, 61]. Simulation results were compared against measured experimental data. It should be noted that, as reported by Hassouni, *et al.*, assuming a Maxwellian EEDF overestimates the ionization rate in the plasma, and slightly underestimates the dissociation rate constants used in the mass transport equations [61]. This results in slightly lower atomic hydrogen densities when compared with experimental data. Moreover, a two-temperature EEDF model did appear to provide slightly better agreement with experimental results and avoided this increased atomic hydrogen mole fraction solution [62]. These simulated results remained in agreement with the experimental data due to large measurement error [61]. The resulting vibrational and gas temperatures also closely matched the experimental data. Thus, a Maxwellian EEDF was deemed valid in describing the EEDF for MPACVD systems and is again applied here. The velocity and energy distributions of all other ions and neutral species are also assumed to be Maxwellian. This is a common approximation, as the energy of these much more massive species is often much lower than that of the electrons, and is less likely influenced by external electromagnetic fields, collisions between species, and other factors.

The energies, and thus average temperatures, of the electrons and ions/neutrals must be tracked and solved simultaneously to ensure accuracy during plasma simulations. Due to their large differences in mass, electrons and ions/neutrals represent two very different systems in terms of kinetic energy. The resultant energies, and thus temperatures, associated with these two species are often different, suggesting their separate solution and tracking during the simulation process. As a result, the well-known two-temperature method as proposed by Mostaghimi, *et al.* is applied [29]. This method more accurately captures these important plasma characteristics than similar single temperature models. It also avoids the unnecessary tracking of individual energies for each separate species within the plasma.

MPACVD systems operating at lower pressures have been well-characterized under the assumption of negligible or zero gas flow influence on the plasma. This has been confirmed via countless numerical simulations agreeing with experimental data where this flow is simply neglected [16, 34]. Although momentum transfer is ignored under these conditions, mass transfer must still take place. This is accomplished through diffusive mass flow, where the plasma particles are transfered throughout the plasma region due to macroscopic gradients in density. In the absence of an average plasma flow or for a negligible hydrocarbon gas flow, this net flow of mass is due purely to these diffusion processes. Thus, the plasma behavior and rate of mass transfer during the deposition process is assumed to be dominated by diffusion forces.

For the currently considered higher pressure operating conditions, these diffusion forces are still expected to dominate the transfer of mass and particles within the plasma. However, the average plasma gas flow is not necessarily expected to remain negligible, and is included in the solution process.

Both electric and magnetic fields influence the behavior of charged species within the plasma according to the Lorentz force equation

$$\vec{F} = -q_{\alpha} \left(\vec{E} + \vec{v}_{\alpha} \times \vec{B} \right) \tag{3.11}$$

where q_{α} is the charge associated with species α . Since the species velocities within MPACVD reactors are expected to remain relatively low, the resulting force due to the cross product of the electron velocity and magnetic flux density may be argued as negligible compared to that of the electric field. Thus, the force on charged particles due to the magnetic flux density is neglected from hereon, simplifying the calculations to follow.

The distributions of all physical quantities, and thus variables, contained in the simulation are approximated as spatially continuous [63]. This approximation suggests the application of a fluid-based simulation method, which assumes a statistical distribution of species and temperatures sampled spatially across pre-determined locations. However, discontinuities may sometimes exist in the numerical solution distribution of certain simulation variables. These are avoided through the increased numerical sampling rate or artificial dampening of the nonlinear solution. For the densities and temperatures present in MPACVD systems, this approximation of a continuous and statistical distribution is valid, and will be applied from hereon.

The particular list of chemical species to track during the simulation must be made. From the typical MPACVD feed gas mixture of molecular hydrogen and methane, numerous chemical species are produced and exist within the plasma [33, 34]. These are produced during the microwave power transfer from the electromagnetic field to the electrons, which then transfer energy to various other ions and neutral species. Some of these species are important precursors to carbon attachment at the growth surface and thus vital to the diamond deposition process [45]. Hundreds of chemical reactions are known to exist in MPACVD systems, and have been characterized elsewhere [16, 34]. The choice of which chemical reactions and species to include in the simulation have been scrutinized and demonstrated to accurately capture the important physics [16, 35, 64]. Here, for the purpose of a much simpler numerical simulation, only hydrogen-based ions and neutral species are considered and tracked [16]. This greatly reduces the number of species and chemical reactions to track and update, simplifies the code structure and solution procedure, and improves the overall numerical efficiency of the simulation. Moreover, since the methane percentage used in the MPACVD deposition process often remains below 10%, the majority of the important electron-heavy species chemical reactions and higher density species are expected to be accurately captured.

In bounded plasma systems, a sheath is known to form at material boundaries. This sheath can have a large impact on the overall behavior and properties of the plasma. It is often on the order of a deBye length, and thus can exhibit length scales much smaller than the overall dimensions of the corresponding plasma. This in turn, often requires very fine numerical resolution in order to accurately simulate. Several approaches for avoiding this fine numerical sampling surrounding this plasma boundary have been proposed, including the *logical sheath* boundary condition [65, 66]. This has been proven to accurately capture the important physics of the sheath region while maintaining sampling rates larger than the deBye length.

In the present model, the boundary conditions will include forcing zero change in the

electron energy, and applying modified species surface reaction and recombination rates. This is a crude approximation to the behavior of the electron energy within the sheath, but avoids the necessity of fine numerical sampling. It also ignores any sort of surface charging which may be present in MPACVD reactors, and may in fact play an important role in the plasma behavior. That is, due to their much greater mobility, the electrons reach the plasma boundaries first and negatively charge these surfaces.

As a result, the charging of the quartz dome in particular could result in electrostatic forces which attract the positive ions and thereby affecting the overall plasma position and behavior. Moreover, the behavior of the species within the sheath layer at the substrate surface is expected to play a vital role in accurately modeling the diamond deposition process and estimating its growth rate. Thus, a more detailed and accurate sheath model would serve as an important improvement on the present numerical solution methods and is left for future implementations of the simulation.

3.4.2 Mass Transport

The mass transport equation represents first and simplest of the three macroscopic transport equations governing the plasma behavior. It relates the net change in each species mass due to chemical reactions with its diffusion throughout the plasma. The mass transport equation may be derived from Generalized Transport Equation[67] by substituting the species mass, m_{α} , for the average general macroscopic variable. Doing so, the mass transport equation becomes

$$\frac{\partial}{\partial t} \left(n_{\alpha} < \zeta >_{\alpha} \right) + \nabla \cdot \left(n_{\alpha} < \zeta \vec{v} >_{\alpha} \right) - n_{\alpha} < \frac{\vec{F}}{m_{\alpha}} \cdot \nabla_{\left(\vec{v} \right)} \zeta >_{\alpha} = \left[\frac{\partial}{\partial t} \left(n_{\alpha} < \zeta >_{\alpha} \right) \right]_{coll} \quad (3.12)$$

with several simplifications readily applied.

First, it is recognized the species mass is a single, scalar value with its average value being equal to itself ($\langle m \rangle_{\alpha} = m_{\alpha}$). The product of $n_{\alpha} < m >_{\alpha}$ was shown to be written

as the volumetric mass density of the species, ρ_{α} . Moreover, the species velocity, \vec{v}_{α} , was already used to represent its average velocity in velocity distribution space, and so is taken as equal to $\langle \vec{v} \rangle_{\alpha}$. Finally, the gradient of species mass in velocity space is assumed to be zero, resulting in the simplified transport equation in Eq. (3.13)

$$\frac{\partial \rho_{\alpha}}{\partial t} + \nabla \cdot (\rho_{\alpha} \vec{v}_{\alpha}) = \left[\frac{\partial \rho_{\alpha}}{\partial t}\right]_{coll} = W_{\alpha}$$
(3.13)

where W_{α} represents the volumetric rate production of mass for species α . Note that the average species velocity, \vec{v}_s , is its total average velocity and remains individual to each chemical species.

Within a multi-component plasma, the total velocity of any species may be treated as a summation of its individual velocity and the average velocity of the plasma as a whole. As a result, the individual species velocity is represented as a change from the average gas, or reference, velocity. This may be expressed mathematically as

$$\vec{v}_s = \vec{v} + \vec{V}_s \tag{3.14}$$

where \vec{v} is the average velocity of the plasma as a whole, and \vec{V}_s is the species velocity associated with a particular species, s. In the present case, this species velocity represents the diffusion velocity.

Substituting the linear summation of the species diffusion and average plasma velocities for the average species velocity in Eq. (3.13) results in Eq. (3.15)

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot \left(\rho_s \vec{V}_s\right) + \nabla \cdot \left(\rho_s \vec{v}\right) = W_s \tag{3.15}$$

where the average plasma flow velocity \vec{v} is typically a known quantity, or may even be negligible for low-flow systems as was often assumed in previous lower pressure MPACVD systems [16,34]. The diffusion velocity for each species is often difficult to calculate or measure directly. Instead, it may be calculated as related to the species diffusion coefficient via

$$\vec{V}_s = -D_s \nabla x_s \tag{3.16}$$

where D_s is the diffusion coefficient associated with species s, and x_s is its mole fraction. The mole fraction is calculated as the fraction of specie number density against the total number density of the plasma

$$x_s = \frac{n_s}{n} \tag{3.17}$$

where n_s is the volumetric number density of specie s at any particular position, and n represents the total volumetric number density of the plasma.

With the diffusion velocity formed in terms of the diffusion coefficient and mole fraction, this quantity may be substituted back into Eq. (3.15). Finally, since a steady-state solution is assumed, the time rate of change in mass is also dropped, resulting in Eq. (3.18)

$$-\nabla \cdot (\rho_S D_S \nabla x_S) + \nabla \cdot (\rho_S \vec{v}) = W_S \tag{3.18}$$

where Eq. (3.18) represents the final form of the mass transport equation.

Here, ∇ · represents the total flux through a closed surface surrounding an infinitesimal volume. The left-hand-side terms represent the flux of mass out of a closed surface via diffusion and convection. The right-hand-side of Eq. (3.18) represents the net volumetric production or consumption rate of mass. Eq. (3.18) governs the change in mass for all chemical species contained in the plasma. Thus, it must be solved N_s times, where N_s is the total number of unique chemical species tracked in the plasma.

3.4.3 Momentum Transport

With the diffusion velocity of each individual species known, the average velocity of the gas flow within the plasma region must likewise be updated. Its behavior is governed separately by the momentum transport equation. This equation has been traditionally ignored in previous lower pressure MPACVD simulations [16, 34]. This was due to its expected negligible contribution to the overall influence on the plasma properties and location. However, this equation must be included in the overall solution scheme when pressure is increased, as the influence of these forces on the plasma behavior are not expected to remain negligible.

The momentum transport equation represents a balance between the rate of change in momentum with the flux of momentum flowing through a closed surface surrounding an infinitesimal volume and the summation of all external forces acting upon said volume. The generalized transport equation is again used as the staring point in this derivation, but this time the species momentum, $m_{\alpha}\vec{v}$, is substituted into the General Transport Equation [67]. As with the mass transport equation derivation, the resultant terms will be individually addressed and simplified in order to simplify and condense the complete differential equation.

Substituting the plasma momentum into the General Transport Equation results in the following expression given in Eq. (3.19)

$$\frac{\partial}{\partial t} (n_{\alpha} < m_{\alpha} \vec{v} >) + \nabla \cdot (n_{\alpha} < m_{\alpha} \vec{v} \vec{v} >) - n_{\alpha} < \frac{\vec{F}}{m_{\alpha}} \cdot \nabla_{(\vec{v})} m_{\alpha} \vec{v} > \\
= \left[\frac{\partial}{\partial t} (n_{\alpha} < m_{\alpha} \vec{v} >) \right]_{coll}$$
(3.19)

where the total plasma velocity average value is again represented by \vec{v} . Once again assuming the species mass is a scalar quantity whose average is equal to its value, Eq. (3.19) is further simplified. Finally, recognizing that the species mass is not a spatially-dependent function, it may be pulled out front of the $\nabla_{(\vec{v})}$ operator resulting in

$$\frac{\partial}{\partial t} \left(\rho_{\alpha} < \vec{v} >_{\alpha} \right) + \nabla \cdot \left(\rho_{\alpha} < \vec{v}\vec{v} >_{\alpha} \right) - n_{\alpha} < \vec{F} \cdot \nabla_{\left(\vec{v}\right)} \vec{v} >_{\alpha} = \left[\frac{\partial}{\partial t} \left(\rho_{\alpha} < \vec{v} >_{\alpha} \right) \right]_{coll} \quad (3.20)$$

At this point, the total velocity of each species may be expanded in terms of its average and

random velocities

$$\vec{v} = \vec{c}_{\alpha} + \vec{u}_{\alpha} \tag{3.21}$$

where \vec{c}_{α} is the random velocity of species α , and \vec{u}_{α} is its average velocity. The velocity gradient operating on the velocity vector results in the identity vector, further simplifying the third term contained in Eq. (3.20). Recognizing $\langle \vec{v} \rangle = 0$, and substituting the expanded velocity terms into Eq. (3.20) yields

$$\frac{\partial}{\partial t}\left(\rho_{\alpha}\vec{u}_{\alpha}\right) + \nabla\cdot\left(\rho_{\alpha}\vec{u}_{\alpha}\vec{u}_{\alpha}\right) + \nabla\cdot\left(\rho_{\alpha}<\vec{c}\vec{c}>_{\alpha}\right) - n_{\alpha}<\vec{F}>_{\alpha} = \left[\frac{\partial}{\partial t}\left(\rho_{\alpha}\vec{u}_{\alpha}\right)\right]_{coll} \quad (3.22)$$

where the average velocity terms inside the divergence operator may be expanded due to their linear and independent nature. The random velocity and volumetric mass density tensor product in the third term of Eq. (3.22) represents the kinetic pressure dyad, \mathcal{P}_{α} [67]. Similar to the EEDF, the velocity distribution is also assumed to be Maxwellian in form. As a result, the pressure dyad reduces to the scalar pressure, p, further reducing its divergence operator to a spatial gradient. The volumetric number density multiplying the average force term may be rewritten as the volumetric mass density multiplying the total acceleration due to external forces. Assuming local charge neutrality, this external acceleration term is only due to gravity, and so may be written as $\rho \vec{g} \cdot \vec{z}$. Finally, Eq. (3.22) may be summed over all species in order to solve for the average plasma velocity, rewritten as \vec{v} and given in

$$\frac{\partial}{\partial t} \left(\rho \vec{v}\right) + \nabla \cdot \left(\rho \vec{v} \vec{v}\right) + \nabla p - \rho \vec{g} \cdot \vec{z} = \left[\frac{\partial}{\partial t} \left(\rho \vec{v}\right)\right]_{coll}$$
(3.23)

The final alteration to Eq. (3.23) comes in the form of the viscous stress tensor. In fluid mechanics, the viscous stress tensor represents the change of fluid motion due to self-interactions dependent on the kinetic viscosity, μ , of the fluid. This can be represented by the collisional term on the right side of Eq. (3.23) and re-written as a divergence operator acting upon the viscosity tensor as

$$\frac{\partial \left(\rho \vec{v}\right)}{\partial t} + \nabla \cdot \left(\rho \vec{v} \vec{v}\right) = -\nabla p - \nabla \cdot \hat{\tau} + \rho \vec{g} \cdot \hat{z}$$
(3.24)

where $\hat{\tau}$ is the viscous stress tensor.

Although compact, Eq. (3.24) is more conveniently expressed and clearly understood when written explicitly in its individual variable components. The chain rule may be applied to the time rate of change in momentum as represented by the first term in Eq. (3.24) yielding

$$\frac{\partial \left(\rho \vec{v}\right)}{\partial t} = \vec{v} \frac{\partial \rho}{\partial t} + \rho \frac{\partial \vec{v}}{\partial t}$$
(3.25)

where the time rate of change of volumetric mass density is forced to zero, which is a result of the time independence assumption from Eq. (3.18). Thus, the total time rate of momentum change may be calculated

$$\frac{\partial \left(\rho \vec{v}\right)}{\partial t} = \rho \frac{\partial \vec{v}}{\partial t} \tag{3.26}$$

In order to set apart only the time rate of change in the plasma velocity, the volumetric mass density divides Eq. (3.24), resulting in the final form of the momentum transport equation

$$\frac{\partial \vec{v}}{\partial t} + \frac{1}{\rho} \nabla \cdot (\rho \vec{v} \vec{v}) = -\frac{1}{\rho} \nabla p - \frac{1}{\rho} \nabla \cdot \hat{\tau} + \vec{g} \cdot \hat{v}$$
(3.27)

where Eq. (3.27) governs the average gas, or plasma, flow velocity throughout the plasma region.

Note in Eq. (3.27) the $\nabla \cdot (\rho \vec{v} \vec{v})$ and $\nabla \cdot \hat{\tau}_s$ terms form rank-two tensors representing both convective and viscous forces acting in both orthogonal and shear directions. They are expressed in the following matrix representations for a generic two-dimensional coordinate frame

$$\nabla \cdot (\rho \vec{v} \vec{v}) = \nabla \cdot \left[\rho \begin{pmatrix} v_r^2 & v_r v_z \\ v_z v_z & v_z^2 \end{pmatrix} \right]$$
(3.28)

$$\nabla \cdot \hat{\tau} = \nabla \cdot \begin{pmatrix} \tau_{rr} & \tau_{rz} \\ \tau_{zr} & \tau_{zz} \end{pmatrix}$$
(3.29)

where v_r and v_z are the average plasma velocity components along the \hat{r} and \hat{z} unit vectors, and τ_{rr} , τ_{rz} , τ_{zr} , and τ_{zz} are the viscosity tensor components representing the shear and bulk forces due to plasma viscosity, respectively. These viscosity tensor terms are calculated [68]

$$\tau_{rr} = -\mu \left(2 \frac{\partial v_r}{\partial r} - \frac{2}{3} \nabla \cdot \vec{v} \right)$$
(3.30a)

$$\tau_{zz} = -\mu \left(2 \frac{\partial v_z}{\partial z} - \frac{2}{3} \nabla \cdot \vec{v} \right)$$
(3.30b)

$$\tau_{rz} = \tau_{zr} = -\mu \left(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right)$$
(3.30c)

$$\nabla \cdot \vec{v} = \frac{1}{r} \frac{\partial}{\partial r} \left(r v_r \right) + \frac{\partial v_z}{\partial z}$$
(3.30d)

where μ is assumed to have spatial dependence, and so is left inside the divergence operator.

This time dependence present in Eq. (3.27) remains in order to accurately update the gas momentum in the presence of the non-linear velocity dyad. This choice will become more clear during the derivation of the numerical framework. However, this is purely due to the choice of numerical solution method, as the final system solution remains steady-state in the absence of turbulent flow.

Finally, the left-hand-side of Eq. (3.27) represents a balance between the total time rate of change in average plasma velocity and the rate of momentum flux across a closed infinitesimal surface due to convective forces. The right-hand-side terms of Eq. (3.27) represent the net rate of volumetric momentum change as a consequence of pressure, viscous, and gravitational forces, respectively [68].

3.4.4 Electron Energy Transport

The energy, and thus temperature, of electrons is expected to be much higher than that of the ions and neutral species at certain operating conditions. This is inferred from their much smaller mass when compared to ions and neutrals. As a result, their kinetic energy increases more quickly due to high frequency oscillations in the presence of electromagnetic fields post collisions and energy transfer before colliding again with heavy species. As mentioned earlier, the electron energy is treated separately from the ion and neutral energy to maintain accuracy by following the two-temperature model. The electron energy transport equation is now derived starting with the Generalized Energy Transport Equation [67].

To begin, the species place holder in the Generalized Energy Transport Equation is replaced with the electron distinction

$$\nabla \cdot (\lambda_e \nabla T_e) + \nabla \cdot \left[\rho_e \vec{v}_e \left(\frac{1}{2} v_e^2 + \frac{3}{2} \frac{k_b T_e}{m_e} \right) \right] + \nabla \cdot (p_e \vec{v}_e) + \nabla \cdot (\hat{\tau} \cdot \vec{v}_e) + \rho_e \vec{g} \cdot \vec{v}_e + \mathcal{P}_{abs} + \nabla \cdot \left[\rho_e h_e \left(\vec{v} - D_e \nabla x_e \right) \right] = \left[\frac{\delta \left(\frac{1}{2} \rho_e < v^2 > e \right)}{\delta t} \right]_{coll}$$
(3.31)

where λ_e is the electron thermal conductivity coefficient.

At this point, the collisional term on the right side of Eq. (3.31) must be explicitly treated for the case of electrons. Numerous physical processes are simultaneously occurring within the plasma during the nominal operation of MPACVD reactors. Some of these processes include the transfer of energy between species through collisions. These collisions between electrons and ions or neutral species represent a kinetic energy loss mechanism and affect the overall electron temperature. Two distinct families of these collision types exist depending on the final state of the heavy species involved and include translational-rotational or vibrational modes, and are denoted Q_{et} and Q_{ev} .

At the same time, another electron energy transfer mechanism is associated with electrons

involved in chemical reactions. These result in a net change of the electron kinetic energy (and decreased temperature) through the activation of these chemical reactions. Energy loss may also be due to the transformation of converted mass or changes in excited energy states. This generic energy change rate is represented in the electron transport equation by Q_{ec} .

Substituting these terms, the time rate of change for the electron kinetic energy as represented by the collisional term on the right side of Eq. (3.31) now becomes

$$\left[\frac{\delta\left(\frac{1}{2}\rho_e < v^2 > e\right)}{\delta t}\right]_{coll} = Q_{et} + Q_{ev} + Q_{ec}$$
(3.32)

which may be back substituted into Eq. (3.31) resulting in the final form of the electron energy transport equation in Eq. (3.33)

$$\nabla \cdot (\lambda_e \nabla T_e) + \nabla \cdot \left[\rho_e \vec{v}_e \left(\frac{1}{2} v_e^2 + \frac{3}{2} \frac{k_b T_e}{m_e} \right) \right] + \nabla \cdot (p_e \vec{v}_e) + \nabla \cdot (\hat{\tau} \cdot \vec{v}_e)$$

+ $\rho_e \vec{g} \cdot \vec{v}_e + \mathcal{P}_{abs} + \nabla \cdot [\rho_e h_e \left(\vec{v} - D_e \nabla x_e \right)] = Q_{et} + Q_{ev} + Q_{ec}$ (3.33)

which governs the energy and thus temperature of electrons during the simulation process. The left-hand-side terms in Eq. (3.33) represent the rate of change in the electron energy due to thermal conduction, kinetic and potential energy related to electron flow, pressure, gravity, electromagnetic fields, and enthalpy, respectively. The three energy exchange terms on the right of Eq. (3.33) represent the time rate of change in electron energy due to collisions between electrons and heavy species in translational-rotational modes, vibrational modes, and their chemical reactions, respectively.

3.4.5 Total Energy Transport

The total energy transport equation is arguably the most important of all the transport equations governing the macroscopic quantities associated with the MPACVD plasma. This is because it relates all macroscopic solution variables in one equation. In this way, it can be thought of as a pseudo master transport equation. Moreover, the majority of the physical processes (including chemical reaction rates, energy transfers rates, diffusion coefficients, etc.) depend on the gas temperature that is governed by this total energy transport equation. These are thusly present in the gas temperature transport equation and influence the gas temperature. As with the electron energy transport equation derivation, the generalized energy transport equation provides the starting point in this derivation.

To begin, a summation over all present species is performed on the individual terms from the Generalized Transport Equation. These will be treated individually and discussed in the following paragraphs. The total rate of energy loss via thermal conduction is calculated by a summation of the three heat flux vectors

$$\vec{q_t} + \vec{q_v} + \vec{q_e} = -\left(\lambda_{tr}T_g + \lambda_v T_g + \lambda_e T_e\right) \tag{3.34}$$

where \vec{q}_t and \vec{q}_v are the heat flux vectors associated with the translational-rotational and vibrational heavy molecular modes, respectively, and λ_{tr} and λ_v represent their thermal conductivity coefficients, respectively. Note in Eq. (3.34) the gas temperature, T_g , is used in both the heat loss due to translational-rotational *and* vibrational modes. This is due to the assumed gas temperature and heavy species vibrational mode temperature equality [16]. These three terms are then substituted back into the total energy transport equation, replacing the single, leading species-dependent heat flux term.

Next, the kinetic and potential energy terms are addressed. The inclusion of this summation of energy over all present species requires only the change of species-based quantities to the average or total macroscopic quantity in each case. For example, the transformation
can be made

$$\nabla \cdot \left[\rho_{\alpha} \vec{v}_{\alpha} \left(\frac{1}{2} v_{\alpha}^{2} + \frac{3}{2} \frac{k_{b} T_{\alpha}}{m_{\alpha}} \right) \right] = \nabla \cdot \left[\rho_{e} \vec{v}_{e} \left(\frac{1}{2} \vec{v}_{e}^{2} + \frac{3}{2} \frac{k_{b} T_{e}}{m_{e}} \right) \right] + \sum_{i=1, i \neq e^{-}}^{N_{s}} \left(\nabla \cdot \left[\rho_{i} \vec{v}_{i} \left(\frac{1}{2} v_{i}^{2} + \frac{3}{2} \frac{k_{b} T_{g}}{m_{i}} \right) \right] \right)$$
(3.35)

where m_i is the mass of the i^{th} heavy species.

The next three terms in the Generalized Energy Transport Equation representing pressure, viscosity, and gravity forces are likewise summed over all species. This again results in the simple removal of their species dependence, and hence subscript.

The absorbed power density term in the Generalized Energy Transport Equation must be treated carefully, as it is the sole term through which the electromagnetic fields influence the plasma properties. The time rate of change in total plasma energy due to the electromagnetic fields is dependent upon the summation over all changes in species accelerations

$$\sum_{\alpha}^{N_s} \frac{1}{2} \rho_{\alpha} \vec{a}_{\alpha, E/M} \cdot \vec{v}_{\alpha} \tag{3.36}$$

This summation may be expanded into its dependence on heavy species and electrons. In particular, the following argument may be made regarding the relative magnitude of influence of these two families. While the electron acceleration is expected to be much greater than that of the heavy species, its product with the electron volumetric mass density negates any large quantity argument. This suggests the summation over all species is necessary to ensure accuracy. However, the electron velocity is in fact expected to be much larger than the heavy species velocities due to the contribution of the electron diffusion velocity. This effect is purely due to its far smaller mass, as is often the case in plasma systems. The large value argument can thus be made when comparing the summation over all total energy changes in heavy species with that of electrons. Approximating the summation over all species in Eq. (3.36) with only the influence due to electrons is thus argued as valid, and once more represented by the absorbed power density as in Eq. (3.33).

The influence of total species enthalpy likewise necessitates the summation over all species. This may be simplified in the following expression as

$$\sum_{i=1}^{N_s} \nabla \cdot \left[\rho_i h_i \left(\vec{v} - D_i \nabla x_i \right) \right] = \nabla \cdot \left(\rho h \vec{v} \right) - \sum_{i=1}^{N_s} \left[\nabla \cdot \left(\rho_i h_i D_i \nabla x_i \right) \right]$$
(3.37)

where the total enthalpy of all species, h, is calculated

$$h = \sum_{i}^{N_S} h_i \tag{3.38}$$

Eq. (3.37) is thus substituted for the species-dependent terms in the total energy transport equation.

Finally, the collisional term is addressed. In the case of total plasma energy, the net energy exchange between all species due to collisions is zero. This is due to the physical requirements of conservation of energy and momentum during any contained physical process. Thus, this collisional term may be neglected in the case of the total energy transport equation. However, the energy loss due to charged species radiation must be included. That is, the de-excitation of electrons radiates energy as phonons. This time rate of energy loss due to high frequency electric fields is denoted as Q_{rad} , and is substituted in for the total energy transport equation.

All necessary additions and substitutions to the generalized energy transport equation

have been made. The result is the total energy transport equation

$$\nabla \cdot \left(\lambda_{tr} \nabla T_g + \lambda_v \nabla T_g + \lambda_e \nabla T_e\right) + \nabla \cdot (p\vec{v}) + \rho\vec{g} \cdot \vec{v} + \nabla \cdot (\hat{\tau} \cdot \vec{v}) + \nabla \cdot \left[\rho_e \vec{v}_e \left(\frac{1}{2} \vec{v}_e^2 + \frac{3}{2} \frac{k_b T_e}{m_e}\right)\right] + \sum_{i=1, i \neq e^-}^{N_s} \left(\nabla \cdot \left[\rho_i \vec{v}_i \left(\frac{1}{2} v_i^2 + \frac{3}{2} \frac{k_b T_g}{m_i}\right)\right]\right) + \nabla \cdot (\rho h \vec{v}) - \sum_{i=1}^{N_s} \left[\nabla \cdot \left(\rho_i h_i D_i \nabla x_i\right)\right] = -\mathcal{P}_{abs} + Q_{rad}$$
(3.39)

where Eq. (3.39) represents the final form of the total energy transport equation.

The left-hand-side terms in Eq. (3.39) represent the time rate of change in the total plasma energy due to heat conduction, pressure, gravity, viscosity, kinetic and potential energy, and enthalpy processes across all species, respectively. The right-hand-side terms represent the gain in electron energy via the electromagnetic heating of the electrons and their loss due to phonon radiation via de-excitation. The gas temperature, T_g , will become the solution variable in Eq. (3.39).

3.4.6 Boundary Conditions

The plasma density at any wall or boundary is known to be non-zero for all plasma species, regardless of mass or charge. As a result, the flux of species mass to the boundaries must balance the total rate of species production at the wall due to surface chemistry processes. This is expressed mathematically as

$$-D_s \nabla x_s = W_{surf,s} + \hat{\nu}_{cat,s} M_s \tag{3.40}$$

where $W_{surf,s}$ is the surface rate of net mass density production, and $\hat{\nu}_{cat,s}$ is the total surface reaction rate. The two terms on the right side of Eq. (3.40) together represent the net rate of mass density production from both surface reactions and chemical reactions at the boundary. These surface rates are calculated as a function of the plasma properties at the boundaries, along with the recombination coefficients

$$W_{surf,s} = \sum_{r=1}^{N_{r,cat}} \nu_{cat,r} \eta_{r,s}^{(2)} M_s$$
(3.41a)

$$\nu_{cat,r} = \sum_{q=1,q\neq H_2,q\neq e^-}^{N_S} \zeta_r x_q \nu_\chi \tag{3.41b}$$

$$\hat{\nu}_{cat,r} = \zeta_r \nu_\chi \tag{3.41c}$$

$$\nu_{\chi} = \frac{c_{tot}}{4} \sqrt{\frac{8RT_g}{\pi M}} \tag{3.41d}$$

where $\nu_{cat,s}$ is the solution-dependent surface reaction rate, ζ_r is the recombination coefficient of catalytic reaction r, and ν_{χ} is the total collision frequency of ions and neutrals at the boundary. A list of surface reactions that are tracked in the simulation of MPACVD plasmas, along with their physical constants and assumptions are detailed in the Appendix and elsewhere [45].

The boundary conditions which apply to the plasma velocity fall into one of two categories: forced and interfacial. Due to the directional nature of the plasma velocity, both normal and tangential boundary conditions must be addressed. These are discussed in detail in the following paragraphs.

Hydrogen gas flows into the experimental MPACVD reactor through the inlets toward the base of the reactor (see Fig. 2.1). It is assumed the gas is flowing at the specified flow rate at this boundary, and is also laminar. Thus, the normal gas flow velocity component is assumed to be forced at this boundary. Moreover, the gas flow is essentially oriented normal to these boundaries.

Unlike the inlet region, the gas flow rate at the outlet region is not forced. However, in order to avoid momentum and gas accumulation, its flow rate may be calculated dependent on the inlet flow rate and the ratio of inlet to outlet surface areas. Moreover, the plasma velocity is also assumed laminar at this boundary. The above considerations suggest a finitevalued, or Dirichlet, boundary condition imposed at the outlet.

All other boundaries represent hard material interfaces either with the quartz bell jar or substrate wall, reactor boundaries, or the substrate surface. The normal component of plasma flow at these boundaries must be zero. At the same time, the tangential plasma flow must also go to zero at these boundaries. This is often referred to as the *no-slip* boundary condition. That is, it is known at a hard material interface the tangential flow at the surface drops to zero.

The effects of the plasma sheath are represented through approximations to physical observables. This includes the assumption that electrons diffusing more rapidly than ions populate the sheath layer and remain at a constant energy across this layer. Such an approximation results in a zeroed normal derivative in the electron temperature approaching all boundaries. Mathematically, this is expressed as

$$\hat{n} \cdot \nabla T_e = 0 \tag{3.42}$$

The gas temperature at the physical boundaries of the MPACVD reactor, and especially at the diamond substrate, is critical to the diamond deposition process. This is even more important to the various mass and heat fluxes directed toward the diamond sample during MPACVD system operation. The relationship between substrate temperature and diamond deposition rates have been documented in several instances for MPACVD systems [5, 21]. Moreover, this relationship has been demonstrated to be crucial to the diamond deposition rate. As highlighted earlier, the solution to the total energy transport equation given in Eq. (3.39) is paramount to the accuracy of the entire solution. Its solution results in an updated gas temperature distribution throughout the plasma region.

Historically, a uniform substrate temperature of 1200 K is often applied to the substrate surface, while all other boundaries are set to 600 K. These values were chosen to match experimental observations [16]. However, as documented experimentally, the substrate temperature is rarely uniform and fluctuates significantly depending on many reactor and operating factors [5]. As a result, forcing a uniform substrate temperature is nonphysical, requiring a more accurate boundary condition be applied. This will be addressed through the inclusion of a substrate temperature calculation.

3.5 Electrical Conductivity

The complex electrical conductivity distribution is calculated based upon the plasma properties. MPACVD plasmas, and most plasmas in general, represent lossy dielectrics in the electromagnetic sense. In this way, the complex electrical conductivity represents the ability of the plasma to absorb electromagnetic power. Due to the steady system assumption and frequency-domain electromagnetic field solutions, the often time-dependent complex electrical conductivity calculation must once again be translated to the frequency domain. The resulting derivation is provided in the following paragraphs.

The collisional equation of motion governing the time rate of change in electron momentum is provided below in Eq. (3.43)

$$\frac{\partial \vec{p}_e}{\partial t} = -q_0 \left(\vec{E} + \vec{v}_e \times \vec{B} \right) - m_e \nu_{eff} \vec{v}_e \tag{3.43}$$

where \vec{p}_e is the electron momentum and ν_{eff} is the effective collision frequency between heavy species and electrons. Again, the magnetic field dependence in Eq. (3.43) may be neglected. Likewise, the time rate of change in the electron mass is zero, and so this term may be pulled out of the partial time derivative and divided through. This results in the following modified equation of motion

$$\frac{\partial \vec{v}_e}{\partial t} = -\frac{q_0}{m_e} \vec{E} - \nu_{eff} \vec{v}_e \tag{3.44}$$

which may now be translated to the frequency domain by replacing the partial temporal derivative operator with $j\omega$, resulting in

$$\frac{\partial}{\partial t} \to j\omega$$

$$j\omega \vec{v}_e = -\frac{q_0}{m_e} \vec{E} - \nu_{eff} \vec{v}_e \qquad (3.45a)$$

where ω is the angular excitation frequency of the incident microwave power. Solving for the electron velocity results in

$$\vec{v}_e \left(j\omega + \nu_{eff} \right) = -\frac{q_0}{m_e} \vec{E}$$

$$\therefore \vec{v}_e = -\frac{q_0}{m_e} \frac{\vec{E}}{\left(j\omega + \nu_{eff} \right)}$$
(3.46a)

Recalling Ohm's Law, it is known that

$$\vec{J_e} = q_e n_e \vec{v_e} = \hat{\sigma}_e \vec{E} \tag{3.47a}$$

$$\therefore \hat{\sigma}_e = \frac{q_e n_e}{\vec{E}} \vec{v}_e \tag{3.47b}$$

Thus, substituting for the electron velocity from Eq. (3.46) into Eq. (3.44) yields the final form of the complex electrical conductivity in Eq. (3.48)

$$\hat{\sigma_e} = \frac{q_0^2 n_e}{m_e} \left(\frac{\nu_{eff} - j\omega}{\omega^2 + \nu_{eff}^2} \right)$$
(3.48)

where the effective collision frequency between electrons and hydrogen species is calculated as

$$\nu_{eff} = \sigma_x n \sqrt{v_{th}^2 + v_e^2} \tag{3.49}$$

with σ_x being the collision cross section for H₂, v_{th} is the electron thermal velocity and v_e

is the total electron speed [16]. Thus, in the case of low operating pressures where flow is neglected, the electron collision frequency is solely dependent on its thermal velocity. This electrical conductivity is used in the calculation of the absorbed power density from Eq. (3.9).

3.6 Inclusion of Substrate Temperature

The gas temperature at the diamond substrate is critical to the diamond deposition process. That is, it has a large effect on the diamond deposition rate and resulting sample quality as documented elsewhere [5,21]. Its accurate representation at physical boundaries is thus important not only experimentally, but crucial to the accuracy of the numerical model as a whole.

The gas temperature in previous MPACVD simulations is often explicitly set along different material boundaries [16, 34]. However, this does not take into account the variations in plasma position and properties, along with substrate conditions, which experimentally are known to vary. Thus, the development of a substrate thermal model is required to accurately capture these changes in substrate temperature. A derivation of the governing equation and boundary conditions for the substrate model is presented in the following paragraphs.

3.6.1 Heat Equation

The conduction of heat across any system is governed by the heat equation as given by

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (\lambda \nabla T) = 0 \tag{3.50}$$

where ρ is the mass density and C_p is the specific heat capacity. Eq. (3.50) relates the time rate of change in the temperature distribution within any infinitesimal volume element to the rate of heat flux flowing through its enclosed surface area. The fact that this expression is set to zero means no sources of heat are present, as is physically relevant to MPACVD systems. The rate of heat conduction within the substrate is expected to be much slower than that within the plasma. Combining this fact along with the long experimental run time suggests a steady-state thermal substrate model is again valid. As a result, the time rate of change in the substrate model is dropped, leaving the governing equation for the substrate thermal model as

$$\nabla \cdot (\lambda \nabla T) = 0 \tag{3.51}$$

Eq. (3.51) is applied from hereon in order to update the absolute temperature distribution within the substrate.

3.6.2 Boundary Conditions

The steady-state heat equation given in Eq. (3.51) yields a trivial temperature solution in the absence of boundary conditions. That is, with no heat sources present, the substrate temperature would necessarily go to zero. Thus, it is important to set these correctly not only to avoid a trivial solution, but also to ensure a single coupled solution within the entire MPACVD system. A derivation of these boundary conditions follows.

The substrate thermal model simulation region extends throughout the substrate pedestal, the substrate itself, the gas outlet cavity, and the quartz wall at the outer radius of the substrate as seen in Fig. 2.1. Temperature is a scalar quantity whose distribution must be continuous across material interfaces. This condition avoids the necessity to treat internal interfaces as boundaries, thus simplifying the boundary considerations to only those lying on the external domain boundaries. The heat flux must likewise remain continuous throughout the substrate and at its boundaries.

Experimentally, the pedestal is water-cooled within its inner-most region. It contains a recirculating flow that is constantly replaced in order to conduct heat away from the growth surface [4]. The substrate pedestal within the same region is assumed to mimic this cooling affect by behaving as a thermal sink with a specified temperature. The remaining region at the bottom of the reactor is approximated with a floating boundary, meaning the temperature is unspecified with zero net heat flow.

The substrate thermal and plasma models are coupled by substituting the total power flux incident at the top substrate surface and outer wall boundaries for these same boundaries in the substrate thermal model. This may be expressed in terms of the heat flow at these boundaries, resulting in the following boundary equation

$$Q_H = -\lambda \nabla T \tag{3.52}$$

where Q_H is the heat flow at the substrate pedestal outer boundaries. This heat flow is a summation of both thermal fluxes and hydrogen energy transfer via bombardment as calculated from the previously derived plasma properties as in Eq. (3.53)

$$Q_H = Q_H^{(x)} + Q_H^{(T)}$$
(3.53)

where $Q_H^{(x)}$ is the heat flow due to hydrogen bombardment energy transfer and $Q_H^{(T)}$ is the heat flow due to the gas temperature gradient.

This heat flow to the substrate surface due to energy transfer via bombardment of atomic hydrogen is calculated as the product of the atomic hydrogen recombination coefficient, the average energy associated with the neutral hydrogen atoms, and the flux rate. As stated previously, this recombination coefficient of hydrogen at the substrate surface is often approximated to be 0.1 in similar models [32, 34]. However, a more accurate approximation which is useful in the present formulation, was proposed by Krasnoperov *et al.* and is applied here [48]. The resulting power flux at the substrate surface due to hydrogen bombardment is given in Eq. (3.54)

$$Q_H^{(x)} = \beta_H \epsilon_H \Gamma_H \tag{3.54a}$$

$$\Gamma_H = -c_H D_H \nabla x_H \tag{3.54b}$$

where β_H is the unitless recombination coefficient of atomic hydrogen at the substrate surface, ϵ_H is the average exothermic energy deposited by hydrogen atoms involved in the dominant surface reaction (104 *kcal/mol*), Γ_H is the atomic hydrogen number flux at the substrate, and c_H is the atomic hydrogen molar concentration [45]. This exothermic energy is associated with the dominant

$$2H \to H_2$$
 (3.55)

diamond surface chemical reaction [45]. This flux is calculated at the substrate surface.

Similarly, the heat flow to the substrate surface due to the gas temperature gradient may be calculated as given above

$$Q_H^{(T)} = -\left(\lambda_t + \lambda_v\right) \nabla T_g \tag{3.56}$$

where the summation of the vibration and translation-rotation thermal conductivities is included. Substituting Eq. (3.56) and Eq. (3.54) into Eq. (3.53) produces the final form of the heat flux boundary condition calculated within the plasma fluid module.

Once the substrate temperature is calculated, the temperature at the boundaries of the plasma region is passed to the plasma fluid module and imposed at the corresponding locations. This coupled formulation of passing the heat flux from the plasma to thermal, and temperature from thermal to plasma ensures not only continuous temperatures, but also continuous fluxes. In this way, the atomic hydrogen flux contribution is not directly influenced as with the gas temperature at the substrate boundaries, but instead indirectly through its physical property dependence on this updated temperature.

CHAPTER 4

SOLUTION PROCEDURE

With the governing equations outlined, the numerical solution procedure is now developed. This will include discussions pertaining to domain discretization, the translation of mathematical expressions to matrix equations, the different solution schemes used in updating the governing equations, and the overall solution scheme.

4.1 Axisymmetric Approximation

The majority of the physical reactor components labeled in Fig. 2.1 exhibit cylindrical symmetry. That is, the cross sectional view provided in Fig. 2.1 may be rotated one full revolution to trace out the three-dimensional geometry. This cylindrically symmetric geometry makes a strong case for exploiting axial symmetry during the simulation process.

The domain of the reactor is discretized using a standard rectangular mesh. Per standard convention, individual nodes are represented by whole integer coordinate pairs (e.g. (m, n)). Here, m and n represent whole integers colocated at the bottom left node of an arbitrary element. This results in edges having coordinate pairs represented by $(m, n + \frac{1}{2})$ and $(m + \frac{1}{2}, n)$ where $\{m, n\} \in \{Z^+\}$ for vertical and horizontal edges, respectively, and $(m + \frac{1}{2}, n + \frac{1}{2})$ for elements. An example of the index pair labeling of all specified mesh features for a generic mesh element is provided in Fig. 4.1.



Figure 4.1: Generic mesh element with labeled geometry feature index pairs.

These index pairs representing the various mesh geometry features seen in Fig. 4.1 will also be cited extensively during the matrix representation and stencil derivations.

4.2 Finite Difference

With the numerical domain now discretized into a set of ordered solution sample locations, the numerical solution of the various equations may be derived. The governing equations contain differential equations, each requiring the discretization and numerical approximation of spatial derivatives. Here, the finite-difference (FD) method is chosen for simplicity, familiarity purposes, and maintaining consistency with previous MPACVD numerical simulation schemes [16, 22, 64].

4.3 Electromagnetics Module

The spatial locations of the electromagnetics module numerical solution samples must be chosen. With the mesh previously defined, this includes the locations of the electromagnetic fields with respect to this mesh. A common sampling approach for electromagnetic fields solved via FD methods is the Staggered Yee mesh [69]. In the Staggered Yee method, the electric field samples are aligned along mesh edges, while orthogonal magnetic fields are sampled at each mesh face, or element centers in the case of the present two-dimensional mesh. This is represented in Fig. 4.2.

		E_{r}		E_{r}	
	E_z	$\overset{H_{\phi}}{\odot}$	E_z	$\overset{H_{\phi}}{\odot}$	E_z
		Er		Er	
ł	E_z	$\overset{H_{\phi}}{\odot}$	E_{z}	$\overset{H_{\phi}}{\odot}$	E_z
		E_{r}		E_{r}	

Figure 4.2: Staggered Yee mesh in two-dimensions.

The advantage of this Staggered Yee mesh is its accurate representation of the curl operators present in Eq. (3.8). For example, the inner curl operator in Eq. (3.8) represents the spatial derivative of the orthogonal magnetic field component evaluated at the electric field location. Since the electric field is chosen to lie tangential to the mesh edges and the magnetic field is directed into the page at the element centers, this curl operation is calculated exactly without the need for numerical estimation through quadrature, averaging, or translation. Likewise, the outer curl operator in Eq. (3.8) represents the orthogonal electric field derivative evaluated at the magnetic field sampling location. This involves calculating both the radially- and vertically-directed derivatives from the mesh edges at the element centers in the present system. Again, this calculation is performed exactly without any required modifications or estimations to the field structure or mesh geometry. Moreover, the Staggered Yee field algorithm maintains the second order accuracy of the curl operator calculation in the case of uniform mesh spacing. Thus, the Staggered Yee mesh provides a distribution of electromagnetic field samples that are simple to assign, are well-defined with respect to the mesh, and result in inherent curl operator calculations.

The choice of the E_r , E_z and H_{ϕ} electromagnetic field components falls out from the coordinate frame, symmetry assumption of the reactor geometry, and known incident power polarization. The electromagnetic field solution is halved to these three components, thus reducing the number of numerical unknowns.

The accurate simulation of the electromagnetic fields is governed by the sufficient sampling of these fields on the mesh. Thus, an accurate sampling rate within the MPACVD reactor is crucial to a successful simulation. This numerical mesh must also accurately capture the geometric features of the reactor to similarly ensure successful representation of the system. A typical electromagnetics domain numerical mesh for the MSU Reactor B (see Fig. 2.1) is provided for reference in Fig. 4.3. Although dense and somewhat difficult to distinguish between adjacent elements, a rectangular grid is clearly depicted in Fig. 4.3.

Two different mesh resolutions are clearly visible along \hat{z} from Fig. 4.3. That is, the solution domain between the top of the bell jar and the antenna probe exhibits much lower mesh resolution. The relative sparsity of sample points in this region was chosen due to its distance from any curved surfaces, source regions, or the plasma solution domain itself. As a result, the electromagnetic fields are expected to remain well-behaved in this region without large fluctuations in field structure or intensity. This decreased mesh resolution also decreases the overall number of unknowns, thus reducing the solution time of the simulation as a whole.



Figure 4.3: Typical electromagnetics numerical solution domain mesh.

The sampling rate of any numerical mesh must be sufficient to capture any effects or changes to the solution variable contained within its domain. In other words, the mesh discretization size must be small enough to accurately capture the solution itself. A good rule of thumb for electromagnetic simulations solved via FD is a minimum mesh discretization size of $\lambda_0/40$. This level coincides with the minimum grid spacing observed in Fig. 4.3, while the higher rate approaches $\lambda_0/100$. Although this increased discretization rate is not necessarily required to accurately capture electromagnetic fields, it will become important in capturing the plasma solution. Since the numerical mesh is shared between electromagnetics and plasma solution domains, the minimum discretization rate is given precedence.

Material properties are assigned at element centers and assumed to remain constant over that entire element. This results in material interfaces being located at mesh edges, which will coincide with the appropriate boundary conditions for the electric fields. Assigning materials to entire mesh elements also ensures no fractional steps or approximations in material transition occur within elements. However, this does result in the need to translate electromagnetic permittivities and electrical conductivities from element centers to edges. This is done by performing a bilinear interpolation of the material properties at the two neighboring elements to each edge and computing their weighted average at the edge location. This ensures accurate translation of material properties in the case of non-uniform mesh spacing, while also approximating this material interface effect.

In the case of an edge lying on a domain boundary, the materials assigned to the corresponding element are also assigned to the edge. This translation of material properties also allows for the calculation of the electrical current density, which is concurrently located and oriented as with the electric fields. The reason for this choice of location and orientation will be more evident in the proceeding derivations.

4.3.1 Finite-Difference Frequency-Domain

The combination of a frequency domain solution and the FD numerical solution method for solving Eq. (3.8) is often referred to as the finite-difference frequency-domain (FDFD) solution method. This is a well-known method in computational electromagnetics, although not as popular as the time-domain formulation, similarly known as the finite-difference timedomain (FDTD) solution method. Previous MPACVD simulations traditionally have employed these FDTD methods for updating the electromagnetic field solutions [16, 34, 35]. However, the field pattern and wave interactions within MPACVD reactors are known to be dominated by certain modes at the excitation frequency [5, 21, 22]. This suggests capturing the lowest order cavity modes is sufficient in representing the majority of the electromagnetic field structure. Moreover, the time-domain solution of these fields is computationally expensive in terms of both scaling and numerical run time. These two disadvantages will be discussed in detail in the following paragraphs.

In FDTD, the electric and magnetic fields are updated at half-integer time steps in a leapfrog manner. The maximum time step (known as the Courant-Fuchs-Levy limit, or CFL condition) allowed in these updates is limited by the discretization rate of the mesh and the wave propagation speed. It specifies the minimum number of solution steps required during one wave period. The disadvantage of this CFL condition is that as the mesh discretization rate increases (and hence mesh spacing decreases), both the number of system unknowns *and* the number of update steps to represent one wave cycle increase. Thus, the overall numerical solution time increases exponentially, or according to a power law using the FDTD method.

The time-averaged absorbed power density which is the only electromagnetic-based quantity present in Eq. (3.33) and Eq. (3.39). Typically, the FDTD simulation is run until this quantity converges to a steady solution [16]. Several dozen wave cycles are often required before convergence including those capturing the initial wave propagation into the cavity. As a result, many calculations are performed unnecessarily making the FDTD method quite inefficient. Instead, the FDFD method may be employed ensuring a steady-state solution (including time-averaged absorbed power) and avoiding the need to simulate several wave cycles.

However, the FDFD method is not without its own disadvantages, which must be addressed. In the matching coaxial structure below and to the outside of the substrate pedestal from Fig. 2.1 the electromagnetic field is known to support transverse electromagnetic (TEM) mode structure with respect to \hat{z} [21]. That is, only the E_r and H_{ϕ} field components are non-zero, while $E_z = 0$. The FDFD formulation does not force E_z to zero anywhere in the solution domain, meaning it can be non-zero in the matching coaxial region. This difference between experimental and numerical results could affect not only the power density profile, but possibly the plasma behavior and its physical properties as well. However, these influences are argued as negligible under nominal operating conditions for MPACVD systems, as the bulk of the power absorption takes place within the plasma body above the substrate top surface.

4.3.2 Equation Discretization

The equation governing the electromagnetic fields as given in Eq. (3.8) may be written in simplified form as

$$\left[\nabla \times \frac{1}{\hat{\epsilon}} \nabla \times - \left(\frac{\omega}{c}\right)^2\right] \vec{H} = 0 \tag{4.1}$$

where $\hat{\epsilon}$ now represents all material dependencies explicitly stated in Eq. (3.8). Eq. (4.1) must now be discretized in terms of the field samples located on the mesh. This will be done by assigning the solution to a generic mesh geometric feature index pair and relating its terms to neighboring indices.

To begin, Eq. (4.1) is first expanded into the electromagnetic field components allowed in the present simulation. Since this includes only the azimuthal magnetic field component, the result is given by

$$\begin{bmatrix} \nabla \times \frac{1}{\hat{\epsilon}} \nabla \times -\left(\frac{\omega}{c}\right)^2 \end{bmatrix} \vec{H} \\ = \left(\frac{\partial}{\partial r} \left[\frac{1}{r\hat{\epsilon}} \frac{\partial}{\partial r} \left(rH_{\phi}\right)\right] + \frac{\partial}{\partial z} \left[\frac{1}{\hat{\epsilon}} \frac{\partial}{\partial z} \left(H_{\phi}\right)\right]\right) - \left(\frac{\omega}{c}\right)^2 H_{\phi} = 0$$
(4.2)

where the curl operators have been expanded in cylindrical coordinates. Eq. (4.1) may now be represented by the field and material quantities as they were assigned on the numerical mesh. This requires the discretization of both the azimuthal magnetic field component and the complex permittivity, $\hat{\epsilon}$.

Magnetic field samples are located at half-integer element centers and may be represented by generic index pairs of the form $(i+\frac{1}{2}, j+\frac{1}{2})$. Eq. (4.2) may then be rewritten in discretized form as

$$\frac{r_{i+\frac{3}{2}}H_{\phi,i+\frac{3}{2},j+\frac{1}{2}} - r_{i+\frac{1}{2}}H_{\phi,i+\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i+1,j+\frac{1}{2}r_{i+\frac{1}{2}}}\left(r_{i+\frac{3}{2}} - r_{i+\frac{1}{2}}\right)\left(r_{i+1} - r_{i}\right)} - \frac{r_{i+\frac{1}{2}}H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} - r_{i-\frac{1}{2}}H_{\phi,i-\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i,j+\frac{1}{2}r_{i+\frac{1}{2}}}\left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}\right)\left(r_{i+1} - r_{i}\right)} + \frac{H_{\phi,i+\frac{1}{2},j+\frac{3}{2}} - H_{\phi,i+\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i+\frac{1}{2},j+1}\left(z_{j+\frac{3}{2}} - z_{j+\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)} - \frac{H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} - H_{\phi,i+\frac{1}{2},j-\frac{1}{2}}}{\hat{\epsilon}_{r,i+\frac{1}{2},j}\left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)} - \frac{\omega^{2}}{c^{2}}H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} = 0 \quad (4.3)$$

where once again, whole integer indices represent nodes and edges, while half-integers represent element centers. Thus Eq. (4.3) relates the magnetic field sample located at $(i + \frac{1}{2}, j + \frac{1}{2})$ to the magnetic field samples at its nearest four neighbors adjacent to its four bordering edges. Moreover, the complex permittivity terms are located at the center of these four adjacent edge segments, with translated values calculated as discussed earlier. These spatial dependencies are visually depicted in Fig. 4.4.

Eq. (4.3) and Fig. 4.4 represent the discretized governing equation for the electromagnetic fields in the bulk region of the MPACVD reactor. That is, Eq. (4.3) is valid for all magnetic field samples away from any numerical domain boundary. However, in the presence of such boundaries, special attention must be paid to the numerical sampling and governing equation in order to ensure an accurate solution. The discretized form of the electromagnetic field boundary conditions are now presented.



Figure 4.4: Magnetic field and permittivity sample locations present in the discretized magnetic field equation. Here, \circ represents the magnetic field sample locations, and \times the permittivities.

4.3.3 Boundary Conditions

The boundary conditions are now numerically discretized and presented in the following paragraphs. Along with these, a third numerical boundary condition related to the artificial termination of the reactor microwave power feed will also be discussed.

The first, and by far the simplest boundary condition to numerically implement in the electromagnetics module is located at the domain boundaries. Electric fields fall to zero intensity well inside a good conductor. Numerically, these conductors are often approximated as PECs, resulting in exactly zero electric fields within such regions. The electromagnetic fields within PECs are thus neglected, and the domain is truncated to include only non-PEC regions, while all domain boundaries (save the axis of symmetry) are assumed to represent PEC interfaces. Since electromagnetic fields lying tangential to any interface must be continuous across that interface, this also requires tangential electric fields lying on any

domain boundary to be zero. Since the electric field is sampled on mesh edges, this forces all electric fields lying on domain boundaries to zero. This is enforced in the electromagnetics module by forcing the following condition

$$E_t|_{PEC} = 0 \tag{4.4}$$

where E_t is the tangential electric field component at the PEC (or domain) boundary.

The discretized governing electromagnetics equation provided in Eq. (4.3) is written in terms of the magnetic field. This likewise requires the domain boundary representation to be written for the magnetic field. This is already explicitly included in the discretized equation, as the contribution from PEC-based magnetic fields, which are already neglected in the calculation, are necessarily zero. Thus, their contribution along with their corresponding reference element term, are neglected in Eq. (4.3). This results in an expected zero-tangential electric field boundary condition when calculated from the magnetic field solution.

Due to the half-plane numerical domain, numerical calculations performed about r = 0must be carefully treated. In order to ensure accurate simulation of a continuous function, the radial component of any vector quantity must be zero at r = 0. Likewise, the rate of change in the radial direction for any vertically-directed vector quantity lying on this boundary must be constant along \hat{r} . Mathematically, these conditions are expressed as

$$A_r \bigg|_{r=0} = 0 \tag{4.5a}$$

$$\left. \frac{\partial A_z}{\partial r} \right|_{r=0} = 0 \tag{4.5b}$$

where A_r and A_z are the radially- and vertically-directed components of some vector quantity, $\vec{A} = A_r \hat{r} + A_z \hat{z}$. These conditions extend to the electric field intensity, which consists of vector components. Thus, the above conditions must be enforced during the solution procedure. However, applying these conditions to Eq. (4.3) results in a singularity at this axis related to the E_z field component. Thus, a new formulation and governing equation is required in this case. This singularity is avoided by making use of the system symmetry, realizing the left-directed neighbor of the magnetic field across the r = 0 axis is equal but opposite the magnetic field value itself. The discrete form of the left-neighboring radial term from Eq. (4.3) may thus be rewritten at the axis of symmetry as in Eq. (4.6)

$$\frac{r_{\frac{1}{2}}^{H} H_{\phi,\frac{1}{2},j+\frac{1}{2}} - r_{-\frac{1}{2}}^{H} H_{\phi,-\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,0,j+\frac{1}{2}}^{H} r_{\frac{1}{2}} \left(r_{\frac{1}{2}} - r_{-\frac{1}{2}}^{H}\right) (r_{1} - r_{0})} = \frac{2H_{\phi,\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,0,j+\frac{1}{2}}^{H} r_{\frac{1}{2}}^{H} (r_{1} - r_{0})}$$
(4.6)

where i = 0 represents the radial index located at the axis of symmetry and $-\frac{1}{2}$ represents the location at the center of the non-physical element radial image across this axis. Thus, this simple multiplication by a factor of two accurately represents the magnetic field boundary condition at the r = 0 axis, as well as the electric field components at this boundary.

A final numerical boundary condition is imposed in order to accurately simulate the electromagnetic field structure within the waveguide feed. The experimental MSU MPACVD system comprises a long microwave waveguide structure which delivers the power to the main reactor chamber as seen in Fig. 2.1. It is usually important to capture these fields during the simulation. However, the fields in this region are not of particular interest and have little effect on the plasma properties. Moreover, the complete discretization of this waveguide would unnecessarily increase the size of the solution domain, thus decreasing the overall numerical efficiency of the solution. In order to avoid simulating these unnecessary field samples, the solution domain is artificially terminated at an arbitrary location at least one free space wavelength away from the main reactor chamber. However, this termination introduces another domain (and hence PEC) boundary, resulting in the non-physical scattering of electromagnetic fields from its surface if left untreated. In order to avoid these non-physical reflections, an absorbing boundary condition is applied.

Here, the perfectly matched layer (PML) as proposed Berenger is applied via stretch-

ing parameters across several layers [70–73]. A detailed derivation of the PML and these stretching parameters are provided elsewhere and summarized here [72, 73]. This boundary condition will end up being applied over a series of successive layers approaching the artificially terminated boundary in the numerical domain. These stretching parameters are given by [72, 73]

$$s_r = \left(1 + \alpha \left[\frac{r - r_0}{r_1 - r_0}\right]\right)^p \left[1 - j\sin\left(\frac{\pi}{2} \left[\frac{r - r_0}{r_1 - r_0}\right]\right)^2\right]$$
(4.7a)

$$s_z = \left(1 + \alpha \left[\frac{z - z_0}{z_1 - z_0}\right]\right)^p \left[1 - j\sin\left(\frac{\pi}{2} \left[\frac{z - z_0}{z_1 - z_0}\right]\right)^2\right]$$
(4.7b)

where s_r and s_z are the stretching parameter functions used in the PML implementation as a function of r and z, respectively, α is the PML scaling coefficient, z_0 is the vertical position of the first PML layer, z_1 is the position of the last PML layer, and p is the PML scaling order. Here, $z_0 < z < z_1$, while the radial stretching function is one everywhere. The PML scaling coefficient and corresponding order often take on values between one and ten, achieving minimal reflections depending on microwave wavelength. Hence, z_1 also coincides with the domain boundary in Eq. (4.7). These stretching parameters modify the material dependencies in Eq. (4.3), resulting in an augmented governing equation given in discrete form as

$$\frac{r_{i+\frac{3}{2}}H_{\phi,i+\frac{3}{2},j+\frac{1}{2}} - r_{i+\frac{1}{2}}H_{\phi,i+\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i+1,j+\frac{1}{2}}r_{i+\frac{1}{2}}\left(r_{i+\frac{3}{2}} - r_{i+\frac{1}{2}}\right)\left(r_{i+1} - r_{i}\right)}\left(\bar{s}_{z,i+1,j+\frac{1}{2}}\right) - \frac{r_{i+\frac{1}{2}}H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} - r_{i-\frac{1}{2}}H_{\phi,i-\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i,j+\frac{1}{2},i+\frac{1}{2}}\left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}\right)\left(r_{i+1} - r_{i}\right)}\left(\bar{s}_{z,i,j+\frac{1}{2}}\right) + \frac{H_{\phi,i+\frac{1}{2},j+\frac{3}{2}} - H_{\phi,i+\frac{1}{2},j+\frac{1}{2}}}{\hat{\epsilon}_{r,i+\frac{1}{2},j+1}\left(z_{j+\frac{3}{2}} - z_{j+\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)}\left(\frac{1}{\bar{s}_{z,i+\frac{1}{2},j+1}}\right) - \frac{H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} - H_{\phi,i+\frac{1}{2},j-\frac{1}{2}}}{\hat{\epsilon}_{r,i+\frac{1}{2},j}\left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)}\left(\frac{1}{\bar{s}_{z,i+\frac{1}{2},j}}\right) - \frac{\omega^{2}}{c^{2}}\left(s_{z,i+\frac{1}{2},j+\frac{1}{2}}\right)H_{\phi,i+\frac{1}{2},j+\frac{1}{2}} = 0 \quad (4.8)$$

where s_z are the element-centered stretching parameters, and \bar{s}_z are stretching parameters translated to the mesh edges via a weighted bilinear interpolation scheme. These stretching parameters must be removed from the material dependence during the electric field calculations that follow.

4.3.4 Matrix Representation

Eq. (4.8) is represented in matrix form, allowing for the simultaneous solution of all unknown magnetic field samples. This is in sharp contrast to the FDTD method where fields are stepped forward in time and dependent on previous solutions. A derivation of this matrix formulation is provided below. Eq. (4.8) may be expressed in matrix equation form as

$$\left[\mathcal{A}_{0} - \mathcal{D}\mathcal{I}\right]\mathbf{H} = \mathbf{0} \tag{4.9}$$

where \mathcal{A} is the $n \times n$ matrix representing the double spatial curl operators and permittivity term on the left side of Eq. (4.8) with n being the number of mesh elements contained in the simulation domain, \mathcal{D} is the diagonal matrix containing the PML stretching parameters and multiplied by the free space wavenumber, \mathcal{I} is the identity matrix, **H** is the $n \times 1$ vector containing the unknown magnetic field solutions, and **0** is a $n \times 1$ vector containing zeros. The filling of \mathcal{A} is dependent on the indexing scheme used to number the magnetic field sampling locations. In general, the coefficients multiplying the five magnetic field samples given in Eq. (4.8) are used to fill the corresponding matrix entries.

The Total-Field/Scattered-Field (TF/SF) formulation is used in simulating the scattering of electromagnetic fields [73]. Many numerical electromagnetic simulations solve for the total field solution spanning the entire simulation domain. This total field is the summation of the incident and scattered electromagnetic fields that resulting from wave reflections and refractions in the presence of materials. This summation may be represented mathematically in terms of the present solution magnetic fields as

$$\vec{H}^{(t)} = \vec{H}^{(i)} + \vec{H}^{(s)} \tag{4.10}$$

where $\vec{H}^{(t)}$, $\vec{H}^{(i)}$, and $\vec{H}^{(s)}$ represent the total, incident, and scattered magnetic fields within the computational domain, respectively.

In order to implement the TF/SF formulation, the numerical solution domain must be separated into regions of total and purely scattered fields. In the present simulation, the total field (TF) region must extend across the entire plasma solution domain to ensure an accurate power absorption profile. This translates to all space contained within the quartz bell jar and that outside the substrate. On the other hand, the scattered field (SF) region must exist removed from the plasma solution domain, which in this case is located within the excitation waveguide at the top of the MPACVD reactor. As a result, the TF/SF boundary is chosen to reside within the waveguide region at the top of the MPACVD reactor, extending



Figure 4.5: Location of the TF/SF regions in the electromagnetics solution domain for the MSU Reactor B configuration. Red is SF, all blue shades represent TF. For interpretation to the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

across the entire waveguide in \hat{r} as shown in Fig. 4.5.

In this way, both the reflected power within the waveguide region, along with the total field and resulting power absorption density, may be calculated accurately. The exact location of the TF/SF boundary within the waveguide is completely arbitrary, but is chosen to reside at least one half wavelength above the main reactor cavity height. This boundary position avoids the significant contribution of decaying higher order modes.

The derivation of the TF/SF matrix equation formulation begins with the choice of a numerical solution in the absence of scatterers or materials [73]. This function, denoted here as \vec{F} , must be continuous and represent a solution to the governing Maxwell's Equations in free space. It is then reshaped into a column vector, \mathbf{f}_{src} . The masking function, \mathcal{Q} , is then filled taking on values of unity along its diagonal only within SF regions. \mathcal{Q} is a square,

 $n \times n$ matrix with zeros everywhere except those diagonal entries stated above. From these two terms, the scattered and total field source vectors may be calculated as $\mathbf{f}_{SF} = \mathcal{Q}\mathbf{f}_{src}$ and $\mathbf{f}_{TF} = (\mathcal{I} - \mathcal{Q})\mathbf{f}_{src}$. Here, \mathbf{f}_{SF} and \mathbf{f}_{TF} represent the scattered and total field source vectors, respectively.

However, the above formulation results in some of the discretized matrix terms representing the SF region being contained in the TF region and vice versa [73]. Since these two regions are incompatible with each other, these discrepancies are resolved by re-introducing the source term back to these quantities and moving its calculation to the right side of Eq. (4.9). The result is a right-hand-side vector in Eq. (4.9) now dependent on the source field

$$\mathbf{b} = (\mathcal{Q}\mathcal{A} - \mathcal{A}\mathcal{Q})\,\mathbf{f}_{STC} \tag{4.11}$$

where \mathcal{A} is the square matrix representing both the spatial operator and material property terms on the left side of Eq. (4.9). The matrix products on the right side of Eq. (4.11) may be efficiently calculated due to the sparse nature of both \mathcal{A} and \mathcal{Q} . In fact, since \mathcal{Q} is a diagonal matrix that is sparse even on its diagonal, these computational steps may scale sub-linearly with the number of numerical solution samples.

With the source vector now formulated, the complete matrix equation may be expressed as

$$\left[\mathcal{A}_{0} - \mathcal{DI}\right]\mathbf{H} = \left[\mathcal{Q}\left(\mathcal{A}_{0} - \mathcal{DI}\right) - \left(\mathcal{A}_{0} - \mathcal{DI}\right)\mathcal{Q}\right]\mathbf{f}_{src}$$
(4.12)

which may be solved for the unknown magnetic field samples contained in **H**. The choice of the electromagnetics matrix equation solution method may now be discussed.

4.3.5 Solution Procedure

There are generally several categories of solution methods that may be applied when solving a matrix equation. These include the direct, iterative, and sparse methods. Each has advantages and disadvantages associated with its implementation, yet sparse methods are the primary solution scheme employed in the current simulation.

Sparse matrix solution methods solve the resulting matrix equation exactly to machine precision and often at much faster rates compared to other methods. However, their solution methods are much more complex and dependent on the particular implementation chosen. Aside from their somewhat complicated data storage formats, sparse matrix solutions represent the best of both worlds of accuracy and efficiency. For this reason, sparse matrix solution methods are chosen for any direct matrix inversion required in the simulation including the solution of Eq. (4.12). Specifically, the MUMPS sparse numerical solver is applied to the current numerical system [74, 75].

The efficient implementation of a sparse matrix solver requires storing the matrix information in sparse format. Matrices may be stored in sparse format by keeping only their non-zero entries. Its percentage of non-zero to total number of entries represents the fill rate of the matrix. For example, the square matrices associated with two-dimensional FD solutions often exhibit a <1% fill rate. This suggests FD method matrix storage and corresponding calculations performed in sparse format would significantly improve the overall numerical efficiency of the solution procedure. This would also cut down on both the memory required to store the matrix information, and the number of numerical computations required during algebraic manipulations.

There are several standard sparse matrix data storage formats. The coordinate list (COO) sparse matrix storage format is chosen here for simplicity. As a result, the COO-formatted matrix information is used to solve for the magnetic fields in Eq. (4.12). This same MUMPS sparse matrix solver will be applied for all required matrix equation solutions throughout the remainder of the simulation.

Once the magnetic field samples have been calculated by solving Eq. (4.12), the electric fields must be calculated. These electric fields will be used along with the electrical conductivity to calculate the absorbed power density profile, which will be passed to the plasma fluid module. The electric fields are calculated via Eq. (3.6) with the PML stretching function dependence now explicitly included as

$$\vec{E} = \frac{1}{\bar{s}\left(\hat{\sigma}_e + j\omega\epsilon_0\epsilon_r\right)} \nabla \times \vec{H}$$
(4.13)

where \bar{s} denotes the generic form of the edge-based PML stretching functions outlined earlier. Expanding Eq. (4.13) into its two components yields

$$E_r = \frac{1}{\bar{s}_z \left(\hat{\sigma}_e + j\omega\epsilon_0\epsilon_r\right)} \frac{\partial H_\phi}{\partial z}$$
(4.14a)

$$E_{z} = \frac{\bar{s}_{z}}{(\hat{\sigma}_{e} + j\omega\epsilon_{0}\epsilon_{r})} \frac{1}{r} \frac{\partial\left(rH_{\phi}\right)}{\partial r}$$
(4.14b)

where \bar{s}_z is the stretching function dependent on the vertical coordinate. The edge-based electric fields are thus calculated via Eq. (4.14). Writing in discretized form, these electric field components located at their respective edge indices are given by

With both the electric and magnetic fields now calculated at their respective numerical mesh locations, the Poynting vector may be calculated. This will be useful in calculating the vector power flux across the simulation domain, and thus the reflected power ratio. Its general form is

$$\vec{S} = \vec{E} \times \vec{H}^* \tag{4.16}$$

where \vec{S} is the electromagnetic poynting vector. From Eq. (4.16), it is clear the calculation of

the Poynting vector depends on the colocation of the electric and magnetic fields. To achieve colocation, the electric fields located at the edges bordering each element are averaged at the element center. This results in element-based electric field samples, which may be used to calculate the Poynting vector along with the element-based azimuthal magnetic field.

As mentioned previously, the reflected power is often experimentally measured and used as an indicator of the effective power coupling efficiency within the plasma. Thus, a similar numerical metric is desired in order to gauge the accuracy of the simulation compared to the experimental system, and to aid in tuning the reactor geometry parameters during the solution procedure. To calculate the total reflected power, the total flux of electromagnetic power is integrated across the waveguide feed and compared to the incident power. This involves integrating the previously-calculated Poynting vector over the surface area of the coaxial waveguide feed. This integration position is located at the top of the reactor in the SF numerical region. It is located at least one quarter wavelength away from the TF/SF boundary to avoid any discontinuities or interpolation errors between these regions. The reflected power integration is thus calculated

$$\mathcal{P}_{ref} = \iint_{r_0}^{r_1} \vec{S} r dr d\phi \tag{4.17}$$

where \mathcal{P}_{ref} is the total reflected power from the MPACVD system, and r_0 and r_1 represent the inner and outer radii of the coaxial waveguide feed, respectively. The reflected power ratio is then calculated as the ratio of the incident power delivered to the system as given by the scaled source vector, \mathcal{P}_{inc} , and this reflected power via

$$R = \frac{\mathcal{P}_{ref}}{\mathcal{P}_{inc}} \tag{4.18}$$

where R is the reflected power ratio.

Finally, the quality factor of the MSU MPACVD reactor may be calculated, which can prove useful in comparing against experimentally measured quality factors [22]. The quality factor of any system is a measure of the system bandwidth at resonance. In MPACVD systems, this value is a measure of how much energy the system can store relative to the power loss at the microwave excitation frequency. It is often used to gauge the reactor performance and design, and is calculated from Eq. (4.19) [22]

$$Q = \frac{\omega \epsilon \iiint \vec{E} \cdot \vec{E}^* d^3 \vec{r}}{\left(\mathcal{P}_{inc} - \mathcal{P}_{ref}\right)}$$
(4.19)

where Q is the quality factor.

4.3.6 Reflected Power Minimization

The MSU MPACVD reactor is tuned during the deposition process to minimize the reflected power. This is done by physically adjusting certain reactor components, namely the main cavity height and antenna probe length. As a result, the reflected power is minimized ensuring maximum microwave power transfer to the oscillating free electrons and heavy species in the plasma. Since this represents an important physical operation, it is important the numerical simulation also mimics this process via a reflected power minimization algorithm as detailed below.

Each adjustment to the physical reactor settings and corresponding numerical domain and mesh requires a new electromagnetic field solution. While the sparse solver described earlier is numerically efficient, this can still take several seconds per solution depending on the computer architecture, number of processors, and domain size. Thus, it is not advantageous to minimize the reflected power at every electromagnetic field solution step. Instead, a certain number of solution steps is skipped before this minimization occurs. Moreover, this allows for the formation and stabilization of the plasma solution before large changes in the absorbed power density profile are imposed.

During reflected power minimization, the electromagnetic fields are first solved within the current reactor configuration and the reflected power saved. The main cavity height is then stepped through a series of evenly spaced positions on either side of the current cavity height, with the reflected power again saved at each position. This results in a set of cavity heights and corresponding reflected power values, which are then searched for the minimum value. The cavity height corresponding to this minimum reflected power is then saved and used as the new cavity height position. Next, the antenna probe length is varied, again for positions on either side of the current antenna probe length. The electromagnetic fields are again solved at each of these positions, along with the reflected power. Finally, the antenna probe length corresponding to the minimum reflected power is likewise saved. The end result is a combination of antenna probe length and main cavity height which minimize the reflected power within the MSU MPACVD reactor. These new probe and cavity settings are then used as the reference positions during the next reflected power minimization update. Before updating the plasma fluid module, the electromagnetics solution is once again run at the minimized cavity height and probe length positions.

Changes in the reflected power calculated during this routine are due solely to adjustments in these physical cavity configuration settings. Although the substrate position is adjustable, it cannot be tuned during experimental operation. Thus, the exclusion of the substrate vertical position adjustment during the reflected power minimization algorithm follows experimental capabilities.

This power minimization routine is repeated throughout the numerical simulation. However, it is often advantageous and results in a more stable final solution when it is applied only after the formation of a stable plasma within the plasma simulation module.

4.4 Absorbed Power

Once the electromagnetic fields have been calculated, the absorbed power density profile must be updated. This quantity will be used in the electron and total energy transport equations. The absorbed power density as derived in Eq. (3.9) will be used here. As with the Poynting vector calculation, the numerical sampling of the absorbed power density is performed at the element centers. This will ensure colocation with the volume source terms prescribed in the plasma transport equations given in Eq. (3.33) and Eq. (3.39). Since the electric fields are sampled along mesh edges, these fields are again be averaged at the element centers. The original complex electrical conductivity passed from the plasma module is already defined at the element centers. This avoids the necessity of translating the already element-based conductivity from the mesh edges back to element centers, which could result in numerical errors. The result is a discretized absorbed power density profile for a generic mesh location

$$\mathcal{P}_{abs,i+\frac{1}{2},j+\frac{1}{2}} = \frac{1}{2} \Re\{\hat{\sigma}_{e,i+\frac{1}{2},j+\frac{1}{2}}\} \times \left[\left(\frac{E_{r,i+\frac{1}{2},j}E_{r,i+\frac{1}{2},j}^{*} + E_{r,i+\frac{1}{2},j+1}E_{r,i+\frac{1}{2},j+1}^{*}}{2} \right) + \left(\frac{E_{z,i,j+\frac{1}{2}}E_{z,i,j+\frac{1}{2}}^{*} + E_{z,i+1i,j+\frac{1}{2}}E_{z,i+1,j+\frac{1}{2}}^{*}}{2} \right) \right]$$

$$+ \left(\frac{E_{z,i,j+\frac{1}{2}}E_{z,i,j+\frac{1}{2}}^{*} + E_{z,i+1i,j+\frac{1}{2}}E_{z,i+1,j+\frac{1}{2}}^{*}}{2} \right) \right]$$

$$(4.20)$$

where $\Re{\{\hat{\sigma}_e\}}$ is the real component of the complex electrical conductivity. This dependence on only the real component of the electrical conductivity mathematically represents the physical power absorbed by hydrogen ions and neutrals via electron collisions. Again, measurable energy transfer only occurs in the presence of these collisional processes. Eq. (4.20) is used to generate a two-dimensional profile of absorbed power density across the entire simulation domain. However, this power density is known to only be non-zero in the regions where $\hat{\sigma}_e \neq 0$, requiring $n_e \neq 0$.

Once the absorbed power density has been calculated, the total absorbed power level must be enforced. Experimentally, the incident microwave power supplied to the MPACVD reactor is set, with the reflected power measured. This means the total absorbed power is not physically enforced, but rather calculated as the difference between incident and reflected powers. Numerically, this total absorbed power level is explicitly set prior to the simulation process, with the incident power scaled to result in this total absorbed power. This is ensured by calculating the total power in the absorbed density profile and scaling the incident electromagnetic fields accordingly. A more detailed description of this scaling algorithm follows.

Upon initialization of the complete simulation, the incident electromagnetic field intensity is set to unity. Once the absorbed power density profile has been calculated, the resultant absorbed power density profile is numerically integrated for the total absorbed power level via Eq. (3.10). The ratio between this value and the specified total power level is calculated as $\mathcal{P}_{tot}/\mathcal{P}_0$ where \mathcal{P}_{tot} is the total absorbed power calculated via Eq. (3.10) and \mathcal{P}_0 is the desired total absorbed power level. All absorbed power density solutions are then scaled by this value, resulting in a modified absorbed power density profile corresponding to the desired total absorbed power. This power ratio is also used to scale the incident source electromagnetic fields at the next electromagnetics module solution step. As a result, the absorbed power density passed to the plasma module always corresponds to the desired total power level. As the coupled solution converges, this scaling coefficient approaches unity.

An advantage of this scaling method and its back substitution in the case of the scaled incident microwave power is the realization of the absolute electromagnetic field intensities. That is, the scaling of the incident electromagnetic source fields results in field intensities which may be directly compared to experimental values.

4.5 Plasma Fluid Module

As with the electromagnetics module, the locations of the various plasma fluid module macroscopic variable samples must first be assigned before proceeding with its numerical solution. The behavior of these physical quantities is governed through the transport equations. Numerically, these relate the influence of fluxes between mesh elements with source terms inside



Figure 4.6: Locations of plasma module samples on numerical mesh.

each mesh element. As a result, the natural choice for the location of scalar plasma module variable samples is element centers. However, the vector flow components are involved in the flux of various quantities between mesh elements. The behavior of these flow components also depends on gradients of scalar quantities, including pressure and viscosity. This suggests sampling the vector flow components at the mesh edges, as will be the case here. Unlike the electromagnetics module, these edge-based vector samples will be oriented orthogonal to the edge segments themselves. This results in a directed flux quantity based on flow components moving between mesh elements where other scalar samples are located. A graphical representation of this configuration is provided in Fig. Fig. 4.6.

Note in Fig. 4.6 the flow components are only defined on their respective oriented edges. That is, the radial flow is only sampled at the vertical edges, while the vertical flow is only sampled at the horizontal edges. This will lead to non-forced shear boundary flows and conditions. The advantage of these particular sample locations detailed in Fig. 4.6 is the flux due to flows between elements is represented exactly with no need to translate or interpolate flux quantities. Moreover, the flow components may be updated based on the various scalar gradients, which are also easily calculated.


Figure 4.7: Numerical mesh within the plasma region for the plasma fluid module.

As with the electromagnetics solution module, the plasma region must be carefully represented and sampled by the plasma domain mesh. The choice of plasma module sample points is equally crucial to the accurate modeling of the MPACVD reactor. Since the electromagnetics solution domain extends throughout the plasma solution domain as well, this mesh has essentially already been produced. However, it is presented here set apart from the electromagnetics domain as given in Fig. 4.7.

The uniform grid spacing shown in Fig. 4.7 is chosen for simplicity and ease of visualization. However, the present simulation is capable of nonuniform mesh discretization schemes as are common in similar MPACVD plasma simulations [16, 34, 76]. This grid spacing also corresponds to roughly $\lambda_0/100$, where λ_0 is the free space electromagnetic wavelength. No direct dependence on the electromagnetic wavelength is required for the plasma fluid module solution quantities. However, familiarity with the simulation and typical operating conditions suggests this spacing is sufficient to ensure the majority of continuous and smooth solution distributions. This particular level of mesh spacing is more than sufficient to capture the important electromagnetic field structure within the MPACVD system.

4.5.1 Equation Discretization

The transport equations are now discretized using the sampling scheme presented in Fig. 4.6. The majority of the transport equations often include many terms and are rather long. Only a representative selection of one scalar and one flow component transport equation will be discretized in the following paragraphs. Moreover, only unique samples of representative scalar and gradient terms will be provided. In this sense, the generic discretization of the transport equations is presented, with their exact forms derived from these.

The mass transport equation governing the behavior of all chemical species seen in Eq. (3.18) is restated here for convenience in Eq. (4.21)

$$\nabla \cdot (\rho_s D_s \nabla x_s) + \nabla \cdot (\rho_s \vec{v}) = W_s \tag{4.21}$$

which may be discretized at any reference generic element-centered index as given in Eq. (4.22)

$$\frac{r_{i+1}\rho_{s,i+1,j+\frac{1}{2}}D_{s,i+1,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_{i})} \left(\frac{x_{s,i+\frac{3}{2},j+\frac{1}{2}}-x_{s,i+\frac{1}{2},j+\frac{1}{2}}}{r_{i+\frac{3}{2}}-r_{i+\frac{1}{2}}} \right) - \frac{r_{i}\rho_{s,i,j+\frac{1}{2}}D_{s,i,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_{i})} \left(\frac{x_{s,i+\frac{1}{2},j+\frac{1}{2}}-x_{s,i-\frac{1}{2},j+\frac{1}{2}}}{r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}} \right) + \frac{\rho_{s,i+\frac{1}{2},j+1}D_{s,i+\frac{1}{2},j+1}}{(z_{j+1}-z_{j})} \left(\frac{x_{s,i+\frac{1}{2},j+\frac{3}{2}}-x_{s,i+\frac{1}{2},j+\frac{1}{2}}}{z_{j+\frac{3}{2}}-z_{j+\frac{1}{2}}} \right) - \frac{\rho_{s,i+\frac{1}{2},j}D_{s,i+\frac{1}{2},j}}{(z_{j+1}-z_{j})} \left(\frac{x_{s,i+\frac{1}{2},j+\frac{1}{2}}-x_{s,i+\frac{1}{2},j+\frac{1}{2}}}{z_{j+\frac{1}{2}}-z_{j-\frac{1}{2}}} \right) + \frac{r_{i+1}\rho_{s,i+1,j+\frac{1}{2}}v_{r,i+1,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_{i})} - \frac{r_{i}\rho_{s,i,j+\frac{1}{2}}v_{r,i,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_{i})} + \frac{\rho_{s,i+\frac{1}{2},j+1}v_{z,i+\frac{1}{2},j+1}}{(z_{j+1}-z_{j})} - \frac{\rho_{s,i+\frac{1}{2},j}v_{z,i+\frac{1}{2},j}}{(z_{j+1}-z_{j})} = W_{s,i+\frac{1}{2},j+\frac{1}{2}}$$

$$(4.22)$$

where the first four lines represent the flux of mass due to diffusion and the last two represent mass flux due to convective gas flow and the production of mass within each mesh element domain. Eq. (4.22) is representative of all scalar transport equations (mass, electron energy, total energy) in that each term in these equations can be derived in the form of one of the terms contained in Eq. (4.21). Thus, the discrete form of all the scalar transport equations comprising the plasma fluid module have been provided.

The momentum transport equation governs the behavior of the vector plasma flow as given in Eq. (3.27). It is restated here for convenience in comparison in Eq. (4.23)

$$\frac{\partial \vec{v}}{\partial t} + \frac{1}{\rho} \nabla \cdot (\rho \vec{v} \vec{v}) = -\frac{1}{\rho} \nabla p - \frac{1}{\rho} \nabla \cdot \hat{\tau} + \vec{g} \cdot \hat{v}$$
(4.23)

Choosing the vertical flow component for its inclusion of the gravity dependence, Eq. (4.23) may be expanded into the individual vertical component flow terms as in Eq. (4.24)

$$\frac{\partial v_z}{\partial t} + \frac{1}{r\rho} \frac{\partial \left(r\rho v_r v_z\right)}{\partial r} + \frac{1}{\rho} \frac{\partial \left(\rho v_z^2\right)}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} - \frac{1}{r\rho} \frac{\partial \left(r\hat{\tau}_{zr}\right)}{\partial r} + \frac{1}{\rho} \frac{\partial \hat{\tau}_{zz}}{\partial z} - v_z g \qquad (4.24)$$

where g is the standard acceleration magnitude. The various terms in Eq. (4.24) must now be condensed into their generic calculation forms for discretization reporting. The time rate of change in the vertical flow must remain, as it will be required in the solution scheme. This leaves three sets of vertical and two radial derivative calculations, each showing the same form related to the derivative calculation. Thus, these divergence terms may be condensed and represented by two divergence terms in either direction (\hat{r} or \hat{z}). Finally, the gravitational term remains as it is unaltered by a spatial operator. Thus, Eq. (4.24) may be written in its representative operator form as in Eq. (4.25)

$$\frac{\partial v_z}{\partial t} = -\frac{1}{r\rho} \frac{\partial \left(r\alpha v_z\right)}{\partial r} - \frac{1}{\rho} \frac{\partial \left(\beta v_z\right)}{\partial z} - v_z g \tag{4.25}$$

where α and β are generic scalar macroscopic variable sampled at the mesh nodes and element

centers, respectively. In this way, Eq. (4.24) may be discretized in a minimal amount of terms. This is given in Eq. (4.26) for a generic horizontal edge index and scalar quantities defined above as given in Eq. (4.26)

$$\frac{v_{z,i+\frac{1}{2},j} - v_{z,i+\frac{1}{2},j}'}{t^n - t^{n-1}} = -\frac{1}{r_{i+1\frac{1}{2}}\rho_{i+\frac{1}{2},j}} \left(\frac{r_{i+1}\alpha_{i+1,j}\bar{v}_{z,i+1,j} - r_i\alpha_{i,j}\bar{v}_{z,i,j}}{r_{i+1} - r_i} \right) \\ - \frac{1}{\rho_{i+\frac{1}{2},j}} \left(\frac{\beta_{i+\frac{1}{2},j+\frac{1}{2}}\bar{v}_{z,i+\frac{1}{2},j+\frac{1}{2}} - \beta_{i+\frac{1}{2},j-\frac{1}{2}}\bar{v}_{z,i+\frac{1}{2},j-\frac{1}{2}}}{z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}} \right) \\ - v_{z,i+\frac{1}{2},j}g \tag{4.26}$$

where v_z is the vertical flow component at the current time sample, t^n , v'_z is the vertical flow at the previous time sample, t^{n-1} , and \bar{v}_z denotes interpolated vertical flow samples at nonmesh edges. These interpolated, or translated, samples are required in order to calculate the divergence terms in Eq. (4.26). However, the vertical flows themselves do not exist at these locations. Instead, weighted averages of the flow components will be calculated at nodes and element centers via bilinear interpolation and used in the update of these flow fields. Eq. (4.26) now represents the discretized form of the two components of the momentum transport equation (Eq. (3.27)) used to update these quantities within the plasma fluid module.

4.5.2 Boundary Conditions

The boundary conditions must now be expressed in numerical form. These will be listed for the scalar solution variables first, then the vector quantities. Just like any other distribution in cylindrical coordinates, the boundary condition for all variables at the axis of symmetry must be treated. However, this boundary is explicitly treated in the numerical representation of scalar distributions by ignoring the flux across this corresponding edge. This assumes



Figure 4.8: One-dimensional mass transport boundary condition schematic for right-edge domain boundary.

a zero-net flux, and thus a symmetric distribution, regardless of the physical variable in question.

There is a single boundary condition governing the termination of the mass transport equation at the domain bounds. It is a finite-valued Neumann condition as given in Eq. (3.40). The mass transport boundary condition involves a gradient in the mole fraction at the domain boundary. Its exact numerical representation is impossible, since the elements outside the domain are not available. Instead, this boundary condition is numerically approximated by translating the boundary to the nearest two elements contained in the domain mesh approaching the boundary. A generic boundary element with a domain border located along its right edge, denoted by the index pair, $N - \frac{1}{2}$, $j + \frac{1}{2}$, is used here although its form is easily translated to any boundary orientation. This right vertical edge boundary condition is represented in the one-dimensional schematic in Fig. 4.8.

The open circles in Fig. 4.8 denote the element centers, while the filled circles are the nodes. Note the right-most node at the coordinate N is lying completely on the boundary.

In order to exactly represent this boundary, the derivative should be calculated at N. This is impossible since the calculation of a numerical derivative requires at least two samples on either side of the derivative evaluation location. Thus, a more reasonable calculation would be to calculate the derivative approaching the boundary as between N and N-1. However, this is also not possible, since the numerical samples are located at the element centers and not the nodes. This boundary condition may instead be calculated using the two nearest element centers via a translation algorithm derived below. The original Neumann boundary condition calculation using the node positions would be calculated according to

$$\nabla A = \frac{A_N - A_{N-1}}{x_N - x_{N-1}} = \gamma$$

where A is some scalar variable defined at the nodes, x is a continuous spatial variable, and γ is some non-zero scalar quantity. As argued earlier, these A values at the nodes are unavailable, and so must be translated to the boundary. This requires calculating these two values using the element-based samples via

$$A_{N} = A_{N-\frac{1}{2}} + \left[\frac{A_{N-\frac{1}{2}} - A_{N-\frac{3}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right] \left(x_{N} - x_{N-\frac{1}{2}}\right)$$
$$A_{N-1} = \frac{A_{N-\frac{1}{2}} + A_{N-\frac{3}{2}}}{2}$$

where the average of the adjacent element-based samples results in A_{N-1} and the slope of the continuous A variable is used to interpolate its value on the boundary node. Plugging these equations in to the original Neumann boundary condition equation results in the generic discretized form of the Neumann boundary condition expression for the scalar transport equations given in Eq. (4.28)

$$\frac{\left[A_{N-\frac{1}{2}}\left(\frac{1}{2} + \frac{x_N - x_{N-\frac{1}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right) - A_{N-\frac{3}{2}}\left(\frac{1}{2} + \frac{x_N - x_{N-\frac{1}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right)\right]}{x_N - x_{N-1}} = \gamma \qquad (4.28)$$

The above expression is valid for non-uniform mesh spacings. However, in the case of a uniform mesh, Eq. (4.28) collapses to the standard numerical derivative of the form

$$\frac{A_{N-\frac{1}{2}} - A_{N-\frac{3}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}$$
(4.29)

where it is now assumed $x_N - x_{N-1} = x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}$. With the general numerically discretized form of the Neumann boundary condition for scalar transport equations available, their exact forms may be expressed. This is represented in Eq. (4.30) for the case of a generic mass transport boundary condition with a domain boundary again at its right edge

$$-\frac{D_{s,i+\frac{1}{2},j+\frac{1}{2}}x_{s,N-\frac{1}{2},j+\frac{1}{2}}\left(\frac{1}{2} + \frac{r_N - r_{N-\frac{1}{2}}}{r_{N-\frac{1}{2}} - r_{N-\frac{3}{2}}}\right)}{\frac{D_{s,i+\frac{1}{2},j+\frac{1}{2}}x_{s,N-\frac{3}{2},j+\frac{1}{2}}\left(\frac{1}{2} + \frac{r_N - r_{N-\frac{3}{2}}}{r_{N-\frac{1}{2}} - r_{N-\frac{3}{2}}}\right)}{\frac{1}{r_N - r_{N-1}}\left(\frac{1}{2} + \frac{r_N - r_{N-\frac{1}{2}}}{r_{N-\frac{1}{2}} - r_{N-\frac{3}{2}}}\right)}$$
$$= W_{surf,s,i+\frac{1}{2},j+\frac{1}{2}} + \hat{\nu}_{cat,s,i+\frac{1}{2},j+\frac{1}{2}}M_{s,i+\frac{1}{2},j+\frac{1}{2}}$$
(4.30)

where the diffusion coefficient, D_s , has been applied at the element center. This usage agrees with the above derivation, as the original derivative is calculated across the element and the diffusion coefficient is necessarily located at the element midpoint. Eq. (4.30) represents the entirety of the boundary conditions related to the mass transport equations for each species.

The discrete boundary condition representing the electron transport equation results in the simple condition of setting the electron temperature at the boundary element equal to its neighboring element as given in Eq. (4.31)

$$T_{e,N-\frac{1}{2},j+\frac{1}{2}} = T_{e,N-\frac{3}{2},j+\frac{1}{2}}$$
(4.31)

This falls out from Eq. (4.28) for a zero-condition Neumann boundary.

Finally, total energy transport equation must be discussed. The solution to this equation results in an updated gas temperature distribution, which is explicitly set at all material interfaces. This even holds for the substrate thermal model, where the energy fluxes to the substrate will be used to solve for the temperature at this boundary. However, within the plasma fluid module, the gas temperature is still set here. Representing a finite-valued Dirichlet boundary condition, the gas temperatures at the node boundary is set via

$$T_{g,N} = \gamma$$

where γ is a non-zero, finite temperature. However, just like the scalar Neumann boundary condition derived above, the temperature is not sampled at the desired node location, but rather the element. Again referring to Fig. 4.8, the scalar quantity at this node may be interpolated via the following

$$A_N = A_{N-\frac{1}{2}} + \left[\frac{A_{N-\frac{1}{2}} - A_{N-\frac{3}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right] \left(x_N - x_{N-\frac{1}{2}}\right)$$

which results in the following equation representing the Dirichlet boundary condition for the gas temperature at the right edge domain boundary

$$T_{g,N-\frac{1}{2}}\left[1 + \frac{x_N - x_{N-\frac{1}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right] - T_{g,N-\frac{3}{2}}\left[\frac{x_N - x_{N-\frac{1}{2}}}{x_{N-\frac{1}{2}} - x_{N-\frac{3}{2}}}\right] = \begin{cases} T_{sub}, & \text{substrate} \\ 600, & \text{else} \end{cases}$$

$$(4.32)$$

where T_{sub} is the gas temperature profile provided by the substrate thermal model at all substrate boundaries. The 600 K temperature that is assumed on all boundaries follows from previous simulations and experimental observations [16].

The momentum transport equation boundary conditions are divided into two categories of orthogonal and tangential flows. Orthogonal flow boundaries denote those mesh edges where the flow component is directed orthogonal to the boundary edge. In the case of a non-inlet or outlet region, which occurs at all physical material interfaces, this flow is forced to zero.

A small feed gas inlet is present in the physical MSU MPACVD reactor toward the bottom of the reactor and on the outer coaxial block wall as seen in Fig. 2.1. For simplicity, this inlet is approximated by setting the entire numerical domain boundary resting at the bottom of the simulation domain to the inlet region. This also ensures laminar flow. This change in inlet location has little effect on the overall flow profile. With the inlet location specified, the flow itself must now be calculated. This corresponds to the vertical flow component due to the inlet region being located on horizontal edges. Experimentally, the inlet flow is set by a flow controller external to the system to a specified flow rate, Q_f . Typical experimental flow rates are often between 100 to 500 standard cubic centimeters per minute, or *sccm*. However, it is first corrected for the pressure difference between standard and operating pressure. This flow rate must also result in a speed by converting from a volumetric quantity to speed via the following calculation

$$v_{in} = \frac{Q_f p_0}{6 \times 10^7 pA} \tag{4.33}$$

where v_{in} is the inlet region speed, Q_f is the specified flow rate at the inlet region, p_0 is standard atmospheric pressure, and A is the total numerical surface area covered by all inlet edge segments. The numerical factor in Eq. (4.33) is due to the conversion from cm^3/min to m^3/s . Once this inlet speed has been calculated, the vertical component of the vector average plasma velocity is explicitly set at the generic inlet edge segment via

$$v_{z,i+\frac{1}{2},j} = v_{in} \tag{4.34}$$

where $i + \frac{1}{2}$, j represents the generic mesh indices of an inlet boundary horizontal mesh edge. An outlet region must physically exist to avoid gas and momentum accumulation. The

MSU MPACVD reactor has outlet gas flow regions located toward the outer radius of the substrate as seen in Fig. 2.1. This location of the outlet region is maintained numerically. Likewise, the speed of the vertical velocity component must be calculated and forced during simulation. Unlike the inlet flow region, this outlet flow speed is not set or known. Instead, the only specification is the avoidance of flow accumulation. To ensure this, the outlet speed is once again calculated using Eq. (4.33) with the surface area now representing the



Figure 4.9: Tangential velocity component sample locations surrounding the domain boundary.

total outlet region surface area. This results in v_{out} , and the final boundary condition for orthogonal flows

$$v_{z,i+\frac{1}{2},j} = v_{out}$$
 (4.35)

where v_z is now within the outlet region.

The tangential velocity components lying adjacent to mesh boundaries must also be considered, but do not physically lie on the domain boundaries. These tangential velocity boundary components are provided in Fig. 4.9.

The physical tangential velocity at any material interface is necessarily zero. This is observed experimentally and is referred to as the *no-slip* or *non-slip* boundary condition. It can be deduced logically when considering the bulk flow of a fluid in the following argument. As a fluid flows across a surface, the frictional forces at the interface counteract the fluid flow on a microscopic length scale. This prohibits the fluid motion, resulting in zero tangential flow, and thus no-slip boundary conditions. This effect propagates away from the interface, resulting in a parabolic speed profile directed orthogonal to this surface.

Numerically, this no-slip boundary condition is not necessarily enforced for all systems. In fact, the opposite, or driven, system will be used in the validation of the fluid model. No-slip boundary conditions may be approximated by forcing the flow at the index N to zero. However, the tangential flow component numerical sample is not located here. Instead, the no-slip boundary condition will be enforced during the simulation by applying a zeroed Dirichlet condition at the nearest tangential flow samples.

4.5.3 Matrix Representation

The generic spatial operator, flux, and source terms representing the scalar transport equations as given in Eq. (4.22) may now be converted to matrix equations. That is, these governing equations are now translated to a generic matrix equation form making their simultaneous solution possible.

The solution variable in Eq. (3.18) is the species molar fraction. This equation is solved for all non-molecular hydrogen and electron species contained in the hydrogen gas mixture. A diffusion flux quantity operates on the gradient of these solution samples, translating to their matrix formulation and representation. As a result, Eq. (4.22) may be written in matrix form as

$$\mathcal{A}_S \mathbf{x}_S = [\mathbf{w}_S + \mathbf{v}_S] \tag{4.36}$$

where \mathcal{A}_s is a square matrix representing the combined numerical diffusion flux operator for species s, \mathbf{x}_s is the solution vector containing the unknown molar fractions, \mathbf{w}_s is a vector containing the net rate production terms, and \mathbf{v}_s is the vector containing the net rate of mass flux due to convective forces via the average gas flow. Thus, the diffusion flux operator, \mathcal{A}_s , represents the calculation of

$$\mathcal{A}_S \approx \nabla \cdot (\rho_S D_S \nabla) \tag{4.37}$$

where the right side of Eq. (4.37) operates on the distribution of mole fraction samples. The numerical calculation of the entries for the last term, \mathbf{v}_s , are calculated by summing the last two lines of Eq. (4.22) related to the convective mass flux dependence. As a result, the k^{th} row entry in \mathbf{v}_s representing the net flux of mass density due to convective forces is

calculated

$$\mathbf{v}_{s,k} = \frac{r_{i+1}\rho_{s,i+1,j+\frac{1}{2}}v_{r,i+1,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_i)} - \frac{r_i\rho_{s,i,j+\frac{1}{2}}v_{r,i,j+\frac{1}{2}}}{r_{i+\frac{1}{2}}(r_{i+1}-r_i)} + \frac{\rho_{s,i+\frac{1}{2},j+1}v_{z,i+\frac{1}{2},j+1}}{\left(z_{j+1}-z_j\right)} - \frac{\rho_{s,i+\frac{1}{2},j}v_{z,i+\frac{1}{2},j}}{\left(z_{j+1}-z_j\right)}$$
(4.38)

where $\mathbf{v}_{s,k}$ represents the k^{th} row entry corresponding to the generic spatial mesh index pair $i + \frac{1}{2}, j + \frac{1}{2}$. In this way, the flux term is not a direct update scheme, but a summation over all mesh edges corresponding to each particular element. This is different than the net rate production of mass vector, which simply requires a direct filling of the vector entries. Rearranging for the convective flux term on the right side of Eq. (4.36) is possible due to its interdependence from the solution molar fractions. That is, the physical dependencies in Eq. (4.38) are purely based on previously updated physical quantities. This allows for the source term to be calculated ahead of time and added as a vector term to the right side of Eq. (4.36). Once again, the matrix entries for \mathcal{A}_s are given in Eq. (4.22) as the terms multiplying the solution molar fractions.

Likewise, the electron and total energy equations may also be represented in matrix equation form as given in Eq. (4.39) and Eq. (4.39b)

$$\mathcal{L}_e \mathbf{t}_e = [\mathbf{k}_e + \mathbf{u}_e + \mathbf{p}_e + \tau_e + \mathbf{g}_e + \mathbf{P} + \mathbf{h}_e + \mathbf{q}]$$
(4.39a)

$$\mathcal{L}_g \mathbf{t}_g = \left[\mathbf{l}_e + \mathbf{l}_v + \mathbf{p} + \mathbf{g} + \tau + \mathbf{k} + \mathbf{u} + \mathbf{h} + \mathbf{P} + \mathbf{q}_{rad} \right]$$
(4.39b)

where \mathcal{L}_e and \mathcal{L}_g square matrices representing the thermal conductivity matrix operators, respectively, and \mathbf{t}_e and \mathbf{t}_g are the solution vectors containing the unknown electron and gas temperature samples, respectively. The remaining vectors represented on the right side of Eq. (4.39) represent the various fluxes and source terms listed in order and described previously in their respective energy transport equations. As with the matrix representation of the mass transport equation, some of these right side vectors are precomputed and represent fluxes across mesh edges. Other vectors on the right side of Eq. (4.39) are source terms that are simply translated to vector form without any computation required. However, unlike the mass transport equation matrix representation, the potential energy terms on the right side of Eq. (4.39) do in fact depend on the solution temperature samples. This would normally require the flux dependencies of this potential energy term to be represented within the square, left side matrix operating on the solution vector. However, the influence of these potential energies on the solution. Thus, their contribution is removed from the operating matrix and instead represented in the right side source vectors. This results in a faster numerical matrix calculation and filling, and provides a much simpler formulation. The matrix equation representations for the scalar transport equations are now available in Eq. (4.36) and Eq. (4.39).

Since the momentum transport equation is nonlinear, it is not solved via a simple matrix solution as with the scalar transport equations. Instead, its solution is more complex, requiring intermediate matrix representations. This matrix representation and filling, along with the momentum transport equation numerical solution, is derived in the following paragraphs.

4.5.4 Solution Procedure

Separating the average flow velocity into its two radial and vertical components results in a set of five separate transport equations governing the plasma fluid module. Furthermore, the mass transport equation must be solved for all non-molecular hydrogen and non-electron species included in the simulation. Instead, these masses are updated via the charge and species conservation equations. With the resulting seven hydrogen species included in the present simulation, this results in a set of eleven governing equations which must be simultaneously updated. The choice of numerical solution procedure for this set of equations is discussed and derived in detail in the following paragraphs. The most important criterion for choosing a solution method is accuracy of the overall simulation. Second, the numerical procedure should be generalizable to the physical structure of the numerical mesh and its representative MPACVD system. Finally, the solution method should be numerically efficient and scale reasonably with numerical size. This suggests a near $\mathcal{O}(\mathcal{N})$ scaling metric for the solution method.

At this point, a distinction should be made between the two classes of governing transport equations in the plasma fluid module. These classes are divided according to their linear or nonlinear representations. In particular, the scalar transport equations form linear expressions, while the momentum transport equation is characterized as a nonlinear equation. This suggests these two classes of transport equations may be solved differently, as is in fact the case here. Further discussion related to the reasoning behind this decision and the particular numerical solution methods are provided in the following paragraphs.

The linear, scalar transport equations will be discussed first. As noted above, these equations are characterized as linear, first order differential equations. This suggests their numerical solution is attainable through simple matrix manipulation and linear algebra. However, the system as a whole must first be considered before choosing a suitable numerical solution method. That is, the complete set of eleven governing equations forms a highly nonlinear system of simultaneous solutions. Even though individual equations are linear, their solutions are interdependent and expected to exhibit nonlinear behavior. Moreover, the physical constants, by which these equations are influenced, are often exponentially dependent on several transport variables. This last fact also suggests nonlinear system dynamics with regards to the overall solution behavior.

As a result, the sparse direct solver is not chosen as the numerical solution method for updating the scalar transport equations. Its superior numerical precision is not advantageous for a nonlinear system with rapidly changing and interdependent solutions. Moreover, its computation time is still slightly more than that required by an iterative method. Instead, an iterative numerical method is chosen to update the scalar transport equations. The choice of which iterative solution method to use must now be made.

One promising nonlinear solution method is Broyden's method, which guarantees convergence for a set of nonlinear equations. However, this similarly requires a large number of numerical calculations, often resulting in an unreasonable computation time. Coupling this with the need to update physical constants, the guaranteed convergence of the particular matrix equation does not guarantee overall system convergence or even a reasonable solution. Thus, Broyden's method was not employed for the solution to the scalar transport equations.

Traditionally, Gauss-Seidel iterative solvers have been applied to solve steady MPACVD systems [16, 32]. The Gauss-Seidel family of numerical solvers are based upon the guess and check methodology, where an approximate solution is calculated and used as the guess in the next iteration. Several implementations and variations of this method have been proposed and developed over the years. One particularly popular implementation for the simulation of MPACVD systems is the Gauss-Seidel Line Relaxation method [16]. This numerical solution method was first applied to a set of coupled velocity moment equations by MacCormack in the late 1980s [77]. The Gauss-Seidel Line Relaxation method essentially applies the Gauss-Seidel method successively along each mesh traversal direction. It has proven highly successful in solving the types of nonlinear systems of equations present when simulating MPACVD systems. However, a rectangular, uninhibited grid is required for accurate numerical evaluation, meaning irregular or non-rectangular-shaped meshes are not allowed. This is unacceptable in the current simulation, as irregularly shaped meshes are required in order to accurately capture system geometry, and improve numerical efficiency and solution accuracy. Instead, the Gauss-Seidel Successive Over-Relaxation (SOR) numerical solution method is employed. SOR is a variation of the Gauss-Seidel solution method, the only difference being the insertion of solution relaxation during the final update step. It was originally developed as a numerical solution method in 1950 by Young [78]. Its advantage over Gauss-Seidel Line Relaxation is its independence of the mesh structure required for solution. SOR often boasts faster convergence rates than the standard Gauss-Seidel method depending on the choice of this relaxation factor. Thus, SOR is chosen as the numerical solution method applied for the scalar transport equations.

However, there are several disadvantages to SOR that must be pointed out. Firstly, even though the convergence rate is often maximized during over-relaxation, under-relaxation is utilized here to avoid divergence of the overall solution. This drastically reduces the effective convergence rate of the numerical solution, but can often avoid its divergence depending on the solution tolerance. That is, an accurate and stable multiphysical model is currently preferred over a faster solution time. Improvements in the numerical solution time could be addressed in future implementations of the present simulation by applying various other iterative solution methods.

A second discussion point is the uniqueness of the overall numerical solution. That is, with the set of coupled transport equations forming a nonlinear numerical system, the final solution is not guaranteed to be unique. Instead, this may represent a local solution that depends on the initial numerical and physical operating conditions. If these conditions, or the solution procedure itself, are changed, a completely new solution may arise. Although unlikely due to the multiphysics nature of the coupled solution between various physical models and the aggressive under-relaxation imposed, large differences in the final solution depending on these initial conditions could arise. However, little change in the final solution is observed when altering the initial conditions under the same physical operating conditions.

Before the SOR solution algorithm is provided, the resulting matrix structure given the choice of sampling scheme must be addressed. Using the finite-difference method, the resulting matrix is penta-diagonal, or two-dimensional tridiagonal in structure. That is, the main diagonal is always nonzero with two nonzero entries for each row on either side of this main diagonal. This results from the second spatial derivatives in both directions, with each element-based scalar solution quantity being related to its nearest four neighboring scalar variables centered at their respective element centers. As a result, each matrix row has at most five nonzero entries. These entries may be split into the \hat{r} - and \hat{z} -going terms by separating out their specific terms and keeping track of the individual main diagonal contributions. In this way, the SOR method as derived below may be applied twice over, once in each direction.

The SOR method is derived in many texts and works, and so is only provided here in final form for convenience. The numerical solution for any matrix equation containing a tridiagonal structure may be calculated via the original, iterative Gauss-Seidel method via forward substitution as given by

$$x_i^{n+1} = \frac{1}{A_{i,i}} \left(b_i - \sum_{j=1}^{i-1} A_{i,j} x_j^{n+1} - \sum_{j=i+1}^n A_{i,j} x_j^n \right)$$
(4.40)

where x_i^{n+1} is the i^{th} solution vector entry at the $(n+1)^{th}$ iteration step, $A_{i,j}$ is the leftside matrix entry in the i^{th} row and j^{th} column, b_i is the i^{th} entry of the source vector, and x_j^n is the j^{th} row entry of the previous solution vector. In this way, the unknown solution vector is successively updated in terms of a previous solution. Upon starting the solution procedure, typically a non-zero solution vector is assumed. The closer this initial guess is to the final solution, typically the faster the overall solution is likely to converge. The right-most term in Eq. (4.40) is then evaluated for the given solution vector row. Once this backward substitution is calculated, the forward calculation of the second summation term is evaluated.

The numerical update scheme presented in Eq. (4.40) forms the basis of the SOR method, with only a slight modification. That is, the numerical solution via SOR is still updated as given in Eq. (4.40), but now the solution is *relaxed*. A combination of the new and old solution vectors now form the final updated solution vector to be used in the next iteration. This may be expressed mathematically as

$$x_{i}^{n+1} = (1-\omega) x_{i}^{n} + \omega x_{i}^{\prime}$$
(4.41)

where ω is the relaxation coefficient, and x'_i is the new solution calculated via the original Gauss-Seidel method given in Eq. (4.40). Relaxation coefficients are typically in the range $0 < \omega < 2$, and heavily influence the convergence rate with these factors depending on the properties of \mathcal{A} . For example, setting $\omega = 1$ clearly results in the original Gauss-Seidel numerical solution algorithm. Moreover, setting $\omega > 1$ denotes over-relaxation, while forcing $\omega < 1$ represents under-relaxation. Due to the stiffness of the present numerical model, under-relaxation is utilized here. The end result is a new solution that is a combination of the previous and current solutions. Thus, the full numerical form of the SOR method is expressed

$$x_i^{n+1} = (1-\omega)x_i^n + \frac{\omega}{A_{i,i}} \left(b_i - \sum_{j=1}^{i-1} A_{i,j}x_j^{n+1} - \sum_{j=i+1}^n A_{i,j}x_j^n \right)$$
(4.42)

where x_i^{n+1} is the new solution.

The determination of these relaxation coefficients is important to the stability, efficiency, and accuracy of the scalar transport equations, and the simulation as a whole. As stated earlier, due to the nonlinear nature of the numerical system, these relaxation constants often approach zero, again representing under-relaxation. They are updated during the solution process itself, with increasing value if the current solution is converging and decreasing value otherwise.

To begin, an initial relaxation coefficient on the order of 0.1% is applied to all scalar solution variables. During the solution process, a maximum scaling parameter is chosen to either increase or decrease each individual relaxation coefficient. This value is typically around 10%, but can vary depending on the physical operating and initial numerical conditions. The determination of whether the individual solution variable is converging or diverging is calculated by comparing the difference between previous and current matrix equation residuals. If the current residual is less than the previous residual, the corresponding relaxation coefficient is increased, otherwise, it is decreased. In this way, individual determination of the relaxation parameters is made and typically avoids divergence of the complete solution. At the start of the next complete iteration step, the same initial relaxation coefficient again resets across all solution variables. A maximum relaxation limit is also specified, typically less than one. This may be reached in the case of a steadily converging solution variable with a large number of allowed iterations. Such a limit diminishes the possibility of a stable solution variable becoming unstable, or the multiphysics solution diverging if the electromagnetic module is not promptly updated.

Finally, since the set of nine scalar transport equations are solved independently, each has its corresponding relaxation coefficients. These individual relaxation coefficients are thus tracked and adjusted according to convergence of the individual solutions. That is, the total error associated with any one of these scalar transport equations may be calculated as

$$\epsilon_{err}^{n+1} = \frac{\sum_{i=1}^{N} |x_i^{n+1} - x_i^n|}{\sum_{i=1}^{N} |x_i^n|}$$
(4.43)

where ϵ_{err}^{n+1} is the total residual error associated with the present scalar transport equation where \mathbf{x}^{n+1} and \mathbf{x}^n are the current and previous solution vectors, respectively. The result is an estimation of the convergence of the solution. That is, if $\epsilon_{err}^{n+1} < \epsilon_{err}^n$, then the solution is assumed to be converging, and its relaxation coefficient is increased. Instead, if $\epsilon_{err}^{n+1} > \epsilon_{err}^n$, then its relaxation coefficient is increased, resulting in a greater dependence on the previous solution. Limits must be imposed on these relaxation coefficients to avoid both convergence that is too slow or too fast. The relaxation coefficient limits imposed here include a minimum (and initial) of 0.005 and a maximum of 0.5. Such limits have been found previously to result in an acceptable balance between efficient convergence and a stable overall solution [16].

Of course, since SOR is an iterative process, many iterations are required before the solution is converged enough to consider it a final solution. Thus, the number of these iterations that are allowed, and also necessary, must be discussed. At this point, the numerical solution to the linear matrix equations expressed in Eq. (4.36) via the SOR method have

been presented. Thus, the nonlinear transport equation numerical solution procedure must now be treated.

The momentum transport equation contains nonlinear dependencies on the flow components related to convection influences. As a result, its numerical solution procedure is not expected to remain efficient or even stable under the SOR numerical method applied in the case of the nonlinear transport equations. In fact, even though SOR could be applied in this case, its solution is not expected to converge efficiently, and may even diverge depending on the relaxation parameter. Thus, the SOR method is not applied to the solution of the momentum transport equation. Instead, the Chorin Projection method is used to solve the momentum transport equation.

The Projection method was first proposed and developed simultaneously, yet independent of each other, by Chorin and Temam in the 1967 [79]. It is an implicit update scheme that splits the nonlinear equation solution into intermediate implicit and explicit solution components tracking individual physical forces. These intermediate expressions must be solved in succession for each iteration, and require either matrix solutions or explicit solution projections. The result is a stable solution to the nonlinear momentum transport equation in a reduced number of iterations compared to purely explicit methods. A more detailed derivation of its solution procedure is presented below.

The momentum transport equation derived in Eq. (3.27) is once again provided for convenience in Eq. (4.44)

$$\frac{\partial \vec{v}}{\partial t} + \frac{1}{\rho} \nabla \cdot (\rho \vec{v} \vec{v}) = -\frac{1}{\rho} \nabla p - \frac{1}{\rho} \nabla \cdot \hat{\tau} + \vec{g} \cdot \hat{v}$$
(4.44)

which may be split into its linear and nonlinear dependencies as in Eq. (4.45)

$$\frac{\vec{v}' - \vec{v}^n}{\delta t} = -\frac{1}{\rho} \nabla \cdot (\rho \vec{v} \vec{v}) \tag{4.45a}$$

$$\frac{\vec{v}^{n+1} - \vec{v}'}{\delta t} = -\frac{1}{\rho} \nabla p - \frac{1}{\rho} \nabla \cdot \hat{\tau} + \vec{g} \cdot \hat{v}$$
(4.45b)

where \vec{v}^{n+1} , \vec{v}' , and \vec{v}^n are the new, intermediate, and previous vector average plasma flow distribution solutions, respectively, and δt is the discrete time step. These two expressions in Eq. (4.45a) and Eq. (4.45b) are sometimes referred to as the *predictor* and *corrector* steps, respectively. Clearly, Eq. (4.45a) contains the nonlinear dependencies and Eq. (4.45b) contains the linear dependencies. The gravitational dependence in Eq. (4.45b) is moved to Eq. (4.45a) to group explicit calculation terms as will be derived below. Finally, the viscous and pressure forces are split once more, resulting in a series of three intermediate solution steps representing the standard Projection method algorithm in Eq. (4.46)

$$\frac{\vec{v}' - \vec{v}^n}{\delta t} = -\frac{1}{\rho} \nabla \cdot \left(\rho \vec{v}^n \vec{v}^n\right) + \vec{g} \cdot \hat{v}^n \tag{4.46a}$$

$$\frac{\vec{v}'' - \vec{v}'}{\delta t} = -\frac{1}{\rho} \nabla \cdot \hat{\tau}'' \tag{4.46b}$$

$$\frac{\vec{v}^{n+1} - \vec{v}''}{\delta t} = -\frac{1}{\rho} \nabla p^{n+1} \tag{4.46c}$$

where \vec{v}'' is a second intermediate flow solution vector. Thus, moving forward linearly in time results in the following relationship between vector flow solutions

$$\vec{v}^n \to \vec{v}' \to \vec{v}'' \to \vec{v}^{n+1}, \qquad t^n \to t^{n+1}$$

$$(4.47)$$

where t^n and t^{n+1} are the times at the numerical solution samples corresponding to the previous and current solutions, respectively. Note in Eq. (4.46) the time-dependence and solution time associated with all important spatial quantities and physical constants have been explicitly provided. This will be important when deriving their respective numerical solution procedures. Also note the density term in all expressions in Eq. (4.46) are calculated at the previous time step, n, and are not expected to change significantly over one numerical time step. As stated previously, Eq. (4.46) represents the set of three intermediate expressions that must be solved at each successive iteration during the Projection method solution.

Explicit time stepping is used to step forward the numerical solution. As a result, the CFL condition must again be satisfied, with the time step now dependent on the magnitude of the flow speed.

Eq. (4.46a) contains the nonlinear flow dependence term represented by the $\vec{v}\vec{v}$ tensor product. An explicit numerical solution is applied to this expression, resulting in an updated intermediate flow quantity, \vec{v}' . The gravitational force is also included in the explicit velocity update, as its flow dependence is due to the previous solution at time n. Thus, the solution to the explicit equation given in Eq. (4.46a) may be translated to discretized form as given in Eq. (4.48) for the generic radial and vertical flow components

$$v'_{r,i,j+\frac{1}{2}} = v^{n}_{r,i,j+\frac{1}{2}} - \frac{\Delta t}{\rho_{i,j+\frac{1}{2}}} \left(\frac{\rho_{i+\frac{1}{2},j+\frac{1}{2}}v^{2}_{r,i+\frac{1}{2},j+\frac{1}{2}} - \rho_{i-\frac{1}{2},j+\frac{1}{2}}v^{2}_{r,i-\frac{1}{2},j+\frac{1}{2}}}{r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}} \right) - \frac{\Delta t}{\rho_{i,j+\frac{1}{2}}} \left(\frac{\rho_{i,j+1}v_{r,i,j+1}v_{z,i,j+1} - \rho_{i,j}v_{r,i,j}v_{z,i,j}}{z_{j+1} - z_{j}} \right)$$
(4.48a)

$$v'_{z,i+\frac{1}{2},j} = v^{n}_{z,i+\frac{1}{2},j}$$

$$-\frac{\Delta t}{\rho_{i+\frac{1}{2},j}} \left(\frac{\rho_{i+\frac{1}{2},j+\frac{1}{2}}v^{2}_{z,i+\frac{1}{2},j+\frac{1}{2}} - \rho_{i+\frac{1}{2},j-\frac{1}{2}}v^{2}_{z,i+\frac{1}{2},j-\frac{1}{2}}}{z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}} \right)$$

$$-\frac{\Delta t}{\rho_{i+\frac{1}{2},j}} \left(\frac{\rho_{i+1,j}v_{r,i+1,j}v_{z,i+1,j} - \rho_{i,j}v_{r,i,j}v_{z,i,j}}{r_{i+1} - r_{i}} \right) - gv_{z,i+\frac{1}{2},j} \quad (4.48b)$$

where the discretized forms of the average plasma flow vector components within the parentheses are all assumed to represent the previous solutions at time step n. Note, the normal and shear terms, along with the densities, are thusly represented at the element centers and nodes, respectively for the modifying terms in Eq. (4.48). This suggests the interpolation of average flow quantities to these non-standard mesh locations. As with previous translation operations, this is performed using bilinear interpolation to nodes, whereas a simple averaging scheme suffices for element-based quantities. Eq. (4.48) represents the first intermediate numerical solution update for the Chroin Projection method for the two velocity components.

The second step is to update the next intermediate flow solution taking into account the viscous forces as given in Eq. (4.46b). To begin, Eq. (4.46b) is expanded into its two orthogonal velocity components, its viscosity tensor expanded as in Eq. (3.30) in terms of these components, and rearranged as given in Eq. (4.49)

$$v_r'' = v_r' - \frac{\delta t}{\rho} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \left[-\mu \left(2 \frac{\partial v_r}{\partial r} - \frac{2}{3} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r v_r \right) + \frac{\partial v_z}{\partial z} \right] \right) \right] \right) \right] + \frac{\delta t}{\rho} \left[\frac{\partial}{\partial z} \left(-\mu \left[\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right] \right) \right]$$
(4.49a)

$$v_{z}'' = v_{z}' - \frac{\delta t}{\rho} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \left[-\mu \left(\frac{\partial v_{r}}{\partial z} + \frac{\partial v_{z}}{\partial r} \right) \right] \right) \right] + \frac{\delta t}{\rho} \left(\frac{\partial}{\partial z} \left[-\mu \left(2 \frac{\partial v_{z}}{\partial z} - \frac{2}{3} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r v_{r} \right) + \frac{\partial v_{z}}{\partial z} \right] \right) \right] \right)$$
(4.49b)

where all velocity components are assumed to be sampled at the t'' intermediate time step unless otherwise noted. The discrete form of Eq. (4.49) is complex and rather lengthy, and is derived separately in Appendix B. It is clear these expressions form a set of coupled equations, suggesting their simultaneous solution in a block matrix form, which may be formulated in terms of generic matrix expressions of the form

$$\left[\begin{pmatrix} \mathcal{I} & \mathbf{0} \\ \mathbf{0} & \mathcal{I} \end{pmatrix} - \begin{pmatrix} \underline{\Delta t} \\ \rho \end{pmatrix} \begin{pmatrix} \mathcal{A}_{rr} & \mathcal{A}_{rz} \\ \mathcal{A}_{zr} & \mathcal{A}_{zz} \end{pmatrix} \right] \begin{pmatrix} \mathbf{v}_r'' \\ \mathbf{v}_z'' \end{pmatrix} = \begin{pmatrix} \mathbf{v}_r' \\ \mathbf{v}_z' \end{pmatrix}$$
(4.50)

where \mathcal{I} is the identity matrix, **0** is a square matrix of size $n \times n$ containing all zeros, and \mathcal{A} represent the block matrices corresponding to the spatial operators containing both the gradient and divergence operators as well as the viscosity dependence.

Thus, the matrix equation in Eq. (4.50) must be solved in terms of the intermediate velocity component sample vectors, \mathbf{v}_r'' and \mathbf{v}_z'' . The \mathcal{A} matrices in Eq. (4.50) are rather sparse, with a maximum of nine non-zero entries per matrix row. This makes the use of the sparse direct solver attractive. Thus, Eq. (4.50) is solved for the second intermediate velocity components via the sparse direct matrix solver.

Finally, the pressure correction must be applied to arrive at the full time step and final solution. This is done by first rearranging Eq. (4.46c) in terms of velocity solution at the full time step

$$\vec{v}^{n+1} = \vec{v}^{\prime\prime} - \frac{\delta t}{\rho} \nabla p^{n+1} \tag{4.51}$$

At this point, both the velocity and pressure samples at the full time step are unknown, resulting in an under-defined equation. To avoid this, the divergence of all terms may be applied, resulting in Eq. (4.52)

$$\nabla \cdot \vec{v}^{n+1} = \nabla \cdot \vec{v}'' - \delta t \nabla \cdot \frac{1}{\rho} \nabla p^{n+1}$$
(4.52)

where notice the time step has been removed from the spatial divergence operator, but the density dependence remains within this operator. In the case of the incompressible flow assumption applied here, momentum cannot be created nor destroyed. Thus, this left side term must vanish since

$$\nabla \cdot \vec{v} = 0 \tag{4.53}$$

leaving the following implicit expression governing the pressure correction

$$\frac{1}{\delta t} \nabla \cdot \vec{v}'' = \nabla \cdot \frac{1}{\rho} \nabla p^{n+1} \tag{4.54}$$

Eq. (4.54) is first expanded into its two velocity and spatial divergence components as given in Eq. (4.55)

$$\frac{1}{\delta t} \left[\frac{1}{r} \frac{\partial \left(r v_r'' \right)}{\partial r} + \frac{\partial \left(v_z'' \right)}{\partial z} \right] = \frac{1}{r} \frac{\partial}{\partial r} \left[\frac{r}{\rho} \frac{\partial p^{n+1}}{\partial r} \right] + \frac{\partial}{\partial z} \left[\frac{1}{\rho} \frac{\partial p^{n+1}}{\partial z} \right]$$
(4.55)

and then expressed in discrete form at a generic index pair $i+\frac{1}{2}, j+\frac{1}{2}$ via

$$\frac{1}{\delta t} \left[\frac{r_{i+1}v_{r,i+1,j+\frac{1}{2}}^{\prime\prime\prime} - r_{i}v_{r,i,j+\frac{1}{2}}^{\prime\prime\prime}}{r_{i+1} - r_{i}} \right] + \frac{1}{\delta t} \left[\frac{v_{z,i+\frac{1}{2},j+1}^{\prime\prime\prime} - v_{z,i+\frac{1}{2},j}^{\prime\prime\prime}}{z_{j+1} - z_{j}} \right] \\
= \left[\frac{r_{i+1} \left(p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1} - p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1} \right)}{\rho_{i+1,j+\frac{1}{2}} \left(r_{i+1} - r_{i} \right) \left(r_{i+\frac{3}{2}} - r_{i+\frac{1}{2}} \right)} \right] \\
- \left[\frac{r_{i} \left(p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1} - p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1} \right)}{\rho_{i,j+\frac{1}{2}} \left(r_{i+1} - r_{i} \right) \left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}} \right)} \right] \\
+ \left[\frac{p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1} - r_{i+\frac{1}{2},j+\frac{1}{2}}}{\rho_{i+\frac{1}{2},j+\frac{1}{2}} - p_{i+\frac{1}{2},j+\frac{1}{2}}^{n+1}} \right] \\
- \left[\frac{p_{i+\frac{1}{2},j+1}^{n+1} \left(z_{j+1} - z_{j} \right) \left(z_{j+\frac{3}{2}} - z_{j+\frac{1}{2}} \right)}{\rho_{i+\frac{1}{2},j+\frac{1}{2}} - r_{i+\frac{1}{2},j-\frac{1}{2}}} \right] \right] (4.56)$$

Once again, the density terms must be translated to the mesh edges as seen from the nomenclature and sample locations in Eq. (4.56). Finally, Eq. (4.56) may be expressed as a matrix equation of the form

$$\begin{pmatrix} \mathcal{A}_r \\ \mathcal{A}_z \end{pmatrix} \mathbf{p}^{n+1} = \frac{1}{\Delta t} \begin{pmatrix} \mathbf{v}_r'' \\ \mathbf{v}_z'' \end{pmatrix}$$
(4.57)

where \mathcal{A}_r and \mathcal{A}_z represent the spatial second derivative operators in the \hat{r} and \hat{z} directions, respectively, and Δt is the full numerical time step. These \mathcal{A} matrices also contain the density dependence as well. Eq. (4.57) is now solved for the pressure at the full time step once again using the sparse direct solver.

However, the boundary conditions related to the pressure must first be addressed. The velocity dependence on the pressure is related to the gradient of the pressure distribution. Thus, to remain consistent with the zero normal flow at material and domain boundaries, the normal gradient of the pressure must also remain zero at these boundaries. This results in a zeroed Neumann boundary condition at all material and domain boundaries, which is mathematically represented as

$$\nabla p^{n+1} \cdot \hat{n}|_{bc} = 0 \tag{4.58}$$

where \hat{n} represents the unit vector directed orthogonal to all boundaries.

Finally, once the full time step pressure has been updated, the full time velocity must also be updated. This is done by reapplying Eq. (4.46c) and updating all non-boundary velocity components using the current pressure solution and the previous velocity solution. The end result is an updated average vector plasma velocity solution at a full time step. At this point, the momentum transport equation error is calculated using Eq. (4.43), and the maximum allowed time step calculated. The previous solution algorithm represents one complete solution cycle over a single time step. In practice, this algorithm is repeated until a given tolerance is reached. This tolerance can vary on the size of the mesh and the nonlinearity of the system, but a maximum error limit of 0.001 typically results in a good balance between final solution accuracy and numerical efficiency. This convergence level is set by the user in the current simulation. The momentum transport equation update may also be terminated after a maximum number of full time step solutions, which is also set by the user.

4.5.5 Solution Algorithm

The plasma fluid module solution algorithm is now discussed and presented. Its major components, the order of the various solutions, and a discussion on these considerations follows.

Before the plasma fluid module begins, the absorbed power density is passed from the electromagnetics solution module. Initialization of the plasma fluid module requires the passing of the various scalar and vector transport equation solutions, along with the corresponding plasma physical properties, from the previous solution.

If this is the first complete iteration of the numerical simulation, then the plasma fluid module has not been run before. These solution variables must then be chosen to reflect some non-zero distributions in order to avoid trivial or non-physical numerical solutions. For example, all mole fractions are chosen as uniform, low-value approaching machine precision. This typically results in all mole fractions of constant 10^{-14} everywhere, except for the molecular hydrogen, which is nearly one. The plasma flow fields are chosen to be zero everywhere except at the inlet and outlet regions. Finally, the gas temperature distribution is solved via the steady heat flow equation given the substrate and quartz boundary temperatures outlined previously. Since it is known to generally result in higher temperatures, the electron temperature is set as uniformly five times this gas temperature distribution. If this is not the first complete solution iteration, then the plasma fluid module has been previously updated, and the previous solutions that were stored at the end of the previous update are read from file.

Next, the physical constants are updated according to these initial distributions. This includes the calculation of the corresponding physical quantities related to plasma composition such as molar, mass, and number concentrations. Once the physical constants have been updated, the transport equations must be solved. The momentum transport equation is solved first, and is expected to exhibit less coupling dependence on the other transport equations. This is primarily due to its dependency on only volumetric mass density and viscosity and not the scalar transport variables (including electron temperature). That is, the electron temperature is known to be tightly coupled to the other transport quantities and is often the underlying influence of nonlinear effects. Moreover, its implicit numerical solution procedure typically results in a more stable solution compared to the iterative processes for the scalar transport equations. Thus, its solution is only updated along with the physical constants. However, the momentum transport equation solution procedure does require convergence to a desired tolerance. Thus, it is solved concurrently until the tolerance level is reached, resulting in a converged average vector plasma velocity distribution. More on this choice of solution order and number will be discussed below.

After the average vector plasma velocity is updated by solving the momentum transport equation, the scalar transport equations must be solved. These equations are solved in the following order. First, the mass transport equations for all non-molecular hydrogen and electron species are solved. Then, the electron energy equation is solved, and finally the total energy transport equation. However, all molar fraction and temperature dependencies in all of these transport equations are based upon the previous solutions. That is, the molar fraction dependence in the energy transport equations related to enthalpy diffusion are taken as the previous mole fraction solutions, and not those current. This ensures the energy transport equations are solved using the physical constants associated with the previous transport quantities, and also helps to avoid a divergent solution.

These scalar transport equations are numerically updated using the SOR method described earlier. Their solutions are then relaxed according to their individual relaxation rates, and their residuals along with the total system error, are calculated. This completes one iterative numerical solution cycle, which is repeated for a set number of iterations as set by the user. After the maximum number of iterations has been reached, the physical constants are updated and the momentum transport equation is once again solved. These solution iterations are often referred to as the *inner* iteration loop structure within the plasma fluid module. Change in the electrical conductivity profile is also tracked as a total error metric when comparing to the distribution upon initialization to the electromagnetics module. This updating of physical constants and transport variables continues until a maximum number of iterations, or the maximum error allowed between successive electrical conductivity distributions, have been reached. These iterative updates and solutions are collectively referred to as the *outer* iteration loop. At this point, the physical constants and electrical conductivity are once again updated and passed to the electromagnetics module.

The choice of number of allowed iterations related to both the scalar transport equation solutions, and the maximum physical constants and transport equation resets is crucial to the stability of the numerical simulation. It essentially represents a balance between allowing the numerical solution to converge toward a solution in an efficient manner, with maintaining a simultaneous solution between different physical modules. That is, the choice of maximum number of inner plasma iterations provides a balance between convergence in the numerical SOR solution with the divergence in the transport quantities before updating their related physical constants. Moreover, the choice of maximum outer iterations relates the need for efficient solution convergence with the divergence of the electrical conductivity. Large changes in the electrical conductivity will inevitably influence the absorbed power density profile and thus, the overall solution. These outer and inner iteration settings will depend on not only the numerical mesh and its resolution, but also the initial plasma solution conditions, and the physical system operating conditions. Typical maximum iteration numbers which have proven in the past to strike a good balance between numerical efficiency and the avoidance of divergent numerical solutions are in the range of 5 to 20 for both settings. The maximum error or residual between successive electrical conductivities should also be set accordingly, with typical relative errors between 1% to 10%. Of course, again, this will depend on the particular system to be simulated. A visual depiction of the plasma fluid module solution



algorithm in flowchart form is provided in Fig. 4.10.

Figure 4.10: Plasma fluid module numerical solution flowchart.

The final step in the plasma fluid module solution algorithm is to calculate the complex electrical conductivity distribution. This is the main coupling mechanism going from the plasma fluid module to the electromagnetics solution module. From Eq. (3.48), it is clearly dependent on primarily scalar transport and related quantities. That is, the vector flow dependence in the electrical conductivity is only present due to the effective collision frequency given in Eq. (3.49). Thus, the electrical conductivity is calculated at the element centers with little interpolation required. As a result, the edge-based plasma velocities are averaged at the element centers given the values at the four corresponding edges. Once the conductivity is calculated, it is passed to the electromagnetics module and used in both the material dependence and the absorbed power density calculation. This concludes the plasma fluid module solution algorithm.

4.6 Substrate Thermal Module

The numerical solution and update of the substrate thermal model is finally visited. This solution results in a physical temperature distribution across and within the substrate pedestal. It is coupled to the gas temperature at the substrate surface from the plasma fluid module. In this way, these two modules form a coupled, multiphysical numerical solution resulting in a more accurate representation of the reactor operation and characteristics.

The numerical sample locations with respect to the mesh must first be defined. The relationship between the temperature and the material properties of the substrate suggest sampling these offset from each other. That is, it is numerically advantageous to sample the temperatures within the substrate one-half mesh cell removed from the physical material assignments. Keeping with the standard of sampling scalar solution quantities at mesh centers as seen in the plasma fluid module, the substrate temperature is also located at the mesh element centers. This leads to the assignment of material characteristics at the mesh edges. Although material assignments are optimally located at the element centers, these are readily interpolated to the mesh edges.

The substrate temperature module is solved completely within the substrate region. This includes the substrate itself, the outflow gas region, and the outer substrate pedestal quartz wall as seen in Fig. 2.1. Once again, the numerical approximation and discretization of the solution domain is critical to the accuracy of this module in representing the physical system. In this case, the choice of mesh is rather straight forward with very little approximation due to the absence of curved material interfaces. As such, the FD sampling scheme is aptly suited to represent this rectangular domain. An example of the substrate temperature module solution domain is provided in Fig. 4.11 for reference.

Although completely nondescript, the numerical sampling mesh shown in Fig. 4.11 is bounded on its top and outer right edges by the plasma domain from 4.7. Moreover, the uniform mesh discretization rate is again chosen for simplicity, with nonuniform mesh spacing



Figure 4.11: Substrate temperature module solution domain (a) sampling mesh and (b) material mapping for the MSU MPACVD Reactor B.

being equally applicable to the solution method.

4.6.1 Equation Discretization

The steady heat equation given in Eq. (3.51) is now discretized given the material and temperature sample locations. This is given for a generic element index pair, $i + \frac{1}{2}$, $j + \frac{1}{2}$, and written in terms of thermal diffusivity in Eq. (4.59)

$$\frac{r_{i+1}\alpha_{T,i+1,j+\frac{1}{2}}\left(T_{i+\frac{3}{2},j+\frac{1}{2}}-T_{i+\frac{1}{2},j+\frac{1}{2}}\right)}{r_{i+\frac{1}{2}}\left(r_{i+1}-r_{i}\right)\left(r_{i+\frac{3}{2}}-r_{i+\frac{1}{2}}\right)} - \frac{r_{i}\alpha_{T,i,j+\frac{1}{2}}\left(T_{i+\frac{1}{2},j+\frac{1}{2}}-T_{i-\frac{1}{2},j+\frac{1}{2}}\right)}{r_{i+\frac{1}{2}}\left(r_{i+1}-r_{i}\right)\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} + \frac{\alpha_{T,i+\frac{1}{2},j+1}\left(T_{i+\frac{1}{2},j+\frac{3}{2}}-T_{i+\frac{1}{2},j+\frac{1}{2}}\right)}{\left(z_{j+1}-z_{j}\right)\left(z_{j+\frac{3}{2}}-z_{j+\frac{1}{2}}\right)} - \frac{\alpha_{T,i+\frac{1}{2},j}\left(T_{i+\frac{1}{2},j+\frac{1}{2}}-T_{i+\frac{1}{2},j-\frac{1}{2}}\right)}{\left(z_{j+1}-z_{j}\right)\left(z_{j+\frac{1}{2}}-T_{i+\frac{1}{2},j-\frac{1}{2}}\right)} = 0$$

$$(4.59)$$

where T is the absolute substrate temperature in Kelvin and α_T is the thermal diffusivity.

4.6.2 Boundary Conditions

The boundary conditions must also be treated, and are now given in discrete form. These can be broken into two categories of Neumann boundary conditions: zeroed and finite-valued. At the axis of symmetry, the radial derivative of the substrate temperature must be zero. As a result, the substrate temperature is numerically calculated via

$$T_{\frac{1}{2},j+\frac{1}{2}} = T_{\frac{3}{2},j+\frac{1}{2}} \tag{4.60}$$

where $\frac{1}{2}$, $j + \frac{1}{2}$ represents the element centers lying one-half mesh cell to the right of the axis of symmetry. Likewise, at the bottom of the pedestal corresponding to the domain boundary, a similar condition is satisfied

$$T_{i+\frac{1}{2},\frac{1}{2}} = T_{i+\frac{1}{2},\frac{3}{2}} \tag{4.61}$$

where again, $i + \frac{1}{2}, \frac{1}{2}$ represents all element centers lying one-half mesh cell above the numerical domain boundary bottom edge within the substrate pedestal.

At the top and right pedestal edges, the total energy flux passed from the plasma module is again applied to the substrate temperature module domain edges. This is a combination of the atomic hydrogen bombardment and energy transfer and the thermal flux from the plasma at these boundaries. It is denoted here as the term Q_H denoting the total heat flow due to the plasma. Thus, for a generic right-edge substrate thermal model boundary representing the boundaries of the plasma and thermal modules located at the one-dimensional element index $N - \frac{1}{2}$, the discrete boundary condition is expressed

$$Q_{H,N} = \lambda_N \frac{\frac{T_{N-\frac{1}{2}} - T_{N-\frac{3}{2}}}{r_{N-\frac{1}{2}} - r_{N-\frac{3}{2}}}$$
(4.62)

where λ_N is the translated thermal conductivity of the substrate material associated with the boundary index N. Again, $Q_{H,N}$ has been supplied via calculations from the plasma fluid module at the adjacent and opposite element across the current edge. Indices and corresponding relationships between adjacent samples are the same as shown in Fig. 4.8.

4.6.3 Matrix Representation

Eq. (4.59) is now expressed in matrix form given in Eq. (4.63) as

$$\mathcal{A}\mathbf{t} = \mathbf{0} \tag{4.63}$$

where \mathcal{A} is the square $n \times n$ matrix containing the spatial divergence and gradient operators, and the thermal diffusivity dependence at the mesh edges, n is the number of elements contained in the substrate mesh, \mathbf{t} is the vector containing the unknown substrate temperature solutions, and $\mathbf{0}$ is a vector containing zeros. The solution to Eq. (4.63) is trivial in the absence of non-zero source terms on its right side. These non-zero values correspond to the substrate right and top boundaries where the thermal flux due to plasma processes are coupled to the thermal model. Eq. (4.63) is solved for the substrate temperature vector using the same sparse direct matrix solver from the electromagnetics module and momentum transport equation in the plasma fluid module.

Finally, the solution substrate temperature at the top and right substrate mesh boundaries must be interpolated to the respective edges and passed to the plasma fluid module. Since the same parent mesh is used to generate all solution module domains, this passing is one-to-one between elements, requiring no interpolation or averaging transverse to the mesh interface. The substrate temperatures are interpolated to the domain boundaries via the following generic solution located at a right boundary

$$T_{N,j+\frac{1}{2}} = T_{N-\frac{1}{2},j+\frac{1}{2}} + \frac{T_{N-\frac{1}{2},j+\frac{1}{2}} - T_{N-\frac{3}{2},j+\frac{1}{2}}}{r_{N-\frac{1}{2}} - r_{N-\frac{3}{2}}} \left(r_N - r_{N-\frac{1}{2}}\right)$$
(4.64)

where T_N is the substrate temperature that is passed to the plasma fluid module resulting in the gas temperature solution being forced to this value at all substrate boundaries. This completes the substrate thermal module solution procedure. Its location and order within the entire simulation algorithm is discussed in the following paragraphs.

4.7 Overall Solution Algorithm

A detailed description and discussion of the complete numerical solution algorithm governing the entire simulation follows. This will cover both the choice of solution method, the order of submodule solutions, and an explanation of advantages and shortcomings to this method.

The overall structure of the simulation is essentially a compartmentalized iterative solver. That is, the electromagnetics, plasma fluid, and substrate thermal modules are all updated simultaneously by passing related field distributions, yet solved individually. This iterative solver ensures simultaneous solutions which approach a single, coupled solution. That is, since the plasma fluid module is comprised of primarily iterative numerical solution methods, their solutions approach steady conditions upon system convergence. However, at any one time during the simulation, especially during the initial phase, these solutions are not necessarily in agreement. This is more so the case with the plasma fluid module and its dependence on both the electromagnetics and substrate thermal modules than the other way around.

Unfortunately, there are several disadvantages associated with this overall solution procedure. Firstly, the iterative procedure does not guarantee a specified convergence rate, or even convergence at all. The complete solution may diverge under certain conditions related to the physical system settings, the mesh resolution, or the numerical solution procedure. It may diverge depending on the initial conditions or the maximum plasma module iterations allowed during the transport update procedures. The simulation also does not guarantee the uniqueness of the final solution, which is a byproduct of the nonlinear system behavior. However, even with these admitted disadvantages, the successful and accurate simulation of MPACVD reactor plasmas will be presented.

To begin the complete simulation, a complex conductivity profile must be assumed and supplied to the electromagnetics module. This ensures a non-trivial absorbed power density profile which is then passed to the plasma fluid module. If this absorbed power density
profile contained all zeros, the energy transport equations would not be driven by the power density. Physically, this would result in zero net energy transferred to the electrons, leading to no species production or other energy transfer. So, in the case of zero initial conductivity, no plasma would form and the simulation would terminate. Thus, an initial complex conductivity profile is required for the simulation to begin.

The choice of this initial conductivity profile is not particularly important to the final solution. However, its distribution will influence the rate of solution convergence and, in the extreme case, whether the simulation diverges before a solution is reached. Thus, it is typically recommended to begin with a conductivity profile which is a reasonable estimate to the expected profile. This estimate should be within one order of magnitude in both size, profile, and absolute values (both real and imaginary components) of this expected profile. As a result, this initial conductivity profile is often centered at the axis of symmetry just above the substrate top surface with gaussian profiles in both \hat{r} and \hat{z} . After this initial conductivity has been supplied to the electromagnetics module, the updated solution from the plasma module is used in all successive conductivity dependent calculations.

A schematic of the complex solution process is provided in Fig. 4.12.

The electromagnetics solution module is outlined in the dashed black box in Fig. 4.12, while the plasma fluid module solution components are outlined in the red dashed box.

After the initial conductivity profile has been chosen, the electromagnetic fields are updated and the absorbed power density profile calculated via the electromagnetics module. This absorbed power density profile is passed to the plasma fluid module, where the various transport quantities are initialized, physical constants calculated, and transport quantities updated. Once these transport equations have converged to the desired error or tolerance, the complex conductivity profile is once again calculated in terms of the updated transport quantities. At this point, the substrate temperature is updated via the substrate thermal module. This temperature distribution is solved using the previously updated gas temperature from the plasma fluid module, with the substrate temperature being passed to the



Figure 4.12: Complete simulation flowchart.

future plasma solution.

As a final step, the total system error is estimated by summing over all transport matrix equation residuals via

$$\epsilon_{tot} = \sum_{t=1}^{N_t} \left(\frac{\sum |\mathcal{A}_t \mathbf{x}_t^{n+1} - \mathbf{b}_t^{n+1}|}{\sum |\mathbf{b}_t^{n+1}|} \right)$$
(4.65)

where N_t is the total number of transport equations solved, \mathcal{A}_t is the left side, square matrix associated with the t^{th} transport equation, \mathbf{x}_t^{n+1} is the transport equation solution at the current iteration step, and \mathbf{b}_t^{n+1} is the current source vector associated with transport equation. In this case, $N_{trans} = 11$ representing the seven mass, two momentum components, and two energy transport equations. The above represents one complete numerical iteration step. This process repeats until either ϵ_{tot} has dropped below the specified maximum system residual error, or the maximum number of allowed iterations, have been reached, the various numerical solution distributions are plotted, and the simulation terminates. Typically, several hundred to thousand such iterations are required for a finely discretized domain simulating higher pressure operating conditions to converge to a total residual of 10%.

CHAPTER 5

VERIFICATION AND VALIDATION

An important step in gauging the accuracy and success of any numerical simulation is its comparison against other known solutions and systems. These systems may represent experimental data, analytic functions or solutions, or previous numerical simulations. This comparison of numerical solutions against other systems is commonly referred to as the *verification* and *validation* process.

The current Microwave PACVD system numerical simulation has numerous interconnected and coupled components, referred to as modules. Its three solution modules are coupled through different physical variables in order to arrive at a single global solution. These modules must be verified and validated individually, along with the entire numerical solution as a whole. These results are presented in the following sections.

5.1 Verification

The verification of individual solution modules is first discussed and presented. This involves verifying the different numerical solution procedures via their related matrix equations. Eigenvalue analysis will be performed on the corresponding matrices. As is standard practice, examples of lowest eigenvalue convergence with increasing mesh resolution are presented.

5.1.1 Electromagnetics Module

The solution to the electromagnetics module is calculated from Eq. (3.8) and Eq. (4.12) in terms of the azimuthal magnetic field. Eigenvalue analysis may performed on the mass matrix in Eq. (4.12) by comparing the lowest mass matrix eigenvalues to the corresponding wavenumbers of an analytic geometry. A cylindrical cavity lined with PEC serves as the analytic geometry as shown in Fig. 5.1.



Figure 5.1: Simple cylinder schematic for verifying Helmholtz matrix equation solution in electromagnetics module.

Supported wavenumbers for the cavity in Fig. 5.1 may be analytically derived [80]. Assuming TM_z polarization, these wavenumbers are given by

$$k_r = \frac{\chi_{0n}}{\lambda_0}, \qquad n \in \mathcal{Z}^+ \tag{5.1a}$$

$$k_{\mathcal{Z}} = \frac{n\pi}{2\lambda_0}, \qquad n \in \{0, \mathcal{Z}^+\}$$
(5.1b)

Mode No.	Analytic	$\lambda_0/20$	$\lambda_0/30$	$\lambda_0/40$
1	386.24058868	385.69556448	385.99816625	386.10419169
2	551.03045703	550.40074519	550.75039349	550.87288775
3	1045.40006209	1043.50082514	1044.55550081	1044.92491456
4	1869.34940386	1861.95567835	1866.06000274	1867.49847970
5	2035.07865405	2021.79786182	2029.16077897	2031.74684394
6	2199.86852241	2186.50304254	2193.91300621	2196.51554000
7	2694.23812746	2679.60312249	2687.71811353	2690.56756681
8	3022.87848233	3000.71925848	3013.01221253	3017.32523434
9	3518.18746923	3498.05797569	3509.22261546	3513.14113194
10	4505.98729751	4452.77070940	4482.26841391	4492.63222899
11	4671.71654770	4636.82155583	4656.17482525	4662.96788659
12	5001.46489722	4923.14226854	4966.47051486	4981.74409267
13	5166.25476558	5087.84744926	5131.22274210	5146.51278874
14	5660.62437063	5580.94752921	5625.02784943	5640.56481554
15	6154.82536288	6088.87300674	6125.43102663	6138.27488123
16	6318.67584939	6209.15765104	6269.80147776	6291.14464717
17	6484.57371240	6399.40238241	6446.53235136	6463.13838068
18	7638.10279087	7538.16596255	7593.48456115	7612.96513533
19	7967.51391476	7845.25994838	7912.96409048	7936.78729942
20	8460.94413798	8259.05137385	8370.71190019	8410.08931311

Table 5.1: Lowest 20 analytic and calculated eigenvalues for a regular PEC cylinder waveguide with varying mesh refinement for the electromagnetics module.

$$k_0 = \sqrt{k_r^2 + k_z^2}$$
(5.1c)

$$\vec{k} = k_F \hat{r} + k_Z \hat{z} \tag{5.1d}$$

where k_r , k_z , k_0 , and \vec{k} are the radial, vertical, magnitude, and total wavenumbers, respectively, χ_{0n} is the n^{th} zero crossing of the zeroeth order Bessel function of the first kind, and \mathcal{Z}^+ is the set of all positive integers. The eigenvalues of the corresponding mass matrix should match these eigenvalues given in Eq. (5.1). All numerical eigenvalues presented in this work were calculated using the MATLAB[®] eigenvalue function, eig. The five lowest zero crossings of the zeroeth order bessel function were also calculated to sixteen digits via MATLAB[®] during the radial component calculations. The results for different uniform mesh spacings are provided in Table 5.1. Clearly, the numerical eigenvalues presented in Table 5.1 are converging to the analytic wavenumbers as the mesh resolution increases. This verifies the correct mass matrix filling within the electromagnetics module.

The material dependence of the matrix solution within the electromagnetics module must also be verified. This is achieved by filling the entire PEC cavity with a homogeneous dielectric and again performing eigenvalue analysis. As a result, the same geometry from Fig. 5.1 is again employed, but now filled with a perfect dielectric. The eigenvalues are calculated in much the same way as in Eq. (5.1), but now with a material dependence as given in Eq. (5.2)

$$k_r = \frac{\chi_{0n}}{\lambda} = \frac{\chi_{0n}}{\lambda_0 \sqrt{\epsilon_r}}, \qquad n \in \mathcal{Z}^+$$
 (5.2a)

$$k_{\mathcal{Z}} = \frac{n\pi}{2\lambda} = \frac{n\pi}{2\lambda_0\sqrt{\epsilon_r}}, \qquad n \in \{0, \mathcal{Z}^+\}$$
(5.2b)

where the total and vector wavenumbers are the same as given in Eq. (5.1). For numerical verification purposes, an arbitrary relative permittivity of $\epsilon_r = 2$ was chosen. The corresponding analytical and calculated numerical eigenvalues for the electromagnetics module matrix equation solution are provided in Table 5.2.

As with the empty cavity results presented above, the calculated mass matrix eigenvalues provided in Table 5.2 converge toward their corresponding analytic values when mesh refinement is increased. Again, this verifies the correct perfect dielectric dependence of the mass matrix filling in the electromagnetics solution module. This is important, as the presence of dielectrics in the MPACVD reactor is vital to the coupling of microwave power to the plasma discharge.

Finally, the accuracy of the mass matrix generation in the presence of a lossy dielectric must be verified. Once again, the same homogeneously filled cylindrical PEC cavity is once again employed. However, the material is now assumed to have a total permittivity matching that of free space, while its complex permittivity is set to an arbitrary value. Eigenvalue analysis is again performed to confirm solution convergence with mesh refinement.

Mode No.	Analytic	$\lambda_0/20$	$\lambda_0/30$	$\lambda_0/40$
1	193.12029434	192.84778224	192.99908312	193.05209584
2	275.51522851	275.20037259	275.37519674	275.43644387
3	522.70003104	521.75041257	522.27775040	522.46245728
4	934.67470193	930.97783917	933.03000137	933.74923985
5	1017.53932702	1010.89893091	1014.58038948	1015.87342197
6	1099.93426120	1093.25152127	1096.95650310	1098.25777000
7	1347.11906373	1339.80156124	1343.85905676	1345.28378340
8	1511.43924116	1500.35962924	1506.50610626	1508.66261717
9	1759.09373461	1749.02898784	1754.61130773	1756.57056597
10	2252.99364875	2226.38535470	2241.13420695	2246.31611449
11	2335.85827385	2318.41077791	2328.08741262	2331.48394329
12	2500.73244861	2461.57113427	2483.23525743	2490.87204633
13	2583.12738279	2543.92372463	2565.61137105	2573.25639437
14	2830.31218531	2790.47376460	2812.51392471	2820.28240777
15	3077.41268144	3044.43650337	3062.71551331	3069.13744061
16	3159.33792469	3104.57882552	3134.90073888	3145.57232358
17	3242.28685620	3199.70119120	3223.26617568	3231.56919034
18	3819.05139543	3769.08298127	3796.74228057	3806.48256766
19	3983.75695738	3922.62997419	3956.48204524	3968.39364971
20	4230.47206899	4129.52568692	4185.35595009	4205.04465655

Table 5.2: Lowest 20 analytic and calculated eigenvalues for filled cylindrical waveguide with varying mesh resolutions and homogeneous permittivity of $\epsilon_r = 2$.

Mode No.	Analytic	$\lambda_0/20$	$\lambda_0/30$	$\lambda_0/40$
1	7.04454840	7.03460786	7.04012694	7.04206071
2	10.05011083	10.03862571	10.04500286	10.04723701
3	19.06679814	19.03215849	19.05139446	19.05813211
4	34.09461031	33.95975808	34.03461586	34.06085189
5	37.11730590	36.87508090	37.00937136	37.05653797
6	40.12286834	39.87909875	40.01424728	40.06171426
7	49.13955564	48.87263153	49.02063888	49.07260937
8	55.13354735	54.72939086	54.95359907	55.03226323
9	64.16736782	63.80023112	64.00386027	64.07532914
10	82.18360927	81.21300514	81.75100662	81.94002973
11	85.20630486	84.56986390	84.92284349	85.04674048
12	91.22050502	89.79199794	90.58225132	90.86082240
13	94.22606745	92.79601579	93.58712724	93.86599869
14	103.24275476	101.78954857	102.59351884	102.87689380
15	112.25636677	111.05347818	111.72025104	111.95450699
16	115.24479605	113.24732064	114.35338869	114.74266158
17	118.27056693	116.71714816	117.57674023	117.87961357
18	139.30950397	137.48678094	138.49572344	138.85102491
19	145.31755355	143.08779368	144.32263310	144.75713884
20	154.31710770	150.63483514	152.67138440	153.38957948

Table 5.3: Lowest 20 analytic and calculated eigenvalues for a homogeneously filled cylindrical waveguide with $\epsilon_r = 1$ and $\hat{\sigma}_e = 1 + j0$ with varying mesh refinements.

The analytic eigenvalues are now dependent on both the permittivity and the conductivity as given in Eq. (5.3).

$$k_r = \frac{\chi_{0n}}{\lambda} = \frac{\chi_{0n}}{\lambda_0 \sqrt{\hat{\epsilon}}}, \qquad n \in \mathcal{Z}^+$$
 (5.3a)

$$k_{\mathcal{Z}} = \frac{n\pi}{2\lambda} = \frac{n\pi}{2\lambda_0\sqrt{\hat{\epsilon}}}, \qquad n \in \{0, \mathcal{Z}^+\}$$
(5.3b)

$$\hat{\epsilon} = \left[1 + \frac{1}{(\sigma_e \omega)^2}\right]^{-1}, \qquad \sigma_e \in \Re$$
(5.3c)

where $\hat{\epsilon}$ is the total real component of the permittivity, σ_e is the electrical conductivity, and \Re is the set of all real numbers. Eigenvalue analysis was performed with results provided in Table 5.3. The lossy dielectric was assumed to have the properties $\epsilon_r = 1$ and $\hat{\sigma}_e = 1 + j0$.

Once again, the calculated mass matrix eigenvalues provided in Table 5.3 converge toward

their respective analytic wavenumbers with mesh refinement. The mass matrix filling in the case of lossy dielectrics in the electromagnetics module is thusly verified as accurate.

5.1.2 Transport Equations

The mass matrix filling for the transport matrix equations within the plasma fluid module must also be verified similarly. These matrix equations will be broken into two categories: vector transport and scalar transport. Since the momentum transport equation contains both explicit and implicit numerical solutions, its verification is unavailable. Instead, the numerical solution to this equation is validated against canonical solutions for simplified flow systems.

Eigenvalue analysis may be performed on the scalar transport equations exactly the same way as seen in the electromagnetics module. The same empty cavity geometry from Fig. 5.1 and corresponding wavenumbers from Eq. (5.1) are utilized and compared against the numerical eigenvalues calculated from the scalar transport mass matrix as provided in Table 5.4.

Once again, the first twenty eigenvalues are captured with convergence during mesh refinement. The scalar transport mass matrix filling is thus verified as accurate.

Of course, the scalar transport matrix solutions are never fully incremented during the plasma fluid module solution procedure. As a result, the SOR numerical solution procedure used in updating the scalar transport equations must also be verified. Since it is an iterative solution method, it is verified against the exact numerical solution of a diagonal matrix equation, with agreement to machine precision expected. Specifically, a positive definite, penta-diagonal square matrix of size 1600×1600 was generated with its entries filled by random numbers between 0 and 1. The resulting matrix equation was first solved using the MUMPS sparse direct solver and then solved via the SOR solution method. An arbitrary

Mode No.	Analytic	$\lambda_0/20$	$\lambda_0/30$	$\lambda_0/40$
1	164.78986835	164.70518071	164.75222724	164.76869606
2	659.15947341	657.80526066	658.55733456	658.82072287
3	980.71259656	977.56612986	979.22975848	979.81250866
4	1145.50246492	1142.27131058	1143.98198572	1144.58120472
5	1483.10881517	1476.26011387	1480.06183649	1481.39428800
6	1639.87206998	1635.37139053	1637.78709305	1638.63323153
7	2463.82141174	2453.82624373	2459.29159498	2461.20679666
8	2636.63789364	2615.02369400	2627.01404628	2631.22104265
9	3287.53142937	3253.57205610	3272.19023028	3278.72607008
10	3452.32129772	3418.27723682	3436.94245753	3443.49476614
11	3617.35049021	3592.58982387	3606.24380477	3611.03355131
12	3946.69090278	3911.37731676	3930.74756485	3937.54679295
13	4119.74670882	4067.07514491	4096.27024766	4106.52803729
14	4770.64024455	4729.83216997	4752.25206678	4760.12035809
15	5100.45930539	5044.64127478	5075.50000615	5086.34054595
16	5924.16932302	5823.46208656	5883.80331151	5905.04045548
17	5932.43526070	5868.59575010	5899.20427657	5909.94711273
18	6911.76305866	6764.61276082	6846.40563292	6875.21649374
19	6913.14785727	6801.02821643	6863.03306999	6884.85296414
20	7076.55292701	6929.31794153	7011.15786017	7039.98518981

Table 5.4: Lowest 20 analytic and calculated eigenvalues for an empty cylindrical cavity with varying mesh refinement.

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relaxation coefficient of 0.1 was specified. SOR numerical solution error was calculated as

$$\epsilon = \sqrt{\sum_{i=1}^{N} \left(b_i^{(0)} - b_i\right)^2} \tag{5.4}$$

where ϵ is the total solution error, N is the number of solution unknowns (1600 in this case), $\mathbf{b}^{(0)}$ is the solution vector calculated via the MUMPS sparse solver, and \mathbf{b} is the solution calculated via the SOR routine. The solution procedure terminated once the SOR error dropped below the double precision tolerance of the computer, or 10^{-16} . Thus, SOR solution procedure was verified as accurate.

5.1.3 Substrate Thermal Model

Finally, the correct mass matrix filling within the substrate thermal module must also be verified. Again, this was carried out via eigenvalue analysis. The standard empty cylindrical cavity from Fig. 5.1 is once again assumed with supported wavenumbers given by Eq. (5.1). The resulting eigenvalues calculated from the substrate thermal module mass matrix are given in Table 5.5.

Again, the first twenty eigenvalues are captured in Table 5.5 with clear convergence toward the analytic eigenvalues during mesh refinement observed. This verifies the mass matrix filling within the substrate thermal module.

5.1.4 Complete Simulation

The verification of the complete, coupled simulation is warranted and provides confidence in the model as a whole. However, due to its complexity, nonlinear behavior, and dependence on numerous physical and numerical variables, the verification of the complete simulation is unavailable. Validating the complete simulation is a more reasonable undertaking and will be discussed in the following section.

Mode No.	Analytic	$\lambda_0/20$	$\lambda_0/30$	$\lambda_0/40$
1	164.78986835	164.70518071	164.75222724	164.76869606
2	659.15947341	657.80526066	658.55733456	658.82072287
3	980.71259656	977.56612986	979.22975848	979.81250866
4	1145.50246492	1142.27131058	1143.98198572	1144.58120472
5	1483.10881517	1476.26011387	1480.06183649	1481.39428800
6	1639.87206998	1635.37139053	1637.78709305	1638.63323153
7	2463.82141174	2453.82624373	2459.29159498	2461.20679666
8	2636.63789364	2615.02369400	2627.01404628	2631.22104265
9	3287.53142937	3253.57205610	3272.19023028	3278.72607008
10	3452.32129772	3418.27723682	3436.94245753	3443.49476615
11	3617.35049021	3592.58982387	3606.24380477	3611.03355131
12	3946.69090278	3911.37731676	3930.74756485	3937.54679295
13	4119.74670882	4067.07514491	4096.27024766	4106.52803729
14	4770.64024455	4729.83216997	4752.25206678	4760.12035809
15	5100.45930539	5044.64127478	5075.50000615	5086.34054595
16	5924.16932302	5823.46208656	5883.80331151	5905.04045548
17	5932.43526070	5868.59575010	5899.20427657	5909.94711273
18	6911.76305866	6764.61276082	6846.40563292	6875.21649374
19	6913.14785727	6801.02821643	6863.03306999	6884.85296414
20	7076.55292701	6929.31794154	7011.15786017	7039.98518981

Table 5.5: Lowest 20 analytic and calculated eigenvalues for an empty cylindrical waveguide with varying mesh refinements for the substrate thermal module.

5.2 Validation

With the accurate filling of the matrix equations in the various modules verified, their resulting numerical solutions must be validated. This includes comparing these solutions with known physical phenomena and tabulated experimental data. As with verification process, the validation of the overall simulation will initially be broken into its individual modules. The validation of the complete simulation is performed by numerical trends and data to physical trends and experimental data under similar operating conditions.

5.2.1 Electromagnetics Module

The electromagnetics module is validated by comparing the numerical field solutions against analytical fields for canonical system geometries. This canonical geometry is most easily realized as an empty cylindrical waveguide as presented in Fig. 5.2.



Figure 5.2: Cylindrical waveguide with $\text{TM}^{(z)}$ polarized incident field for validating electromagnetics module solution.

A $\text{TM}^{(z)}$ -polarized electromagnetic wave is assumed traveling downward from the top of the waveguide. The analytic electromagnetic field solutions are given in Eq. (5.5) [80].

$$H_{\phi} = \frac{\mu_0}{\epsilon_0} J_1(k_r r) \exp\left(jk_z z\right) \tag{5.5a}$$

$$E_r = J_1(k_r r) \exp\left(jk_z z\right) \tag{5.5b}$$

$$E_z = J_0(k_r r) \exp\left(jk_z z\right) \tag{5.5c}$$

These solutions provided in Eq. (5.5) may be used for direct comparison with the numerical solutions.

An infinite cylindrical waveguide as shown in Fig. 5.2 is numerically unattainable. Instead, it is truncated and lined with PMLs on either end as presented in Fig. 5.3 [70, 73].



Figure 5.3: Cylindrical waveguide for quantifying reflections from PMLs and validating the electromagnetics module numerical solution.

The incorporation of the PMLs introduces a numerical reflection artifact, which must be quantified. In order to do this, the resulting electromagnetic field solutions must be calculated purely in the presence of the PMLs. These solutions are all provided in Fig. 5.4, along with the initial traveling wave.

In order to quantify the reflection from the PMLs, the magnetic field magnitude may be





Figure 5.4: Real components of the (a) TF/SF source vector, (b) azimuthal magnetic (H/m), and (c) radial and (d) vertical electric field (V/m) intensities for the canonical waveguide solution.

compared between the scattered and total field regions as

$$R_{PML} = \frac{|H_{\phi}^{(s)}|^2}{|H_{\phi}^{(i)}|^2} \tag{5.6}$$

where R_{PML} is the reflection coefficient from the PMLs, and $|H_{\phi}^{(s)}|^2$ and $|H_{\phi}^{(i)}|^2$ represent the maximum scattered and incident magnetic field intensities, respectively. The incident magnetic field intensity is equal to the maximum of the first-order Bessel function of the first kind (approximately 0.575) divided by the free space impedance as given by

$$\eta_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} \approx 1.526 \times 10^{-3} \tag{5.7}$$

where η_0 is the free space impedance. The maximum scattered magnetic field intensity within the scattered field region is extracted as 6.168 $\times 10^{-6}$ H/m. Thus, the reflected power ratio may be calculated

$$R_{PML} = \frac{|6.168 \times 10^{-6}|^2}{|1.526 \times 10^{-3}|^2} = 1.633 \times 10^{-5}$$
(5.8)

resulting in a total reflected power percentage due to the numerical domain truncation via PMLs of approximately 0.16%. This result is very small, and translates to a maximum absorbed power error of roughly 3 Watts for a MPACVD system operating at 2.0 kW. This validates the incorporation of the PMLs in the electromagnetics solution procedure. The accurate incorporation of both the PEC and axis boundaries were similarly validated within the electromagnetics module. Finally, the numerical results provided in Fig. 5.4 validate the electromagnetic field solutions for the electromagnetics module for an empty cavity.

The electromagnetic field solutions must also be validated in the presence of both lossless and lossy dielectrics. In order to validate the electromagnetics module numerical solution in the case of lossless materials, a dielectric material fills the lower half of the numerical domain. A schematic of this partially filled lossless dielectric waveguide is provided in Fig. 5.5.



Figure 5.5: Cylindrical waveguide with lossless dielectric region for validating the electromagnetics module numerical solution.

The supported analytic electromagnetic field distributions may be calculated and used for comparison [80]. The resulting numerical electromagnetic solutions for $\text{TM}^{(z)}$ polarization and $\epsilon_r = 4$ are provided in Fig. 5.6.

As expected, the wavelength of the electromagnetic fields in the lossless dielectric region of Fig. 5.6 is one half that of the free space region. In order to validate the lossless material response of the numerical solution, both the wavelength and reflected and transmitted field intensities are quantified and compared to their corresponding analytic values. Here, the wavelengths were determined to be within 2% of their analytically calculated values. These relationships remained valid for both magnetic and electric fields in the scattered and total field regions. Likewise, the magnitude of both the electric and magnetic fields were observed to agree with the analytical amplitudes to within 2% for both regions. These results were reported for a relatively coarse mesh discretization rate of twenty sample points per free space wavelength, and validate the electromagnetics solution in the presence of a lossless dielectric.





Figure 5.6: Real components of the (a) TF/SF source vector, (b) azimuthal magnetic (H/m), and (c) radial and (d) vertical electric field (V/m) intensities for the lossless material $(\epsilon_r = 2)$ validation.

Table 5.6: Comparison of analytic and measured skin depth values for wave propagation into a lossy material with $\epsilon_r = 1 - j0.1$ for mesh discretization of $\Delta = \lambda_0/20$.

Resolution	$\delta(m)$
Analytic	6.158497226941845E-002
Simulation	6.118213428571451E-002

The electromagnetic field solutions in the presence of a lossy dielectric must also be validated. The same geometry from the lossless dielectric system is employed, but now with a complex permittivity, in this case chosen to be $\hat{\epsilon}_r = 1 - j0.1$. The resulting electromagnetic field intensities exponentially decay as the wave propagates into the lossy material with a skin depth given by

$$\delta = \frac{1}{\alpha} = \frac{c}{\omega\sqrt{0.1}} \approx 0.062m \tag{5.9}$$

This decay of electromagnetic field strength is observed in Fig. 5.7.

The skin depth was calculated by measuring the distance from the lossy dielectric surface to the point where the electric field magnitude dropped to 1/e of its surface value. For comparison, both the analytic and numerically extracted distances are listed in Table 5.6.

The numerical and analytic skin depth data provided in Table 5.6 agree to within 0.65% error. Thus, the accurate solution of the electromagnetic fields in the presence of a lossy dielectric are validated for the electromagnetics module.

As a final validation of the electromagnetics module, the field solutions and power distribution within the MSU Microwave PACVD reactor may be analyzed. This will include a qualitative analysis of the electromagnetic fields in the absence of a lossy dielectric (representing the plasma). Numerical electromagnetic field solutions in the presence of a plasma discharge will be presented later.

Electromagnetic fields within the MSU MPACVD reactor are known to be dominated by $TM_{013}^{(z)}$ -like modes in the main cavity [5, 21, 22]. Simulated electromagnetic field solutions in the absence of a plasma discharge are provided in Fig. 5.8.





Figure 5.7: Real components of the (a) TF/SF source vector, (b) azimuthal magnetic (H/m), and (c) radial and (d) vertical electric field (V/m) intensities for the lossy material ($\epsilon_r = 1 - j0.1$) validation.



Figure 5.8: (a) Discretized MSU MPACVD schematic with magnitudes of the (b) azimuthal magnetic (H/m), and (c) radial and (d) vertical electric field (V/m) intensities for the validation fo the unfilled reactor. In (a), red denotes the TF/SF interface, green the silica bell jar and substate walls, and blue the plasma and reactor regions. White denotes metal (PEC). The color scales for the electric fields are the same.

Within the main cavity, three electric field maxima are present at the outer reactor wall in the $|E_r|$ solution from Fig. 5.8. This confirms the $\text{TM}_{013}^{(z)}$ -like mode dominance. Similarly, the corresponding two maxima along the reactor axis in the $|E_z|$ solution also suggest the $\text{TM}_{013}^{(z)}$ mode dominates. The combination of all these factors suggest the total electromagnetic field solution in the absence of a plasma discharge within an approximated MSU MPACVD reactor is validated.

5.2.2 Plasma Fluid Module

The numerical solutions within the plasma fluid module are now validated. Unlike the electromagnetics module, this includes both the physical constants and matrix equation solution variables. These physical constants are addressed and validated first.

Some of the physical constants present in Eq. (3.18) may be compared directly against reported data under similar conditions [16, 35, 45, 64, 81]. Two such constants include the species mass diffusion and the chemical reaction coefficients, the exact calculation of which are provided in the appendix.

The species mass diffusion coefficient is based upon Kinetic Theory and gas dynamics, and as a result is dependent on many separate plasma properties [81]. Several approximations have been previously substituted for these calculations and are often implemented in MPACVD simulations [35, 64]. These simplified diffusion coefficient expressions require much less information and computation time, but are not nearly as accurate. The latter can lead to large errors in the final system solution. Two simplified diffusion coefficient models have been reported by Koldanov, *et al.* and Mankelevich, *et al.* [35, 64]. As a comparison between these simplified diffusion expressions and that calculated in the current simulation, the ratio between these values are recorded over the range of typical operating conditions. The resulting ratios of current simulation to both the Koldanov and Mankelevich approximated mass diffusion coefficients are shown in Fig. 5.9.

Clear differences between the present and simplified diffusion models are apparent from



Figure 5.9: Comparison of present to approximated mass diffusion coefficients as used by (a) Koldanov, *et al.* and (b) Mankelevich, *et al.* [35, 64].

Fig. 5.9. That is, the wide range of ratios between present and the approximated diffusion models suggest large differences in the resulting calculations. One possible reason for this discrepancy is that the species diffusion coefficient is not completely–or even well–characterized within microwave discharges in MPACVD systems. This makes it difficult to definitively choose one model over another. However, the two simplified diffusion models and that used in the present work are of the right order of magnitude over a large range of expected operating temperatures and pressures. Their ratios do not deviate by more than one order of magnitude for the majority of the typical operating conditions range, as well. Thus, this qualitative agreement is taken as a validation of the species diffusion coefficient calculation.

Calculated chemical reaction rates associated with MPACVD hydrogen-based plasmas may also be validated against experimental data [16, 34, 45–47, 64, 82–85]. Several reactions at various locations throughout the plasma solution domain were compared to those stated in the literature under the same temperature, pressure, and density conditions [16, 45]. Agreement to within machine precision was observed, validating the chemical reaction calculations.

The momentum transport equation in Eq. (3.27) resembles the Navier-Stokes equation. Thus, this equation may be validated against canonical Navier-Stokes solutions for simple geometries. One of the most common canonical problems is the driven cavity system as shown in Fig. 5.10.

The coordinate frame chosen in Fig. 5.10 is the Cartesian frame, as is typically assumed. Thus, the momentum transport equation solution will first be validated against the Cartesian coordinate frame solution, and later the cylindrical solution will be supplied. Also, the gravitational force present in Eq. (3.27) is turned off, and the volumetric mass density and viscosity distributions are assumed constant. The resulting numerical vector velocity solution to the momentum transport equation is presented in Fig. 5.11.

As expected, a circulating flow is supported with the fluid circulating about a center vortex. Two turbulent regions are observed to exist in the two lower corners as expected. This solution may be compared directly with numerical results reported elsewhere [86] by



Figure 5.10: The canonical driven cavity system used to validate the momentum transport equation.



Figure 5.11: Numerical vector velocity solution in units of m/s to the momentum transport equation for the driven cavity canonical system in Cartesian coordinates.



Figure 5.12: Validation of driven cavity numerical solution for two Reynolds numbers against reported data. [86]

tracking the horizontal flow component at the horizontal midpoint across the vertical domain as provided in Fig. 5.12.

The numerical vector flow solutions at the two given Reynolds numbers are in excellent agreement with the previously reported results as shown in Fig. 5.12 [86]. With 40 numerical samples in each direction, agreement to within 1% is observed. This validates the momentum transport equation in Cartesian coordinates.

However, the MSU MPACVD reactor exhibits cylindrical symmetry, and so the numerical simulation must also be validated in the cylindrical coordinate frame. Since a similar driven cavity solution does not exist in cylindrical coordinates, flow through a cylindrical pipe is used for validation.

Schematics of laminar flow through both square and cylindrical pipe canonical systems are provided in Fig. 5.13.

The resulting numerical solutions for both square and cylindrical systems are provided in Fig. 5.14.



Figure 5.13: The laminar flow through a pipe in the (a) Cartesian and (b) cylindrical coordinate frames.

As expected, the flow speed at the center of the Cartesian coordinate frame system is greater than that present at the axis of symmetry in the cylindrical coordinate system. This is due to the cylindrical pipe having roughly twice as much area for the fluid to flow through compared to the square pipe. These results validate the solution of the momentum transport equation under uniform fluid properties in cylindrical coordinates.

Finally, the mass transport equation solution must also be validated inhomogeneous viscosity and mass density. To do so, a Gaussian distribution for both density and viscosity is assumed as shown in Fig. 5.15. The relative scaling between the density and viscosity mimics typical MPACVD plasma values. The resulting vector flow solution was again calculated for matching inflows and outflows of 1 m/s as given in Fig. 5.16.

The solution in Fig. 5.16 is very similar to that given for the constant density solution from Fig. 5.14. However, a slight difference in flow speed and direction is observed toward the right half of Fig. 5.16 as the gas flow speed is slightly greater than that from the constant density and viscosity plot. This is undoubtedly due to the variable density and viscosity distributions. These results validate the numerical solution to the momentum transfer equation in the



Figure 5.14: Numerical vector velocity solutions in units of m/s to the momentum transport equation for the laminar pipe flow canonical systems in (a) Cartesian and (b) cylindrical coordinates.



(a)



Figure 5.15: (a) Mass density (kg/m^3) and (b) viscosity $(Pa \ s)$ distributions for the validation of the variable density momentum transport solution.



Figure 5.16: Vector velocity solutions in the presence of (a) constant and (b) variable density and viscosity distributions to the momentum transport equation. Units are given in m/s.



Figure 5.17: Right toroid used for validating the substrate thermal module and related boundary conditions.

presence of variable density and viscosity.

5.2.3 Substrate Thermal Model

Finally, both the internal temperature solution flux boundary conditions were validated utilizing the unit cylinder shown in Fig. 5.17.

The analytic temperature at the right side of the numerical domain may be calculated in terms of the heat flux boundary conditions as

$$T_2 = T_1 - Q_H \frac{\Delta x}{\lambda} \ln\left(\frac{r_2}{r_1}\right) \tag{5.10}$$

where T_1 and T_2 are the temperatures at the left and ride side of the numerical domain, Q_H is the heat flux, Δx is the mesh spacing, and r_1 and r_2 are the inner and outer radii of the forced temperature and boundary flux on either side. The resultant analytic temperature at the right side of the domain becomes $\approx 1387 \ K$. The corresponding numerical solution to this system is provided in Fig. 5.18.



Figure 5.18: Numerical solution for cylindrical toroid of thickness 1 m used to validate the substrate thermal model.

The numerical solution at the right side of Fig. 5.18 agrees with the analytic temperature to within 20 K. This discrepancy is simply due to interpolation error when plotting. When comparing colocated solutions, these two values agree to machine precision. Thus, the substrate temperature module is validated in the case of heat flux boundary conditions in cylindrical coordinates.

5.2.4 Complete Simulation

The complete numerical simulation may finally be validated, but first the reproducibility of the geometry configurations is addressed. These reported data can be imprecise at times, and error bars will be reported when appropriate and available [40]. Similarly, the exact reactor configurations used during data extraction are often partially reported. This makes the simulation of the MPACVD reactor under the exact same conditions difficult or even impossible. Of course, this may lead to a inaccurate simulation, which makes the validation between the experimental data and the numerical results appear inaccurate. Keeping these points in mind, the validation of several important simulated quantities against experimental data is described below, and will include:

- Radial electric field intensity at the reactor wall
- Quality factor of the reactor at a lower pressure
- Average gas temperature and electron density in the plasma
- Average vector plasma flow solutions in the presence of the plasma
- Maximum substrate temperature at the growth surface

The electric field intensity at the reactor wall was previously measured by Tan and Grotjohn and is used for comparison here [22]. Measurements varying along \hat{z} were recorded using a field probe during plasma operation under lower pressure operating conditions. The MSU MPACVD reactor geometry used for the $|E_r|$ measurements by Tan and Grotjohn was approximated and discretized as presented in Fig. 5.19 [22].

The original electric field data was recorded at an absorbed power level of 1.5 kW and a pressure of 50 Torr which were again enforced during simulation [22]. The substrate thermal model was not included. The resulting $|E_r|$ numerical solution along the wall, compared against the measured data, is provided in Fig. 5.20.

Very good agreement between the simulated and experimental data is observed in Fig. 5.20. In particular, three maxima are captured in both the experimentally measured data and in the numerical solution. This confirms the $\text{TM}_{013}^{(z)}$ -like mode dominates in the main cavity of the reactor. Furthermore, agreement of maxima and minima locations along \hat{z} suggests wavelength and good reactor configuration match. Finally, the magnitudes of the simulated and experimental electric field intensities also agree. Also, the simulated quality factor of 119.3 agrees with the experimental value as reported by Tan and Grotjohn of ≈ 100 [22]. These characteristics from Fig. 5.20 suggest the complete numerical simulation is validated with regards to the electromagnetic module.



Figure 5.19: Schematic of MSU MPACVD reactor used for $E_r|_{wall}$ measurements. [22]



Figure 5.20: Comparison of measured and simulated $|E_r|$ component along the outer wall of the MSU MPACVD reactor.



Figure 5.21: Schematic of the modified MPACVD reactor used during the measurement of T_q and n_e at low pressures.[40]

Plasma fluid module based variables may also be used to validate the complete simulation. Here, the gas temperature and electron volumetric number density are used as measured by Grotjohn, *et al.* [40]. Line-of-sight averages of these two quantities were recorded over a range of pressures at a constant absorbed power level. The modified MPACVD reactor provided in the original work was approximated and discretized as shown in Fig. 5.21 [40].

Replication of the line-of-sight experimental data was achieved by integrating across the plasma within a cylinder. A visual depiction of this beam configuration with respect to the plasma is provided in Fig. 5.21 with corresponding mathematical representation of this integration calculation within the beam across the plasma region is given by

$$\chi = \frac{\int_0^{R_b} \int_0^{2\pi} \int_0^{r_b} X(r', z') r' dr' d\phi' dz'}{\int_0^{R_b} \int_0^{2\pi} \int_0^{r_b} r' dr' d\phi' dz'}$$
(5.11)
where χ is the scalar average value of the chosen solution variable, X, r_b is the radius of the microwave beam, and R_b is the maximum outer radius marking the boundary of integration inclusion in the weighted average sum. These general coordinates may be translated to the standard cylindrical coordinate frame via

$$\chi = \frac{\int_{z_0 - r_b}^{z_0 + r_b} \int_0^{R_b} X(r, z) \frac{2}{\pi} \cos^{-1} \left(\frac{|z - z_0|}{r_b}\right) \tan^{-1} \left(\frac{r_b}{r}\right) r dr dz}{\int_{z_0 - r_b}^{z_0 + r_b} \int_0^{R_b} X(r, z) \frac{2}{\pi} \cos^{-1} \left(\frac{|z - z_0|}{r_b}\right) \tan^{-1} \left(\frac{r_b}{r}\right) r dr dz}$$
(5.12)

Finally, the discrete form of Eq. (5.12) becomes

$$\chi^{(i)} = \frac{X(r,z)\frac{2}{\pi}\cos^{-1}\left(\frac{|z_m - z_0|}{r_b}\right)\tan^{-1}\left(\frac{r_b}{r_m}\right)\left(r_2^2 - r_1^2\right)|z_2 - z_1|}{\frac{2}{\pi}\cos^{-1}\left(\frac{|z_m - z_0|}{r_b}\right)\tan^{-1}\left(\frac{r_b}{r_m}\right)\left(r_2^2 - r_1^2\right)|z_2 - z_1|}$$
(5.13)

where r_2 , r_1 , z_2 , and z_1 are the radial and vertical coordinates at the right/top and left/bottom edges of the i^{th} mesh element, respectively, and r_m and z_m are the radial and vertical coordinates at the element midpoints, respectively.

The approximate beam radius and vertical position are given in the original work by Grotjohn, *et al.* and so are used here, while a radial beam extent of 1 *cm* was imposed [40]. Plots of both gas temperature and electron density experimental and averaged numerical data at a total absorbed power level of 400 Watts are provided in Fig. 5.22. Experimental error bars are included in Fig. 5.22 to represent the approximately 20-30% uncertainty in the physical data [40].

Several important observations are made when comparing the experimental data and numerical results in Fig. 5.22. First, both gas temperature and electron density increase for increasing pressure as expected. The simulated gas temperature results agree with the experimental data to within the reported uncertainty for pressures below 30 Torr. Above 30 Torr, the simulated gas temperature exceeds the experimental data. Similarly, the simulated electron densities are generally greater than their experimental counterparts. These discrep-



Figure 5.22: Comparison between experimental and averaged numerical simulation data of (a) gas temperature (K) and (b) electron density (cm^{-3}) for the modified MSU MPACVD reactor at 400 W. Experimental data taken from [40].



Figure 5.23: Validation of substrate temperature module simulation versus experimental data at low and high pressures in the MPACVD reactor.

ancies may in part be due to several factors including differences in reactor configuration and geometry; inaccurate substrate position; and the simplification of the numerical approximation to the experimental measurement technique. With these acknowledged differences, the observed trends of increasing gas temperature and electron density with increasing pressure suggest the complete simulation is validated with respect to the plasma fluid module solution quantities.

Finally, the substrate temperature solutions must be validated within the complete, coupled simulation. This is done by comparing the simulated substrate temperature results at the substrate top surface to experimental data as reported in the literature [5]. Such results are presented for various operating conditions in Fig. 5.23.

The maximum simulated substrate temperature results given in Fig. 5.23 are slightly lower than the experimental data reported by Hemawan, *et al.* at lower pressures, yet the upward trend and rate of increase agree well [5]. At 200 Torr, the simulated substrate temperature increases much more rapidly than the measured data at similar absorbed power levels. These differences could be due to several factors including high calculated reflected power (denoting a detuned geometry); the over-simplification of the internal substrate structure and introduction of a spacer layer; and the omission of a diamond sample and recessed sample holder. These would all undoubtedly affect the simulation results and thus could explain the small differences observed between the numerical and experimental data in Fig. 5.23. In light of these small differences, the general agreement between the simulated results and experimental data validates the complete simulation with respect to the substrate temperature.

CHAPTER 6

RESULTS

This chapter presents data on the simulation of MPACVD reactors at moderate pressures. These results will be presented and discussed in order of the numerical solution algorithm and its corresponding modules. All results presented from hereon are assumed to be taken directly from fully coupled multiphysics simulations unless otherwise noted.

6.1 High-pressure example

The multiphysics numerical solution of the MSU MPACVD Reactor B configuration is first solved for power and pressure combinations of 180 Torr and 2.2 kW. An inlet gas flow rate of 400 *sccm* is specified. These operating conditions represent typical values during MPACVD diamond deposition experiments. A minimum numerical mesh element width within the plasma region of $\lambda_0/150$ (roughly 0.8 mm) is used. The numerical results presented include those related to the electromagnetic, plasma fluid, and substrate temperature solutions.

6.1.1 Electromagnetics module

The magnitude of the complex electrical conductivity solution given in Fig. 6.1 is confined to the immediate region surrounding the reactor axis of symmetry. Its maximum conductivity



Figure 6.1: Magnitude of electrical conductivity numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.2 kW and 180 Torr. Units are given in S/m.

amplitude is slightly less than $3.0 \ S/m$ suggesting a much high rate of spatial electromagnetic absorption and scattering. However, the relatively narrow conductivity profile in Fig. 6.1 means the electromagnetic waves are still able to penetrate the discharge before decaying significantly. This narrow conductivity profile is more narrow than those typically observed at lower pressures [16].

The resulting magnitudes of the various electric and magnetic fields are provided in Fig. 6.2 with interesting features readily apparent. In general, the electromagnetic field intensities for the higher pressure results are greater than those observed at lower pressures [22]. The radial electric field pattern presented in Fig. 6.2 exhibits a $TM_{103}^{(z)}$ -like structure with three clear maxima located at the outer reactor wall. This radial component intensity is significantly higher in the immediate region just outside the plasma ball surrounding the reactor axis of symmetry. This is indicated by the lighter blue false coloring extending from the substrate surface toward the top inner surface of the quartz bell jar at a radius of roughly



Figure 6.2: Plots of (a) radial and (b) vertical electric (V/m), (c), azimuthal magnetic (H/m), and (d) total electric field (V/m) components from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW.

5 mm in \hat{r} . A small increase in radial electric field intensity is also witnessed just above the substrate surface.

The vertical component of the electric field exhibits high field strength in the immediate vicinity of the substrate surface with its overall solution distribution agreeing with that of the lower pressure result. That is, this vertical component intensity varies between roughly 25,000 V/m at the substrate surface, drops to below 10,000 V/m within the main plasma ball which coincides with the maximum electrical conductivity magnitude, and then increases again approaching the top wall of the quartz bell jar when moving along \hat{z} . Both the radial and vertical electric field component intensity solutions presented in Fig. 6.2 remain nonuniform within the plasma region. This suggests the plasma has a strong influence on the electromagnetic fields, which in turn effects the absorbed power profile.

All of these observations and characteristics come about from the combination of the electrical conductivity and electromagnetic field numerical solutions, and result from the increased operating power and pressure. As a result of the increased operating pressure, the plasma is more tightly confined to the reactor axis. Moreover, the increased absorbed power level results in increased electron and hydrogen species dissociation within the plasma. This, in turn, results in an increased electrical conductivity magnitude and altered electromagnetic field structure.

Finally, the volumetric absorbed power density numerical solution is presented in Fig. 6.3 where its maximum reaches slightly more than $2.3 \times 10^8 \ W/m^3$. This maximum absorbed power density is on the same order as values observed at similar operating conditions and reactor configuration reported elsewhere [5]. The absorbed power density profile is clearly concentrated near the substrate surface surrounding the reactor axis. This profile extends upward toward the inner surface of the top quartz bell jar. It even increases moving away from the plasma ball toward this location. This suggests the electromagnetic energy is primarily being transferred to the electrons near the substrate surface, which may in turn ultimately increase the rate of diamond deposition through the production of other ions and



Figure 6.3: Plots of absorbed power density (a) across the full MPACVD reactor and (b) a detail of the plasma region. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. The color scales are the same for both plots. Units are given in W/m^3 .



Figure 6.4: Molecular hydrogen mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.

radicals.

6.1.2 Plasma fluid module

The nine mole fraction, vector average gas flow, and electron and gas temperature distributions are presented in Fig. 6.4 through Fig. 6.15. These profiles were extracted from the same coupled, multiphysics simulation presented in the previous section detailing the electromagnetic field solutions.

The molecular hydrogen mole fraction drops to a little less than 40% at the center of the plasma ball as given in Fig. 6.4. Conversely, the atomic hydrogen mole fraction reaches slightly greater than 60% as seen in Fig. 6.5. The atomic hydrogen clearly dominates the gas mixture when comparing produced species. Thus, the molecular hydrogen feed gas is predominantly dissociated into atomic hydrogen at moderate pressures. This is in agreement with previous experimental observations and numerical results at lower pressures [4, 16, 35,



Figure 6.5: Atomic hydrogen mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.

40]. The numerical solution for both the molecular and atomic hydrogen mole fractions are tightly confined to the reactor axis. This is clear from the rapid decrease in molecular hydrogen, and rapid increase in atomic hydrogen mole fractions extending outward along \hat{r} . These mole fractions reach roughly 10% of their respective minimum/maximum values at roughly 2 cm from the axis, respectively. This is in sharp contrast to previous simulation results at lower pressures and powers where these mole fractions have been observed to extend much further toward, and even past, the outer radius of the substrate pedestal [16, 33]. The combination of increased operating pressure and reactor configuration settings are attributed to affecting this change in the solution profile.

Both the first and second excited atomic hydrogen mole fraction numerical solutions seen in Fig. 6.6 and Fig. 6.7 exhibit maxima of approximately 6.5×10^{-9} and 8.4×10^{-11} . As with absorbed power density and the previously discussed hydrogen mole fractions, these excited atomic hydrogen mole fractions are tightly confined to the reactor axis. Moreover, the vertical position of the maxima reported for these excited hydrogen mole fractions is shifted



Figure 6.6: First excited atomic hydrogen mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.



Figure 6.7: Second excited atomic hydrogen mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.



Figure 6.8: H^+ ion mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.

upwards, away from the substrate surface. This suggests the density of these particular hydrogen species are present in limited quantities near the deposition surface at moderate pressures.

The proton mole fraction solution shown in Fig. 6.8 is also tightly confined to the reactor axis with a maximum mole fraction reaching more than 3×10^{-8} . The vertical location of this maximum mole fraction is shifted upwards along \hat{z} and away from the substrate surface. The positive molecular hydrogen ion (H_2^+) solution increases to 1.565×10^{-11} as seen in Fig. 6.9. It shares some similarities with the proton mole fraction in that it is now concentrated along the reactor axis, and even begins to exhibit significant concentration roughly midway between the substrate and bell jar surfaces. However, unlike the previous ion solution, the H_2^+ ion remains in significant concentration just above the substrate surface. The location of the maximum value of the H_3^+ ion is shifted toward the center of the plasma ball, and its overall distribution is more concentrated at the r = 0 axis as seen in Fig. 6.10. Similarly, its concentration remains significant just above the substrate surface.



Figure 6.9: H_2^+ ion mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.



Figure 6.10: H_3^+ ion mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.



Figure 6.11: H^- ion mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.

The maximum value of the H^- ion reaches more than 7.7 $\times 10^{-9}$. Similar to other mole fraction solutions, its overall distribution and shape is elongated along \hat{z} .

Finally, the electron mole fraction solution closely follows the H_3^+ trends given the dominance of that ion with respect to the total density of all ions in the plasma. The vertical location of this maximum mole fraction is removed from the substrate surface several millimeters, and its overall distribution is now more closely confined to the reactor axis.

As quantitative convective flow data have not been previously reported for MPACVD reactors at these moderate pressure operating conditions, considerable attention will be paid to describing these data in detail. The vector average gas flow at the gas inlet region extending along the bottom edge of the solution domain in Fig. 6.13 contains an upward direction component. The flow just above the inlet region is already downward directed suggesting the gravitational forces acting on the gas mixture away from the plasma ball dominate. Such gravitational dominance is expected, as the gas is significantly cooler in this region outside the substrate pedestal and below the substrate top surface as is shown in the



Figure 6.12: Electron mole fraction solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.



Figure 6.13: Vector average gas flow solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Color denotes speed while the arrow denotes flow direction. Units are in m/s.

gas temperature plot in Fig. 6.15. Moreover, with an inlet flow of $\sim 2 \ mm/s$, the gas flow throughout the plasma region is primarily free convection-driven.

The hydrogen feed gas is strongly upward directed along both the outer surface of the substrate pedestal, and the inner surface of the quartz bell jar walls. These flow streams represent the primary method for momentum and feed gas transport to the plasma region. A vortex is present in this lower and outer substrate region just above the inlet as evident from the swirling vector pattern and low overall gas flow speed located at a radius of roughly $4 \ cm$. The flow begins to turn back upward after the cooling gas initially falls under the force of gravity with moderate speed close to the substrate outer wall.

The flow picks up speed at the top and outer substrate radius in order to conserve momentum in its flow around this corner. Some of the gas mixture then flows through the outlet region toward the outer radius of the substrate top surface and evacuates the reactor system. The hydrogen gas mixture which does not exit the reactor flows tangential to the substrate surface toward the reactor axis. At the r = 0 axis, the average gas flow is heated from the increase in gas temperature, causing it to decrease in density, become buoyant, rise, and flow upward toward the quartz bell jar inner surface. Once heated within the plasma ball, the gas mixture begins to cool and starts to exits the plasma region. Flowing back along the top quartz bell jar surface in the positive \hat{r} -direction, the gas mixture cools and starts to succumb to the gravitational force resulting in the downward direction. This influence of both buoyant and gravitational forces leads to an overall circulating flow pattern, creating a vortex outside the plasma ball and substrate.

The electron temperature solution provided in Fig. 6.14 shows a maximum temperature of roughly 13,770 K. Due to the increased operating pressure and total microwave power, the energy transfer rate from electrons to heavy species is increased. This in turn results in a decreased average electron energy (and therefore temperature) within the plasma, as the electrons will transfer their kinetic energy to the heavy species more rapidly before gaining significant microwave energy.



Figure 6.14: Electron temperature solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in K.

The electron energy solution distribution again reaches its maximum value at the top surface of the substrate and decreases from this value along the positive \hat{z} direction. However, this higher pressure electron temperature solution does not decrease nearly as quickly as lower pressure distributions reported elsewhere [16, 33]. Instead, the electron temperature remains close to its maximum value within a very short length from the top quartz bell jar surface. Although the electron temperature remains close to the maximum temperature moving toward the outer radius of the substrate along \hat{r} , it first decreases before increasing again.

The gas temperature solution shown in Fig. 6.15 reaches a maximum of $3654 \ K$. This value is consistent with the expected trend of increasing gas temperature with absorbed power and operating pressure often reported at lower pressures [16, 34, 35, 40]. It is due to the increased energy transfer from the electrons to the translational, rotational, and vibrational modes of the hydrogen molecules in the plasma. The gas temperature distribution



Figure 6.15: Neutral species and ion temperature solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in K.

is slightly more elongated along \hat{z} than its lower pressure counterpart [16, 34]. However, the gas temperature does remain at significant temperature levels extending outward in \hat{r} past the substrate radius. This elongated gas temperature shape is not commonly reported in the literature at lower pressures, but may be commonplace at higher pressures.

A very small change in relative local pressure is shown in the pressure difference plot in Fig. 6.16. In this case, the operating pressure is $2.4 \times 10^4 Pa$, or approximately 180 Torr with a maximum deviation from the baseline operating pressure is less than $1.5 \times 10^{-5} Pa$. This suggests very low flow speeds present during system operation.

The volumetric number density distributions associated with the atomic hydrogen and electron species, along with the total gas density, are provided in Fig. 6.17 to Fig. 6.19. The maximum gas density shown in Fig. 6.17 reaches almost $3 \times 10^{24} m^{-3}$. This total gas number density is more confined near the reactor axis, while at the same time more removed from the immediate vicinity of the substrate surface. The number density remains high even



Figure 6.16: Absolute pressure difference solution from 180 Torr ($\sim 2.4 \times 10^4 Pa$) for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in Pa.



Figure 6.17: Volumetric total number density solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in m^{-3} .



Figure 6.18: Volumetric atomic hydrogen number density solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in m^{-3} .

below the vertical position of the substrate and to its outside, although the plasma density is significantly lower in this region.

Many differences are observed when comparing the atomic hydrogen volumetric number density from Fig. 6.18 to the previous total gas number density. This is clear from the change in maximum number densities, where a more than ten times decrease going from the total to atomic hydrogen solutions is present. Moreover, the solution distribution itself is more tightly packed at the reactor axis. These effects are echoed by the atomic hydrogen mole fraction solution discussed in preceding paragraphs and shown in Fig. 6.5.

The electron volumetric number density numerical solution as shown in Fig. 6.19 also depicts a narrow distribution. Similar to the atomic hydrogen number density solution discussed in the preceding paragraph, this behavior is also found in the electron mole fraction solution given in Fig. 6.12. Furthermore, the decrease of roughly five orders of magnitude between the atomic hydrogen and electron number density solutions echoes their corresponding mole fraction solutions. These solution variables and related physical quantities provide



Figure 6.19: Volumetric electron number density solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in m^{-3} .

significant insight into the behavior and characteristics of plasmas within MPACVD systems when operating at higher pressure and power conditions.

Finally, the internal substrate temperature distribution is shown in Fig. 6.20. Its maximum temperature is located at the substrate top surface with almost uniform temperature, and then gradually decreases traveling down its outside radius. Similarly, a sharp transition from high to low temperature is observed across the spacer region at approximately 5 cm in the vertical direction. The maximum substrate temperature of 1438 K is much greater than values reported in the literature [5]. Differences are attributed to the over-simplified nature of the present simulation in terms of the actual physical structure and material properties. The calculated reflected power also remained relatively high for this simulation, at 37%, which may suggest a detuned MPACVD reactor, and thus less than optimal power transfer.



Figure 6.20: Substrate temperature solution for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in K.

6.2 Extreme high-pressure example

Numerical solutions at 180 Torr and 2.2 kW were presented in the previous section, and represent typical MSU MPACVD system operating conditions [5, 21]. This operating pressure is only slightly above the generally accepted lower pressure/higher pressure boundary of 150 Torr. Moreover, MPACVD experiments have recently been conducted at pressures approaching 300 Torr with total absorbed powers approaching 3 kW [5, 21]. Diamond deposition rates often change significantly at these operating conditions, which suggest the plasma properties are also altered [5]. Thus, results of a second simulation run at the upper limit of these operating conditions (300 Torr and 2.5 kW) are also presented. The numerical mesh spacing was decreased to roughly 500 μm in the plasma region and the resulting numerical solutions are presented and described in the following paragraphs.



Figure 6.21: Magnitude of electrical conductivity numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units are given in S/m.

6.2.1 Electromagnetics module

As expected, the complex electrical conductivity shown in Fig. 6.21 is roughly 70% greater than the electrical conductivity depicted from the 180 Torr simulation, peaking at slightly under 5 S/m. This increased complex conductivity is due to the increase in total microwave absorbed power leading to an increased ionization rate within the plasma, and an increased electron density. As a result, the complex conductivity increases and effects the electromagnetic field distribution. Comparing this extreme high pressure result to the 180 Torr results from Fig. 6.1, the present electrical conductivity amplitude is even more tightly confined to the reactor axis. The maximum absolute electrical conductivity translates to a relative permittivity of more than 25, suggesting significant electromagnetic wave scattering and influence.

The numerical electromagnetic field solutions at 300 Torr depict many similar traits to



Figure 6.22: Plots of (a) radial and (b) vertical electric (V/m), (c), azimuthal magnetic (H/m), and (d) total electric (V/m) field components from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 300 Torr and absorbed power of 2.5 kW.

those given previously at 180 Torr. For example, the incident electromagnetic wave is indeed $TM^{(z)}$ -polarized, a $TM^{(z)}_{103}$ -like cavity mode dominates the solution in Fig. 6.22, and the electric field is primarily vertically directed just above the substrate. At a maximum electrical conductivity of almost 5 S/m, the electric field strength within the bulk of the plasma ball is significantly reduced from previous results. The vertical electric field intensity drops to roughly 20% of its maximum value within this region. This represents a large decrease in field strength over a very short length extending from the top of the substrate to the center of the plasma ball, which then increases once more at the top bell jar wall. The radial electric field intensity is confined to the outer region of the plasma, suggesting it penetrates only slightly into the plasma. Similarly, the radial electric field is nonzero just outside the reactor axis just above the substrate top surface. This coincides with a very high vertical electric field intensity at this location, leading to an increased total electric field intensity. This, in turn, results in a very high absorbed power density just above the substrate surface, as will be discussed in the following paragraphs.

The vertical component of the electric field intensity falls off significantly traveling along the top substrate surface along \hat{r} . Moreover, this elevated vertically-directed field intensity extends upward several millimeters into the plasma region. Once again, this suggests increased microwave power absorption extending to regions away from the substrate. Finally, the vertical component of the electric field is also elevated at the top bell jar inner surface. This is unexpected and not common during experimental operation, as this leads to an increased absorbed power density and therefore electron temperature at this location. Experimentally, this can lead to the unwanted heating of the bell jar, which may even damage the bell jar and entire MPACVD system.

The resulting volumetric absorbed power density profile is presented in Fig. 6.23. Similar to the previous numerical results, the absorbed power density is highest several millimeters above the substrate top surface. Again, this is expected as the maximum microwave absorbed power within MPACVD systems is typically just above the substrate surface where the



Figure 6.23: (a) Volumetric absorbed power density numerical solution (b) with detail for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. The same color scale applies to both. Units are given in W/m^3 .

production of ions and electrons leads to the most efficient deposition. Moreover, the power density has risen to a maximum of roughly $3.4 \times 10^8 W/m^3$, which exhibits good agreement with reported experimental values [5].

The absorbed power density decreases moving along \hat{z} as is expected. However, unlike the previous volumetric absorbed power solution, the power density observed in Fig. 6.23 increases on the other side of the plasma ball toward another maximum. Again, this signals the unwanted heating of the electrons away from the substrate surface which could damage the physical reactor. As a result, the reflected system power is also expected to be very high, and suggests sub-optimal tuning of the MPACVD reactor. Finally, the power density profile in Fig. 6.23 shows a discontinuous distribution with finger-like regions of increased absorbed power observed. This is a numerical artifact due to the rate of mesh discretization stemming



Figure 6.24: Molecular hydrogen mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.

from the balance of production and diffusion fluxes within the plasma transport equations.

6.2.2 Plasma fluid module

As with the previous solution, the molecular hydrogen mole fraction solution presented in Fig. 6.24 reaches a minimum value at the center of the plasma ball, while it is maximum outside the plasma region. Likewise, the atomic hydrogen mole fraction solution from Fig. 6.25 is maximum within the plasma, and decreases to negligible amounts away from the substrate. Notice at this operating pressure and total absorbed power level that the minimum molecular hydrogen mole fraction is less than 5% while the atomic hydrogen conversely reaches a maximum mole fraction of more than 95% at the same location. This confirms the vast majority of the molecular hydrogen feed gas is being dissociated into atomic hydrogen, a trend that was also observed for the 180 Torr operating conditions. As was seen in the 180



Figure 6.25: Atomic hydrogen mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.

Torr numerical solutions, the atomic and molecular hydrogen mole fraction distributions are again elongated along the reactor axis. This is again a result of the increased operating pressure resulting in confined plasma located at the reactor center.

Unlike the previous excited atomic hydrogen solutions, the maxima of the first excited atomic hydrogen mole fraction distribution presented in Fig. 6.26 is almost 20 times greater, and the second excited solution in Fig. 6.27 more than 10 times greater than the corresponding high order results. This confirms increased electron energy promotion within the plasma, which is expected due to the increased microwave absorbed power. That is, increased absorbed power translates to an increase of energetic electrons in the plasma, which in turn leads to a greater number of excited hydrogen atoms via chemical reactions. Unlike the previous solution, both excited hydrogen mole fractions are very tightly confined to the reactor axis. As a result, the excited mole fraction solutions are greater in magnitude and narrower. Of interest is the increased distance between the region of greatest excited atomic



Figure 6.26: First excited atomic hydrogen mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.



Figure 6.27: Second excited atomic hydrogen mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.



Figure 6.28: Proton ion mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.

hydrogen density and the substrate surface. The excited atomic hydrogen mole fraction at this surface is also higher than the previously presented results. A similar trend is observed in many other mole fraction solutions, suggesting increased diamond deposition rates at such operating conditions.

The hydrogen ion mole fraction solutions presented in Fig. 6.28 through Fig. 6.31 all reach greater maximum values than their predecessors, which is again expected. However, as with the excited atomic hydrogen mole fractions, their solution distributions are significantly altered from their corresponding lower pressure results being more concentrated toward the center of the reactor axis. Of notable significance is the much greater H_3^+ ion mole fraction distribution, with almost a ten-fold increase in maximum value over its 180 Torr counterpart. This suggests the electron concentration, and thus energy transfer from the electromagnetic power to the electrons and ions, are much greater. However, even at these very high absorbed power levels, this ion and corresponding electron mole fractions



Figure 6.29: H_2^+ ion mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.



Figure 6.30: H_3^+ ion mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.



Figure 6.31: H^- ion mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.

remain much lower than the atomic hydrogen mole fraction, which is found to dominate species concentrations independent of the physical operating conditions. Again, the H_3^+ ion mole fraction distribution is also observed to extend upward to the inner surface of the top quartz bell jar. Its presence in this region confirms its direct dependence on the absorbed power and resulting production via chemical reactions and recombination processes away from the substrate.

Once again, even though the H_3^+ ion mole fraction solution drops off significantly at the substrate surface, its number density remains high at approximately 10% of this maximum value at the surface. The H^- ion also exhibits an unusual mole fraction distribution numerical solution in that it appears to separate into upper and lower concentration regions. That is, the H^- ion mole fraction is greatest just above the substrate surface and just below the upper quartz bell jar surface.

However, with the tightly confined plasma densities observed in these figures, uniform



Figure 6.32: Electron mole fraction numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr.

diamond deposition is not guaranteed, and may not even be expected. At this point, the tuning of the MPACVD system becomes important as the adjustment of the physical reactor geometry will significantly affect the plasma shape and properties. As stated previously, these adjustments are commonplace and often necessary to maintain uniform deposition across the substrate surface during the deposition process. These *in situ* adjustments are available within the simulation by minimizing the reflected microwave power during the electromagnetics module update by altering the reactor cavity height and antenna probe length.

Finally, as is typical with both previously depicted electron mole fraction solutions, the 300 Torr electron mole fraction solution given in Fig. 6.32 closely matches the H_3^+ ion distribution in shape and value. Moreover, the increased maximum value results in an increased overall volumetric number density. This maximum value remains low even at this higher operating pressure and absorbed power level and confirms that even at the upper



Figure 6.33: Vector average gas flow numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in m/s.

limit of current operating conditions, the plasma remains very weakly ionized as is typical of MPACVD systems [16, 34, 35, 40].

The vector average gas flow numerical solution provided in Fig. 6.33 is very similar in characteristics and behavior to its corresponding results at 180 Torr. For instance, the inlet gas flow once again has little influence on the overall gas flow throughout the plasma region at the bottom of the reactor. Moreover, the gas flow is once again upward directed just outside the substrate pedestal and outer quartz bell jar walls, while it is downward directed between these regions. Above the vertical position of the substrate surface, the gas flow is circulatory about a vortex located above the outer substrate radius with upwardly flow at the reactor axis. At 300 Torr and 2.5 kW, the maximum flow speed occurs not at the outer quartz bell jar wall, but at the center of the reactor. Thus, the upward flow of momentum and gas species lies directly above the diamond sample where it can arguably influence the plasma properties most significantly. Since this upward flow is obviously not driven



Figure 6.34: Electron temperature numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in K.

by the forced gas flow at the inlet region, it is an example of free convection and buoyant forces. The operating conditions of 300 Torr and 2.5 kW absorbed power represent the upper limit of currently reported MPACVD system operating conditions. Thus, the maximum gas flow of roughly 7 cm/s represents the expected upper limit of gas flow speeds in MPACVD reactors. Of course, this upper limit of average gas flow speed depends heavily on the reactor geometry and operating mode. However, for the MSU MPACVD systems considered, this assumption is expected to remain valid for the foreseeable future as operating pressures and total absorbed power levels continue to increase.

The electron temperature solution provided in Fig. 6.34 reaches a minimum temperature of roughly 11,600 K, which is much less than the minimum temperature reported in each of the previous higher pressure example solution. Once again, the electron temperature is expected to decrease with increasing operating pressure and total absorbed power level due to the increased transfer of energy from the electrons to the heavy hydrogen species via


Figure 6.35: Gas temperature numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in K.

collision processes. However, unlike the previous electron temperature results, the current distribution remains almost constant along the entire reactor axis line extending from the substrate surface to the inner surface of the top quartz bell jar. This suggests the electrons remain significantly energetic even far removed from the substrate, and thus deposition, surface which would lead to a decreased deposition rate in an experimental system. Thus, while unwanted and even avoidable, this solution is once again provided for comparison and reference purposes as an example of an non-tuned reactor and the effects thereof.

The gas temperature distribution from Fig. 6.35 are similar to those reported for the 180 Torr simulation results seen in Fig. 6.15. That is, the distribution shape, location of maximum temperature, rate of temperature decrease outward along \hat{r} , and temperature at the plasma region boundaries are all very similar. One key difference is the maximum gas temperature, which is now 4176 K. Although not experimentally reported elsewhere thus



Figure 6.36: Difference in local pressure numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in *Pa*.

making validation difficult, the trend of steadily increasing maximum and average gas temperature with operating pressure and total absorbed microwave power is expected. Again, this is due to the increased energy transfer from the high frequency electron oscillations to the translational, rotational, and vibrational modes of the molecular hydrogen atoms. This is a direct result of the combination of both increased operating pressure and total absorbed power.

Once again, the maximum variation observed in Fig. 6.36 is incredibly small, thus confirming low average gas flow speeds. For instance, the maximum difference in the local pressure solution never reaches more than 10^{-5} Pa, which represents a deviation on the order of several parts-per-billion. Thus, even at these extreme operating conditions close to the upper limit in both pressure and total absorbed power, the difference in local pressure within the plasma region during operation remains incredibly low. This confirms the previous conclusion accompanying the average gas flow solution that at even higher pressures



Figure 6.37: Total gas volumetric number density numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in m^{-3} .

and powers the gas flow would expected to remain at relatively low speeds.

Both the total and atomic hydrogen volumetric number densities from Fig. 6.37 and Fig. 6.38, respectively are similar to their corresponding previously presented solutions at slightly lower pressure. These include the overall shape of the solution distributions and location of corresponding maximum values. Once again, the increased operating pressure and total absorbed microwave power results in increased maximum total and atomic hydrogen number densities, with likewise an increased minimum total volumetric number density. These are due to the combination of both the increased pressure translating to higher densities, as well as indirectly via the increased absorbed power level which in turn leads to increased gas temperatures and thus densities. The result of only slightly increased maximum densities over those reported in the 180 Torr results again confirm the trend of increasing density with absorbed power and pressure reported elsewhere [16, 40].

The maximum electron volumetric number density as shown in Fig. 6.39 reaches more



Figure 6.38: Atomic hydrogen volumetric number density numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in m^{-3} .



Figure 6.39: Electron volumetric number density numerical solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in m^{-3} .



Figure 6.40: Substrate temperature solution for the MSU MPACVD "Reactor B" configuration operating at 2.5 kW and 300 Torr. Units given in K.

than $1.25 \times 10^{19} m^{-3}$, which is more than double the maximum electron density reported in the 180 Torr case. This mimics the electron mole fraction trend of increasing maximum value with pressure and absorbed power levels. Moreover, this electron number density is again tightly confined to the reactor axis with a maximum value occurring just off the r = 0axis and decreasing rapidly along \hat{r} . Its extension of non-negligible levels from the substrate surface to the inner surface of the quartz bell jar along the \hat{z} -axis also agrees with the electron mole fraction solution. Once again, this suggests the detuned nature of the reactor and undesirable expected decreased diamond deposition rate.

The substrate temperature solution is provided in Fig. 6.40 depicting a maximum of 2060 K. Once again, the substrate temperature is maximum at the top surface, which is in close proximity to the plasma. This temperature also decreases along the outer substrate pedestal wall, approaching roughly 700 K at the bottom of the reactor.

6.3 Power and pressure combinations

The plasma characteristics at different power and pressure combinations are expected change with these operating conditions. For example, the combination of both increasing power and pressure should result in essentially a consistent plasma size or volume. This is often observed and enforced experimentally (along with other reactor configuration settings) in order to maintain a consistent plasma volume and uniform deposition [5, 21]. At the same time, the plasma intensity and luminescence is expected to change significantly due to higher power densities. This in turn is expected to result in increased gas temperatures, and electron and atomic hydrogen mole fractions.

The corresponding numerical results at these increasing power and pressure conditions are presented in the following paragraphs. Important physical variable solutions are presented. The specific operating conditions for each are specified, but all reside in the higher pressure operating regime, ranging from 180 to 240 Torr. The operating pressure is increased in 20 Torr increments, resulting in four such sets of numerical solutions. Along with increasing pressure, the total absorbed power is increased from 2 kW to 2.3 kW in 100 Watt increments. The MSU MPACVD Reactor B configuration was again utilized for all results.

The radial and vertical electric field intensities shown in Fig. 6.41 and Fig. 6.42 do not vary significantly with increased power and pressure. This is expected, as the shape and location of the plasma also do not change significantly over these power and pressure ranges suggesting minimal affect on the electromagnetic fields. Moreover, although the conductivity itself does increase at these conditions, this does not translate to a large change in electric field structure or waveform. Again, a $\text{TM}_{103}^{(z)}$ -like mode is observed to dominate the field structure in Fig. 6.41. Many other similar characteristics are also observed at these conditions. Finally, the maximum field intensities within the plasma region again reach 25 kV/m as was observed in the case of the corresponding high pressure results presented earlier.

A marked and consistent change in the simulated absorbed power density solutions is





Figure 6.41: Radial electric field intensity solutions for (a) 180 Torr, 2.2 kW, (b) 200 Torr, 2.1 kW, (c) 220 Torr, 2.2 kW, and (d) 240 Torr, 2.3 kW. Shown for MSU MPACVD Reactor B. Units are given in V/m.



Figure 6.42: Vertical electric field intensity solutions for (a) 180 Torr, 2.2 kW, (b) 200 Torr, 2.1 kW, (c) 220 Torr, 2.2 kW, and (d) 240 Torr, 2.3 kW. Shown for MSU MPACVD Reactor B. Units are given in V/m.

0.00

r (m)

(d)

0.000

0.000

0.00 + 0.000

r (m)

(c)



Figure 6.43: Absorbed power densities for (a) 180 Torr, 2.2 kW, (b) 200 Torr, 2.1 kW, (c) 220 Torr, 2.2 kW, and (d) 240 Torr, 2.3 kW. Shown for MSU MPACVD Reactor B. Units are given in W/m^3 .

observed in Fig. 6.43. That is, the formation and increase in absorbed power at the top of the plasma region just inside the top surface of the quartz bell jar is evident. An increased electron density and thus electrical conductivity also corresponds to this location. This suggests the reactor may be detuned as the plasma pulling away from the substrate surface and forming at the top of the quartz bell jar. Experimentally, this would be avoided by adjusting the reactor configuration as the increased power residing at this top surface would draw from that at the substrate surface. This would would likely result in a decreased diamond deposition rate. Moreover, the increased power absorption at the quartz dome surface may cause overheating of the quartz dome, which could ultimately cause it to melt. Thus, this operating condition and resulting plasma mode is not recommended for experimental observation. Again, this is confirmed by the calculated reflected powers of 57%, 65%, 84%, and 56%, respectively.

The atomic hydrogen mole fraction solutions remain quite high at these operating conditions, indicating very high dissociation of the hydrogen feed gas. This is evident in the maximum atomic hydrogen mole fraction reaching to almost 88% at 2.3 kW and 240 Torr in Fig. 6.45. An increased atomic hydrogen mole fraction is a result of the increased absorbed power density as described previously. As a result, the atomic hydrogen flux to the substrate surface would also be expected to increase, and possibly lead to an increased diamond deposition rate. However, its narrow distribution above the substrate suggests uniform deposition may be difficult for this particular reactor tuning.

The electron densities in Fig. 6.46 and Fig. 6.47 exhibit very narrow distributions tightly confined to the axis of symmetry. Moreover, these solutions steadily increase in maximum value along with increased absorbed power and pressures. This is expected, as the increased power density leads to increased ionization rates, which also increases the plasma density. The maximum electron density approaching $10^{19} m^{-3}$ in Fig. 6.47 is reasonable compared to electron densities reported elsewhere at lower pressures [4, 35, 40]. Moreover, the position of the maximum electron density is also observed to rise with increasing power and pressure.





Figure 6.44: Atomic hydrogen mole fraction solutions at (a) 180 Torr, 2 kW and (b) 200 Torr, 2.1 kW from the plasma module. Shown for MSU MPACVD Reactor B.





Figure 6.45: Atomic hydrogen mole fraction solutions at (a) 220 Torr, 2.2 kW and (b) 240 Torr, 2.3 kW from the plasma module. Shown for MSU MPACVD Reactor B.



Figure 6.46: Electron densities at (a) 180 Torr, 2 kW and (b) 200 Torr, 2.1 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in m^{-3} .



Figure 6.47: Electron densities at (a) 220 Torr, 2.2 kW and (b) 240 Torr, 2.3 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in m^{-3} .

This follows the absorbed power density shown in Fig. 6.43. Finally, the electron density solution becomes more discontinuous moving up in pressure. This again is a numerical consequence due to the choice of mesh discretization and is thus not physical. This artificial limit was imposed due to the serial structure of the simulation, and the choice and availability of processing hardware. Future implementations and versions are suggested to avoid these shortcomings through the use of parallel processing and other methods as suggested in Chapter 8.

Marked changes are observed across the vector average gas flow solutions presented in Fig. 6.48 and Fig. 6.49. For instance, the flow speeds in different regions surrounding the plasma change significantly with operating conditions. That is, as the absorbed power density and pressure increase, the flow speeds similarly increase above the substrate surface. This is particularly noticeable along the axis, at the outer substrate corner, and just inside the curved quartz dome corner. At these three locations, the flow speed steadily increases along with operating pressure. Of course, these are physically due to the increase in gas temperature, which in turn results in a decrease in gas density within the plasma, and ultimately increases the flow speed. That is, while this increased flow due to decreased gas density is observed at the reactor axis, the flow outside the expected plasma region is due to cooling gas and gravitational effects. As a result, the recirculating pattern observed throughout the solution domain intensifies with increasing speeds.

Of course, several characteristics and regions remain unaffected by this change in absorbed power and pressure as well. These include the inflow and outflow regions, along with the entire spatial region below the vertical substrate surface.

This increased upward gas flow at the reactor axis of symmetry within the expected plasma region was observed and during the high pressure results. Again, the maximum gas flow speed remains low, not rising above 5 cm/s within the expected plasma region.

The maximum electron temperature solutions presented in Fig. 6.50 and Fig. 6.51 generally decrease with increasing pressure. Again, this is expected as the increased pressure





Figure 6.48: Vector average gas flows at (a) 180 Torr, 2 kW and (b) 200 Torr, 2.1 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in m/s.





Figure 6.49: Vector average gas flows at (a) 220 Torr, 2.2 kW and (b) 240 Torr, 2.3 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in m/s.





Figure 6.50: Electron temperature solutions at (a) 180 Torr, 2 kW and (b) 200 Torr, 2.1 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in K.





Figure 6.51: Electron temperature solutions at (a) 220 Torr, 2.2 kW and (b) 240 Torr, 2.3 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in K.

results in increased plasma density, thus increasing the electron collision frequency. This means the electrons transfer their energy to neutrals and ions more quickly and thus the electrons have less time to gain energy before their next collision event. As a result, their most probable energy is decreased, resulting in a lower temperature. The electron temperature distribution changes only slightly across these high pressure operating conditions, with the majority of the energy confined to the reactor axis. A slight increase in electron temperature is observed toward the outer radius of the substrate surface, but remains lower than that at the reactor center.

Finally, the maximum gas temperature observed in the gas temperature solutions from Fig. 6.52 and Fig. 6.53 consistently increase with operating pressure and absorbed power. From the previous discussion, this is expected, as the increasing absorbed power translates to an increased rate of dissociation in the atomic hydrogen and thus plasma energy. The gas temperature distribution does not change significantly across this range. Moreover, this maximum gas temperature generally agrees with a slowly increasing temperature typically observed in MPACVD systems at lower pressure conditions [16, 35, 40].

6.4 Effects of reactor geometry

Up to this point, several numerical solutions have been presented at individual operating conditions. These results have served to present and exemplify the typical results associated with this wide range of physical conditions imposed during the simulation. However, no such results have yet been provided demonstrating the various effects of the system geometry on the plasma behavior. To accomplish this, several series of simulation results are now presented to demonstrate the important influence these geometric features have over the plasma properties. Two lesser, yet still important, plasma influences related to the reactor geometry are the substrate vertical position and the reactor cavity height. Several multiphysical simulation results are presented detailing the effects on the plasma properties with





Figure 6.52: Gas temperature solutions at (a) 180 Torr, 2 kW and (b) 200 Torr, 2.1 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in K.





Figure 6.53: Gas temperature solutions at (a) 220 Torr, 2.2 kW and (b) 240 Torr, 2.3 kW from the plasma module. Shown for MSU MPACVD Reactor B. Units are in K.

regards to these features. The substrate radius, and finally a complete reactor configuration alteration are presented. In particular, these effects will be presented within the higher pressure regime, as this is important to future experiments with lower pressure results available elsewhere [16, 22, 35].

6.4.1 Substrate position

The vertical position of the substrate within the MSU MPACVD class of reactors is known to significantly affect the plasma properties and power coupling [5]. It is physically adjustable prior to deposition, but not during. This is also the case in the numerical simulation with the vertical position being set prior to the simulation run. Its numerical adjustment is not available due to the unsatisfactory interpolation required that would significantly affect the simulation results, and possibly lead to divergent solutions. This adjustment is often necessary to ensure efficient microwave power coupling to the plasma, to maintain contact between the plasma and the substrate, and to maximize deposition uniformity during the system operation.

Experimentally, the substrate vertical position is often not quoted as an absolute distance from the bottom of the reactor, but instead related to the vertical position of the top-most outer coaxial block. Thus, the difference between these two characterizes this setting, with the outer coaxial block being the reference height. For example, a setting of -5 mm, which is often typical during an experimental run, would translate to the substrate vertical position being 5 mm lower than the outer coaxial block vertical position. This same nomenclature is used here in the following paragraphs.

In the following series of plots, the substrate position is varied from null to -6 mm in 2 mm increments. All of these results were extracted from a single multiphysics solution for a MSU MPACVD Reactor B configuration operating at 180 Torr and 2.2 kW. The substrate thermal model was not included in the results, improving numerical efficiency and singling out the effects due to substrate position alone. For comparison, the radial and vertical electric field

distributions at these substrate positions are provided in Fig. 6.54 and Fig. 6.55.

As seen from Fig. 6.54 and Fig. 6.55, significant changes to the electric field intensity component solutions are not readily apparent. That is, these electric field solutions are very similar in structure, value, and distribution almost completely throughout the entire simulation domain. However, several small differences between solutions at the various substrate positions are apparent. For instance, the maximum radial electric field intensity at the outer substrate pedestal wall below the top substrate surface decreases significantly with decreasing substrate position. With very little change in the vertical electric field solution in this region, this suggests the power coupling into the plasma is more efficient at the lower substrate and bell jar surfaces along the reactor axis decrease in magnitude with decreasing substrate position. This is attributed to the increased distance between these two surfaces allowing for a less compact plasma distribution, and thus power absorption and plasma density.

Subtle changes to the absorbed power distribution are also apparent as shown in Fig. 6.56. As the substrate position is lowered with respect to the outer coaxial block level, the maximum absorbed power density decreases more than 10%. This is significant to the plasma properties and overall behavior of the reactor as will be discussed related to the plasma solution results presented in the following paragraphs. Moreover, this decrease in maximum power density suggests a more distributed power absorption profile accompanying the lower substrate positions. Again, this will be presented along with the plasma fluid module solution results. With regards to the overall absorbed power density distribution, very little change in this structure is observed regardless of substrate position.

The most significant changes to the electromagnetic solutions with regards to substrate position were related to the absorbed volumetric power density distributions, with a more distributed density corresponding to the lower substrate positions. However, the overall effect of this substrate position was not readily apparent aside from the maximum power



Figure 6.54: Plots of radial electric field intensities for substrate positions of (a) 0 mm, (b) -2 mm, (c) -4 mm, and (d) -6 mm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in V/m.

r (m)

(d)

r (m)

(c)



Figure 6.55: Plots of vertical electric field intensities for substrate positions of (a) 0 mm, (b) -2 mm, (c) -4 mm, and (d) -6 mm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in V/m.





Figure 6.56: Plots of absorbed power densities for substrate positions of (a) 0 mm, (b) -2 mm, (c) -4 mm, and (d) -6 mm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in W/m^{-3} .

density. To demonstrate the effects of substrate position on MPACVD reactor operation even further, several plasma-related solution quantities are now presented. These include several solution mole fractions, the average gas flow, temperatures, and densities.

Similar to the microwave absorbed power density distribution plots shown in Fig. 6.56, very little structural or spatial change to the atomic hydrogen mole fraction solutions is observed in Fig. 6.57 and Fig. 6.58. However, the maximum solution values as denoted by the top color scales suggest an increase of more than 10% from the null to -6 mm substrate positions. This is again similar to the percent relative change in the maximum absorbed power density solution, albeit the inverse relationship, which is expected due to the strong dependence of the rate of hydrogen dissociation on the absorbed power density. Nevertheless, this again represents a significant change in the plasma properties suggesting that adjusting a single reactor component by as little as 6 mm can affect the maximum plasma atomic hydrogen mole fraction by more than 10%.

The effect of substrate vertical position is also observed in the change in the total power deposited to the top substrate surface as shown in Fig. 6.59. It is clear a nearly linear relationship is present in this total power flux measurement depending on the substrate position. This suggests the power delivered to the substrate via hydrogen bombardment increases as the substrate is lowered. However, this must be balanced with the measured reflected power in order to maximize the overall diamond deposition rate.

Unlike the atomic hydrogen mole fraction solution, the electron mole fraction solutions presented in Fig. 6.60 and Fig. 6.61 exhibit no such clear trend in maximum value. Moreover, their distributions are all narrowly confined around the reactor axis, yet are slightly different in terms of maximum value positions. Again, this is due to the discontinuous solution distribution, which is a numerical artifact of the relaxation process. Thus, the comparison of maximum values here is not necessarily warranted or valid. This same behavior is also present in the electron density distribution.

Again, the average gas flow velocity solutions presented in Fig. 6.62 and Fig. 6.63 show





Figure 6.57: Atomic hydrogen mole fraction numerical solutions for substrate positions of (a) 0 mm and (b) -2 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW.





Figure 6.58: Atomic hydrogen mole fraction numerical solutions for substrate positions of (a) -4 mm and (b) -6 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW.



Figure 6.59: Total power deposited on top substrate surface due to hydrogen bombardment for various vertical substrate positions in the MSU MPACVD Reactor "B" configuration operating at 180 Torr and 2.2 kW.

very little change in the overall flow distribution as a whole. Notice in these plots the color scales have all been normalized to the same $5 \ cm/s$ maximum for easy comparison. However, both the upward flow at the reactor axis within the plasma ball, and the downward directed flow outside the substrate radius both increase slightly with lowered substrate position. This is a direct result of the increased gas temperature and decreased gas density in the upward directed region, and decreased gas temperature in the downward flow case. As a result, the substrate position appears to have very little effect on the overall, circulating flow pattern during operation. However, as this position is either raised or lowered, the gas flow within the plasma region is also affected due to changes in the gas temperature and mass density.

As with all numerical solution quantities in which the diffusion and conduction fluxes are dominated by source terms, the electron temperatures from Fig. 6.64 and Fig. 6.65 are again discontinuous and uneven. As a result, their maximum temperatures present from their color scales tend to provide an inaccurate depiction of the affect of substrate position on electron temperature. In spite of this, little change is observed between numerical solutions for the





Figure 6.60: Electron mole fraction numerical solutions for substrate positions of (a) 0 mm and (b) -2 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW.





Figure 6.61: Electron mole fraction numerical solutions for substrate positions of (a) -4 mm and (b) -6 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW.





Figure 6.62: Average gas flow velocity numerical solutions for substrate positions of (a) 0 mm and (b) -2 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in m/s.





Figure 6.63: Average gas flow velocity numerical solutions for substrate positions of (a) -4 mm and (b) -6 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in m/s.





Figure 6.64: Electron temperature numerical solutions for substrate positions of (a) 0 mm and (b) -2 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in K.




Figure 6.65: Electron temperature numerical solutions for substrate positions of (a) -4 mm and (b) -6 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in K.

various substrate positions, and so is assumed to have little effect on this quantity.

Finally, a clear trend in increasing gas temperature with lowering substrate position is deduced from Fig. 6.66 and Fig. 6.67. This increase in maximum gas temperature from $3680 \ K$ to $3696 \ K$ represents a relative change of less than 0.5%. However, this difference is significant enough to correspond to the previously discussed maximum atomic hydrogen mole fraction increase of more than 10%. Likewise, this temperature increase does affect the average gas flow, which from previous paragraphs was observed to have a small change in behavior with respect to substrate position.

Finally, the reflected power coefficient for the various substrate settings is presented in Fig. 6.68. It is clear the substrate position has a large effect on the relative percentage of microwave power reflected from the reactor. As discussed in the preceding paragraphs, the result of this increased reflected power is a decrease in coupling efficiency and maximum absorbed microwave power density. Thus, the substrate position clearly affects the reflected power coefficient. These reflected power ratios of more than 40% are far greater than typically observed during MPACVD operation, and thus suggest sub-optimal tuning at the specified operating conditions.

From these numerical solution data, plots, and discussion, the vertical positioning of the substrate clearly affects the system behavior and operation. This, in turn, affects the plasma properties and as a result is expected to significantly affect the diamond deposition rate and perhaps even the quality of the synthetic diamond sample. This dependence on the substrate position and the resultant plasma properties under such conditions presented in the previous numerical results are generally in agreement with previously reported experimental data at similar conditions [5].

6.4.2 Reactor cavity height

It may seem obvious that the vertical positioning, and therefore size, of the plasma region is significant to the overall behavior and properties of the plasma during operation. However,





Figure 6.66: Gas temperature numerical solutions for substrate positions of (a) 0 mm and (b) -2 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in K. 225





Figure 6.67: Gas temperature numerical solutions for substrate positions of (a) -4 mm and (b) -6 mm for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW. Units are given in K. 226



Figure 6.68: Power reflection coefficient for several substrate positions for the MSU MPACVD "Reactor B" configuration operating at 180 Torr and 2.2 kW.

even minute changes to the system geometry configuration significantly removed from the plasma region can also affect the system operation. The most common of these is the reactor cavity height. Changing the reactor cavity height is known to significantly affect the electromagnetic field structure, and thus the absorbed power and plasma properties. As an example to this effect, many similar numerical solutions are now presented for support of this statement. These numerical solutions are presented in a similar pattern compared to the substrate position discussed previously.

As can be seen in Fig. 6.69 and Fig. 6.70, there is very little change in both components of the electric field solution. Any discernible differences are further masked by the imposed equal color scales in an effort to demonstrate the fields within the main reactor cavity. These fields would otherwise be overshadowed by the much more intense electromagnetic fields within the coaxial waveguide at the top of the figures. Thus, from this brief, albeit mundane conclusion, the effect of the reactor cavity height on the electromagnetic fields, and therefore absorbed power and plasma properties, may be naively accepted as negligible. However, this is not the case as clear differences in these numerical solutions are observed as given in the absorbed power density solutions in Fig. 6.71.

The maximum volumetric absorbed power density as given in the color scales associated



Figure 6.69: Plots of radial electric field intensities for reactor heights of (a) 20.0 cm, (b) 20.2 cm, (c) 20.4 cm, and (d) 20.6 cm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in V/m.



Figure 6.70: Plots of vertical electric field intensities for reactor heights of (a) 20.0 cm, (b) 20.2 cm, (c) 20.4 cm, and (d) 20.6 cm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in V/m.





Figure 6.71: Plots of absorbed power density distributions for reactor heights of (a) 20.0 cm, (b) 20.2 cm, (c) 20.4 cm, and (d) 20.6 cm from the electromagnetics module. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in W/m^3 .

with Fig. 6.71 generally decrease with increasing cavity height. Moreover, this decrease represents a change in maximum power density of slightly more than 10%. This relative ratio between maximum absorbed power densities between the two most extreme cavity heights is approximately equal to the relative ratio of absorbed power densities observed during similar changes in the substrate vertical positioning. The similarity between these two numbers with regards to the very different and significantly separated reactor geometry configuration surfaces suggests perturbations of several millimeters of metallic horizontal surfaces can affect the power distribution, and ultimately plasma properties, more than 10%.

The fact that the maximum absorbed power density is decreasing with increasing cavity height suggests this distribution is becoming more spread out as the cavity size is increased. Since the reactor geometry within the plasma region remains constant, this redistribution of power is expected to result in a decrease of species production and densities. Similarly, the gas temperature will also be expected to decrease as will be discussed in the following paragraphs.

This significant change in the maximum absorbed power density profile once again suggests similar effects are expected to the plasma fluid module solution variables. As a result, these variables are once again presented and discussed in terms of the effect the reactor cavity height has on the plasma properties. Unlike the previous substrate position results, the adjustment to the reactor cavity height is removed from the plasma region, and thus any changes to the plasma properties are completely due to an external reactor configuration parameter.

The maximum atomic hydrogen mole fractions observed in Fig. 6.72 and Fig. 6.73 increase with corresponding decreases in maximum absorbed power densities. This is unexpected, yet the observation of a decreasing maximum absorbed power density may not be correct. That is, although the maximum absorbed power density does in fact continuously decrease with increased cavity height, the power density within the center of the plasma ball is not





Figure 6.72: Plots of atomic hydrogen mole fraction solutions for reactor heights of (a) $20.0 \ cm$ and (b) $20.2 \ cm$ within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of $2.2 \ kW$.





Figure 6.73: Plots of atomic hydrogen mole fraction solutions for reactor heights of (a) $20.4 \ cm$ and (b) $20.6 \ cm$ within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of $2.2 \ kW$.

able to be precisely extracted from Fig. 6.71. Instead, a second set of plots providing the same solution over only the plasma region would aid in this distinction and analysis, and is presented in Fig. 6.74 and Fig. 6.75.

The maximum absorbed power density from Fig. 6.74 and Fig. 6.75 is located just above the substrate surface. With the maximum absorbed power decreasing here, the microwave power is instead being absorbed more within the plasma ball than elsewhere. As a result, the absorbed power density distribution indeed relates to an increase in atomic hydrogen mole fraction.

The electron mole fraction solutions again do not exhibit significant changes in their distributions as seen in Fig. 6.76 and Fig. 6.77. That is, all plots are narrow in distribution about the reactor axis with maximum mole fractions that are approximately similar. Again, these slight differences in the electron mole fraction scales can be attributed to their oscillatory and discontinuous numerical solutions. Thus, any change to the electron mole fraction, temperature, and number density due to an adjustment in the reactor cavity height is difficult to discern.

As can be seen from Fig. 6.78 and Fig. 6.79, a decrease in average gas flow outside the plasma and about the outer substrate corner increases with the decrease in absorbed power density. This is expected, not as a result of the absorbed power density, but instead related to the increase in gas temperature and corresponding decrease in gas density in these regions. As a result, the buoyant and gravitational forces are more prominent, and affect the average flow.

A clearly increasing maximum gas temperature with rising cavity height is observed across Fig. 6.80 and Fig. 6.81. This again suggests the decrease in maximum absorbed power density results in an increased power density within the bulk plasma region, leading to increased hydrogen dissociation and energy transference to the hydrogen kinetic modes, thus raising the gas temperature. The reactor cavity height only slightly alters the maximum gas temperature value by much less than 0.5%. Moreover, the numerical distributions are





Figure 6.74: Plots of absorbed power density distributions for reactor heights of of (a) 20.0 cm and (b) 20.2 cm within the plasma region. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in W/m^3 .





Figure 6.75: Plots of absorbed power density distributions for reactor heights of of (c) 20.4 cm and (d) 20.6 cm within the plasma region. Shown for MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in W/m^3 .





Figure 6.76: Plots of electron mole fraction solutions for reactor heights of of (a) $20.0 \ cm$ and (b) $20.2 \ cm$ within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of $2.2 \ kW$.





Figure 6.77: Plots of atomic hydrogen mole fraction solutions for reactor heights of (a) 20.4 cm and (b) 20.6 cm within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW.





Figure 6.78: Plots of average gas flow velocity solutions for reactor heights of of (a) 20.0 cm and (b) 20.2 cm within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in m/s.





Figure 6.79: Plots of average gas flow velocity solutions for reactor heights of (a) 20.4 cm and (b) 20.6 cm within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in m/s.





Figure 6.80: Plots of gas temperature solutions for reactor heights of of (a) 20.0 cm and (b) 20.2 cm within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in K.





Figure 6.81: Plots of gas temperature solutions for reactor heights of of (a) 20.4 cm and (b) 20.6 cm within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW. Units are given in K.



Figure 6.82: Plot of the reflected power ratio for various reactor heights within the MSU MPACVD Reactor B at a pressure of 180 Torr and absorbed power of 2.2 kW.

very similar across the different reactor height settings.

Finally, the microwave reflected power given in Fig. 6.82 confirms the trend of increasing absorbed power density within the plasma ball by presenting the opposite trend of decreasing reflected power. That is, this decrease in reflected power conversely suggests an increase in power transferred to the plasma via the electrons and their collisions with hydrogen species. The reflected power values themselves are quite high being between 47% to 65%. Again, this is not typical of experimental reflected power coefficients, but is reasonable in a numerical simulation where the reactor has not been tuned to minimize this reflected power.

From the results presented in the previous paragraphs and corresponding figures, adjusting the reactor cavity height clearly affects the plasma properties. This is seen not only in the power coupling from the microwave source into the plasma, but also in the plasma properties itself; most notably the atomic hydrogen and gas temperatures. More specifically, increasing the cavity height by a mere 6 mm may affect the atomic hydrogen molar fraction by more than 10%. Since atomic hydrogen plays an important role in the diamond deposition, this alteration is significant to the total operation of the MPACVD reactor.

6.4.3 Reactor Configuration

The strong, nonlinear dependence of important plasma properties in the physical reactor geometry was observed to be dependent even on millimeter changes in either the substrate position or reactor height. It would thus be expected that more drastic changes to the reactor configuration, such as the alteration of the entire MPACVD system configuration and physical layout would affect the overall solution even more. These differences have been previously reported over a wide range of reactor configurations [5, 21, 76]. However, the majority of these data were reported while operating at lower pressures. Similar higher pressure results are now briefly outlined in the following paragraphs for comparison and reference. The MSU MPACVD reactors will be primarily used due to familiarity and the existence of experimental data, consisting of configurations "A", "B", and "C". Results could similarly be obtained for other reactor configurations.

Although "A" and "B" are clearly different reactors as noted by their associated letters, only the substrate pedestal wall radius is altered. More specifically, this pedestal radius is decreased in Reactor "B" compared to "A" by almost a factor of two. As a result, numerical simulation data are not expected to vary significantly between these two configurations. On the other hand, Reactor "C" is strikingly dissimilar from Reactors "A" and "B", suggesting the plasma solutions are also dissimilar. Results are given for various simulated physical quantities across all three reactor configurations for comparison.

The two electric field component solutions are provided in Fig. 6.83 and Fig. 6.84.

As expected, the electric field solutions presented in Fig. 6.83 and Fig. 6.84 are quite similar between reactors "A" and "B", while that of "C" is markedly different. For instance, the largest change seen going from Reactor "A" to "B" is the increase in radial field intensity below the substrate position, and the increase in vertical electric field intensity within this same region. This means the electromagnetic energy below the substrate vertical position changes from being directed radially to vertically. However, as it is very far away from



Figure 6.83: Plots of radial electric field intensities for MSU MPACVD reactor configurations (a) A, (b) B, and (c) C from the electromagnetics module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in V/m.



Figure 6.84: Plots of vertical electric field intensities for MSU MPACVD reactor configurations (a) A, (b) B, and (c) C from the electromagnetics module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in V/m.

the plasma ball position, the absorbed power density here is extremely low and thus is not expected to significantly affect the overall power distribution.

Both radial and vertical electric field intensities seen in Fig. 6.83 and Fig. 6.84 for the MSU MPACVD Reactor "C" are very different than their counterparts. The radial electric field appears to exhibit a $\text{TM}_{202}^{(z)}$ -like mode structure with two maxima residing above the substrate along \hat{z} . Likewise, the presence of a removed minimum in \hat{r} from the axis toward the top of the reactor suggests this second radial mode excitation. Within the plasma region, the radial electric field is more uniform than the previous configurations, while this intensity drops to almost zero within the plasma at the reactor axis. The radial electric field once again drops off roughly as 1/r below the substrate at the outer pedestal. The vertically-directed electric field once again reaches very high levels at the substrate surface and the top of the quartz bell jar. However, outside the substrate radius, this field component drops significantly, possibly resulting in a decreased absorbed power density here. Finally, E_z is much lower within the plasma region, which is a result of increased conductivity and thus increased electron density. More on these quantities will be provided in upcoming paragraphs.

Little change is observed between the power density results presented in Fig. 6.85 for MSU MPACVD Reactors "A" and "B". However, those results corresponding to Reactor "C" show very large differences to the other two solutions. That is, the same power and pressure combination used for the previous two configurations results in greater power density present along the top surface of the bell jar. However, it does provide an example of a combined unstable system and operating conditions. Moreover, this power density is also even more heavily concentrated at the reactor axis, which is likely due to a combination of a reduced substrate radius, increased pressure, and increased plasma region volume. Thus, the absorbed power density observed for Reactor "C" is clearly altered from the other configurations. As a result, the various plasma properties are also expected to vary significantly as discussed below.



Figure 6.85: Plots of absorbed power density for MSU MPACVD reactor configurations (a) A, (b) B, and (c) C from the electromagnetics module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in W/m^3 .





Figure 6.86: Plots of atomic hydrogen mole fraction for MSU MPACVD reactor configurations (a) B and (b) C from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW.

The plasma quantities calculated using reactor configurations "A" and "B" were very similar, and thus "A" results are omitted here in order to allow for easy comparison with the "C" results. As seen in Fig. 6.86, the distributions, location, and maximum values of the simulation results for the atomic hydrogen mole fraction are very different between Reactors "B" and "C". For instance, while the "B" atomic hydrogen mole fraction is more round and spherical in shape, the "C" distribution is more narrow being tightly confined to the reactor axis. Moreover, its maximum mole fraction is almost 40% greater than that of Reactor "B". Finally, these changes in distribution and maximum value confirm the previously reported findings of decreased operating microwave power required for Reactor "C" in order to achieve the same plasma volume and density of that in Reactor "A" or "B" [21].

As with the atomic hydrogen mole fraction results, the electron mole fraction numerical results in Fig. 6.87 depict a much more narrow electron mole fraction with slightly increased maximum value for Reactor "C" compared with its counterpart in "B". Similar to the previous results for altered substrate and reactor heights, the electron mole fraction and density is not exponentially-dependent on the absorbed power density as is the atomic hydrogen. Thus, the small increase in electron density follows as expected.

Marked differences in the vector average gas flow solutions are shown in Fig. 6.88 and Fig. 6.89 as noted by both changes in maximum gas speed and the overal solutions. For instance, the maximum gas flow within the plasma increases moving from MSU MPACVD Reactors A to B, and to C, respectively. Moreover, a more complex flow pattern is observed for Reactor C with increased gas flow located at the reactor axis, outer substrate corner, and just inside the top quartz dome surface. Similarly, the vertical flow below the top substrate surface also changes between these configurations. The overall circulating pattern of flow with upward direction within the plasma region remains throughout. As these results presented in Fig. 6.88 and Fig. 6.89 all correspond to the same pressure and absorbed power levels, the reactor configurations clearly have a marked affect on the average gas flows within the MPACVD system.



(a)



Figure 6.87: Plots of electron mole fraction for MSU MPACVD reactor configurations (a) B and (b) C from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW.





Figure 6.88: Plots of vector average gas flow for the MSU MPACVD reactor configurations (a) A and (b) B from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in m/s.



Figure 6.89: Plot of vector average gas flow for the MSU MPACVD reactor configurations C from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in m/s.

The electron temperature simulation results corresponding to Reactor "C" as given in Fig. 6.90 is more confined to the reactor axis with much cooler temperatures approaching the substrate radius along its top surface. Moreover, this temperature is much cooler below the substrate vertical position compared to the Reactor "B" results. Again, this is a result of the decreased electromagnetic field presence, and thus absorbed power density within this region and is dependent on the reactor geometry itself. Interestingly enough, the maximum electron temperatures, and thus the temperatures at the substrate surfaces, agree to within 2%, denoting very little difference in the electron energy here.

Finally, the increased absorbed power density also results in increased gas temperature comparing "B" and "C" results in Fig. 6.91. This agrees with the much larger relative increase in the atomic hydrogen mole fraction presented previously. The elongated distribution with higher temperatures residing higher within the plasma region also confirm the changes in absorbed power density and electron mole fraction.

Clearly the reactor configuration, geometry settings, and parameters present during the





Figure 6.90: Plots of electron temperature for MSU MPACVD reactor configurations (a) B and (b) C from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in K.



Figure 6.91: Plots of gas temperature for MSU MPACVD reactor configurations (a) B and (b) C from the plasma fluid module. Shown for a pressure of 150 Torr and absorbed power of 2 kW. Units are given in K.

simulation can significantly affect the plasma properties, and thus diamond deposition rate. As a result, the reactor design must carefully be chosen, analyzed, and vetted to ensure efficient and hight quality diamond deposition.

6.5 Power Minimization

As described earlier, several of the important physical reactor components are often adjusted during the deposition process in order to minimize the measured reflected power. This reflected power is an indication of the power absorption efficiency into the plasma and the resultant matching within the reactor. It also can be used as a diagnostic for indicating an unstable plasma or reactor configuration. In this way, the effect of the minimization of power plays an important role in ensuring the successful and efficient deposition of diamond.

The accurate capture of this power minimization and its related effect on the plasma properties and location is also important. This is demonstrated by simulating similar reactor configurations under the same operating conditions, but only allowing one to actively minimize the reflected power during the solution procedure. That is, in one case, the reactor cavity height and probe antenna length are chosen to be 21.0 cm and 2.5 cm respectively. These settings represent a typical set of configuration parameters for the MSU MPACVD systems. During the power minimization simulation, the cavity height and antenna probe length are adjusted in order to achieve a minimum reflected power. As a result, the minimized values are 20.7 cm and 3 cm for the cavity height and antenna length, respectively. Clearly, these settings do not change much, but result in large differences in calculated reflected power. The resulting differences between the plasma solutions are attributed solely to the differences in reactor configurations. This test was performed at the higher pressure operating conditions of 180 Torr and 2.2 kW for the MSU MPACVD Reactor B. Plots of several physical constants are provided and described in the following paragraphs. Both simulations are run at operating conditions of 180 Torr and 2.2 kW.



Figure 6.92: Plots of radial electric field intensities for MSU MPACVD Reactor B with (a) minimized and (b) non-minimized reflected powers from the electromagnetics module. Units are given in V/m.



Figure 6.93: Plots of vertical electric field intensities for MSU MPACVD Reactor B with (a) minimized and (b) non-minimized reflected powers from the electromagnetics module. Units are given in V/m.

The radial and vertical component electric field intensities shown in Fig. 6.92 and Fig. 6.93 exhibit many differences between field solutions. For the radial electric field solution, the field intensity is much greater within the waveguide region in the case of the non-minimized power solution. This increased field intensity confirms a greater reflected power, which in this case is roughly 30% higher than that of the minimized power solution. Similarly, this field intensity at the outer top region of the reactor is much greater for the non-minimized power solution. Again, this suggests more energy is remaining within the cavity and not being transferred to the plasma and aiding in the deposition process. For the vertical electric field intensity, the electric field is again much greater in the immediate region surrounding the antenna probe in the case of the non-minimized power solution compared to that of the minimized power.

Similar traits shared between both of these solutions include relatively unchanged field structures within the plasma region. Moreover, the intensities or amplitudes of these fields within the plasma region do not change significantly between these solutions. This suggests the plasma solution and related quantities may also exhibit little change between the two solutions. Although unexpected from an experimental standpoint, the fact that these solutions remain unchanged could be due to the relatively high reflected power ($\sim 40\%$) even for the minimized power solution. More on these plasma solution quantities will be discussed in the following paragraphs.

The absorbed power density solutions shown in Fig. 6.94 exhibit small changes in both maximum power density and location of this maximum. That is, the maximum absorbed power density is slightly higher in the case of the non-minimized reflected power. Moreover, the location of this maximum is closer to the substrate surface than in the actively minimized reflected power solution. This indicates that more power is being transferred to the electrons, and thus plasma ions and radicals as well, closer to the substrate and at a higher rate. However, the overall absorbed power density profiles are very similar, which again suggests the plasma solutions will also remain similar.


Figure 6.94: Plots of absorbed power densities for MSU MPACVD Reactor B with (a) minimized and (b) non-minimized reflected powers from the electromagnetics module. Units are given in W/m^3 .

Again, very little difference between both the maximum and solution distribution for the atomic hydrogen mole fractions are observed in Fig. 6.95 when comparing the reflected power solutions. The only clear difference is the slight change of maximum atomic hydrogen solution with the non-minimized reflected power value being slightly greater. This represents only a 0.62% relative difference between the two maximum values again confirming very little difference between the two solutions.

Very similar numerical solutions are again encountered comparing both the electron and gas temperatures, and vector average gas flow solutions. However, the electron mole fraction and densities exhibit stark contrasts in maximum value when comparing their solutions. These distributions are provided and discussed in the following pages.

Similar to the electron mole fraction, the electron density solutions shown in Fig. 6.96 exhibit very dissimilar maximum values between the minimized and non-reflected power minimized numerical solutions. In this case, the adjusted reactor configuration resulting in





Figure 6.95: Plots of atomic hydrogen mole fraction for MSU MPACVD Reactor B with (a) minimized and (b) non-minimized reflected powers from the plasma fluid module.





Figure 6.96: Plots of electron number density for MSU MPACVD Reactor B with (a) minimized and (b) non-minimized reflected powers from the plasma fluid module. Units are given in m^{-3} .

a minimized reflected power leads to a sharp increase in maximum electron number density. However, this is in contrast to the absorbed power density solution where the two solutions were very similar. Since the absorbed power density is closely related to the electron number density, this represents an oscillating solution with insufficient mesh discretization. That is, although the solution maxima do not agree, their overall shape and absolute density values are expected to remain in good agreement to within the uncertainty associated with one solution iteration.

As a final observation on reactor geometry configuration adjustment and its affect on the plasma properties, the energy flux to the substrate may be calculated and compared between the two cases. These solutions are presented below.

The energy fluxes shown in Fig. 6.97 exhibit small changes between solutions, particularly at the axis of symmetry. For instance, while the energy flux due to atomic hydrogen bombardment is slightly greater at this location in the case of a non-minimized reflected power reactor geometry configuration, it is slightly lower for the thermal conduction energy flux. Since the energy due to thermal conduction is roughly five times that due to the atomic hydrogen bombardment, the total energy flux to the substrate is greater when the reactor is tuned to minimize reflected power. This confirms the experimental practice of actively minimizing reflected power during diamond deposition. Of course, since hydrocarbons are not included in the present simulation, these may also affect the flux to the substrate and may even further confirm the minimization of reflected power practice. However, the above discussion has confirmed that even minute changes of reactor geometry configuration (3 mm in this case) can have observable affects on the plasma properties, the resulting energy flux to the substrate, and likely the deposition rate.





Figure 6.97: Plots of energy flux from (a) thermal conduction and (b) atomic hydrogen bombardment at the substrate surface. Units are given in W/m^2 .

6.6 Convergence

The convergence of the complete numerical solution is vital to both the accuracy and efficiency of the simulation as a whole. This includes not only the rate of convergence within the various modules consisting of numerous equations, but also the minimum convergence levels attainable. The simulation only terminates once satisfactory convergence has been achieved. However, this level of satisfaction is determined by the user with numerous conditions spanning several solution variables within the plasma fluid module. The intricacies of the simulation convergence, examples of its calculation and levels during simulation, and physical interpretation will be presented below.

The passing of physical quantities between solution modules after successive updates results in an overall guess-and-check-style iterative solution procedure. As a result, the system is expected to slowly converge toward a single solution, but may require many updates to achieve this. The overall simulation convergence toward a single, stable solution is not guaranteed. However, with the correct choice of relaxation coefficients applied to the most unstable numerical equations, reasonably stable convergence is often achieved. Various plasma fluid module transport equation residuals, representing the system convergence, are provided in Fig. 6.98 and Fig. 6.99. These convergence rates are typical of those achieved for the stated relaxation quantities with null initial solution and higher pressure operating conditions.

The most important numerical residuals calculated from the plasma fluid module transport equations are presented in Fig. 6.98 and Fig. 6.99. These data represent the scaled, absolute difference between left and right hand sides of their respective matrix equations. That is, the absolute value of these residuals closely mimics their maximum solution values within their numerical distributions. Thus, the numerical error associated with the H_3^+ ion mole fraction is much lower than the atomic hydrogen mole fraction simply due to the large difference between their maximum solution values. In order to somewhat normalize



Figure 6.98: Numerical transport equation residuals plotted against total iteration number for the MSU MPACVD Reactor B operating at 180 Torr and 2 kW.



Figure 6.99: Numerical transport equation residuals plotted against total iteration number for the MSU MPACVD Reactor B operating at 300 Torr and 3 kW.

the error calculations across all variables, the temperature errors were divided by the upper temperature range of $30,000 \ K$.

Note in Fig. 6.98 and Fig. 6.99, the error associated with many of the variables changes rapidly over the first several iterations. Starting from the numerical condition of null initial solution, the various mole fractions and temperatures are undergoing large changes in both their distribution shapes and absolute values. This eccentric convergence continues for several iterations until a stable plasma begins to form above the substrate as characterized by a gently increasing error across solution variables until 500 to 750 iterations. Once a stable plasma has formed, the solution converges toward a single solution by undergoing small changes over the next several hundred to thousand iterations. The simulation terminates once all specified convergence limits are met for the solution variables.

The errors associated with the higher pressure and power simulations are generally greater than those associated with the lower pressure and power conditions. This is due simply to the increase in ion and species production, and an increase in gas temperature at higher pressure and power conditions. As a result, the error calculated for these simulations is necessarily greater.

The atomic hydrogen and gas temperature numerical errors are relatively well-behaved and continue to decrease after plasma formation. This is in contrast to the H_3^+ ion, electron temperature, and total errors which plateau once a plasma forms. Again, this is a result of their local oscillations within the spatial distributions and discontinuous solutions. It is a direct result of insufficient mesh discretization coming from a source term dominating over that species or temperature flux.

Finally, the total plasma residual is dominated by the electron temperature regardless of operating conditions as indicated by a relatively constant and increased T_e residual in Fig. 6.99. This suggests the numerical solution, and thus physical MPACVD system, is heavily influenced by the EEDF within the plasma.

CHAPTER 7

ANALYSIS AND DISCUSSION

The following analysis is presented to provide a more detailed description, and underlying reasoning, behind the numerical results provided in Chapter 6. Significant attention is paid to the role of convective flows within MPACVD systems at moderate operating pressures and the substrate temperature during the deposition process. Both quantitative and qualitative analysis is provided and compared at typical operating conditions within the MSU MPACVD reactors. Comparisons with previous experimental and numerical simulations are also made.

7.1 Electromagnetics

Many interesting characteristics of the electromagnetic fields within the plasma reactor during operation have been outlined in Chapter 6. These include the overarching themes (regardless of operating conditions or minute tuning of the reactor configuration) of maximum electric field intensity residing just above the substrate surface, this maximum electric field being primarily vertically directed at the substrate surface, and the electric fields below the substrate are significantly diminished from those above the substrate. On top of these, the MSU MPACVD Reactors A and B were indeed found to support $TM_{103}^{(z)}$ -like field structure as observed at the outer reactor walls. Overall, the electromagnetic fields (and thus absorbed power density, and ultimately plasma characteristics) were clearly sensitive to the reactor configuration parameters during operation. As expected, the reactor configuration and geometry played an important role in these characteristics. Even small changes of a few millimeters made to reactor surfaces (even those removed from the plasma region) were observed to significantly affect the plasma properties. For instance, the lowering and raising of the reactor cavity height 6 mm resulted in a 10% change in maximum atomic hydrogen mole fraction within the plasma as given in Fig. 6.72 and Fig. 6.73. Since atomic hydrogen is a precursor to the carbon deposition process, this increase is expected to significantly affect the rate of diamond deposition during the experimental run.

7.2 Absorbed Power

The maximum absorbed power level often resides just above the substrate surface in the case of stable plasmas. However, for those plasmas elongated vertically along the reactor axis, or formed at the top of the bell jar, this was not necessarily observed. Instead, for unstable or detuned solutions, the absorbed power density often reached a maximum at the top bell jar surface and centered at the axis of symmetry. Moreover, the microwave absorbed power density was observed to closely influence the electron temperature solution. This is expected and often observed, as the microwave power is primarily transferred to the electrons via their interactions with the electromagnetic fields, and then to the rest of the plasma via collisions with heavy species [16]. Finally, the microwave power is absorbed at non-negligible levels outside and below the substrate surface. However, these absorbed power densities are still very low compared to the maximum absorbed power density residing just above the substrate surface. In turn, this results in very little hydrogen dissociation or plasma ionization below the substrate, resulting in a relatively confined and stable plasma above the substrate.

7.3 Plasma Fluid Module

A more detailed analysis of the plasma fluid module solution and related quantities is now presented. This will primarily focus on the two important contributions of the present work: the influence of convective flows and the substrate temperature at moderate pressures.

7.3.1 Validation

The numerical average gas flow results were never validated in the case of the fully coupled, multiphysics simulation. Since no known experimental data on these flows exists, these flows at moderate pressures will be validated against previous simulations. The average gas flow velocity component profiles just above the substrate surface were simulated and presented previously by Yamada, *et al.* [36]. Although these results utilized a much different reactor configuration, they provide a basis for comparison in both spatial distribution, sign, and magnitude.

Comparing the numerical results presented in Chapter 6 with the results of Yamada, *et al.*, similar magnitudes and orientation of the flow are observed [36]. These results provide a validation of very low average flow components near the substrate. Furthermore, the radial component is observed to be negative in sign just above the substrate top surface, signaling a flow back toward the reactor axis. Finally, the vertical flow is consistently upward-directed within the plasma. The agreement between these several characteristics is taken to validate the momentum transport solution, and average convective gas flow results, in the case of moderate pressure MPACVD systems.

7.3.2 Effect of average gas flow

The effect of the average gas flow on the overall plasma properties, stability, and location within MPACVD reactors at pressures exceeding 150 Torr is of significant interest and is one of the primary thrusts of this work. Thus, a detailed analysis of this effect via numerical simulations is warranted. This is done by quantifying the three gas flow-related forces affecting the plasma; convection, buoyancy, and gravitation. These are analyzed in the following paragraphs over a range of operating pressures, absorbed power levels, and for several solution variables. They are analyzed for their influence in the respective scalar transport equations for both mole fractions and temperatures. Finally, a direct comparison between the relative size of these forces is provided.

Unlike buoyant or gravitational forces, the force of convection may be oriented along any direction. In order to quantify the force of convection and its role within the plasma discharge during MPACVD system operation, the related flux across mesh edges is calculated. Here, both mass and energy are tracked and compared with their respective maximum fluxes, which are calculated as

$$\vec{\Gamma}_{m,s} = \rho_s \vec{v} \tag{7.1a}$$

$$\vec{\Gamma}_e = \tilde{E}\vec{v} = \frac{E}{V}\vec{v} = \frac{1}{2}\rho v^2 \vec{v}$$
(7.1b)

where $\Gamma_{m,s}$ and Γ_e represent the mass and energy fluxes, respectively, \tilde{E} is the plasma volumetric energy density, and V is the volume associated with individual mesh elements. Since many terms contained in Eq. (7.1) are element-centered, they are translated to their respective edges via a bilinear interpolation scheme. In this way, both the mass and energy fluxes may be directly compared to their diffusive flux counterparts as given in the scalar transport equations. Moreover, these fluxes provided in Eq. (7.1) follow directly from their respective transport equations from Eq. (3.18) and Eq. (3.39). Vector plots of both the mass and energy fluxes across the entire plasma domain are provided in Fig. 7.1 and Fig. 7.2.

The convection flux vector plots provided in Fig. 7.1 and Fig. 7.2 clearly follow closely to the average vector gas flow solution. That is, both energy and mass convection fluxes exhibit vortices centered at the outer region of the plasma with upward-directed flux within the plasma and downward going outside. The slight differences between the local values of these convective fluxes are due to changes between mass and kinetic energy density within





Figure 7.1: Vector energy (a) convection and (b) conduction fluxes within the plasma region for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in kg/s^3 .





Figure 7.2: Vector mass (a) convection and (b) diffusion fluxes within the plasma region for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW. Units are given in $kg/m^2/s$.

the plasma region. Moreover, convective fluxes are present throughout the entire plasma region, albeit at much smaller levels far away from the plasma.

Comparing both the maximum and average energy conduction and mass diffusion fluxes with their respective convection fluxes further exemplifies the small effect the average gas flow has on the transport of these quantities. As a result, the gas flow influence on the overall plasma properties and characteristics is very small. The absolute difference between the maximum conduction and convection energy fluxes spans more than twelve orders of magnitude. Likewise, the separation between the maximum convection and diffusion mass fluxes is more than eight orders of magnitude within the plasma, as the diffusion color scale is truncated in Fig. 7.2. Since both the mass diffusion (in the case of atomic hydrogen) and energy conduction terms are known to dominate over their respective source transport equation terms, the role of the convection fluxes due to the average gas flow are confirmed to be insignificant.

Reviewing these convective forces specifically in terms of their vertical components results in the specific treatment of gravitational and buoyant forces. Using the same convection flux plots provided in Fig. 7.1 and Fig. 7.2, the effect of these gravitational and buoyant forces on the plasma properties may be discussed as follows.

Simulations suggest the average gas flow within the plasma changes direction from downward to upwardly-directed depending on operating pressure and absorbed power level. This is a result of an increased gas temperature, and thus decreased gas density, yielding a much larger buoyant force (or likewise smaller gravitational force) at increased operating pressures. Moreover, the gas flow outside this plasma region can either be downwards or upwards directed, as is the case of lower pressure operation.

In the case of lower pressure operation with a decreased gas temperature, the average gas flow is downward directed within the plasma. This results in the further transport of mass toward the substrate surface, as the diffusion flux is necessarily downward directed toward this surface in the presence of a plasma. As a result, the mass flux to the substrate is expected to be greater than in the case of no gas flow. When operating at higher pressure conditions, the gas flow is upward directed within the plasma region, which may naively be interpreted as reducing the mass flux to the substrate compared to lower pressure operation. However, due to the much greater atomic hydrogen mole fraction at these conditions, the flux to the substrate is much greater than that at lower pressures. Thus, even with a slightly reduced mass flux toward the substrate due to the upward-directed average gas flow, this flux is still much greater than that observed at lower pressures.

It is clear from this analysis that convective fluxes, buoyant, and gravitational forces are all present throughout the plasma region regardless of operating conditions. This results in the transport of both mass and energy throughout the solution domain. Due to their relatively small influence on the physical quantities when compared to their respective diffusion or conduction fluxes, the gas flow within MPACVD reactors is not expected to contribute significantly to the properties or position of the microwave discharges even at higher pressures approaching 300 Torr.

A final recommendation may be made relating to the inclusion of the average gas flow in the multiphysics simulation of MPACVD reactors. Due to the insignificant amount this average gas flow affects the overall plasma behavior and characteristics at the given conditions, it is beneficial to estimate its relevance during numerical simulation and question its inclusion in the solution process. The employed matrix inversion solution requires a significant amount of processing power and physical memory, especially for dense meshes. On top of this, its inclusion also results in a slightly less efficient rate of convergence for the overall solution, and can contribute numerical instability and noise. As a result, the numerical solution of the average gas flow (and thus momentum transport equation) within the present simulation is not recommended for operating conditions where a plasma is known to remain experimentally stable.

It should be mentioned that the above statements are only valid for the combination of operating conditions and reactor geometries included in the present work. In fact, these effects may become significant under the right conditions that have not yet been simulated.

7.4 Atomic Hydrogen Diffusion Coefficient

As stated earlier, the atomic hydrogen mole fraction and resulting volumetric number density are important to the diamond deposition process. Thus, the atomic hydrogen mole fraction solution and distribution is vital to accurately simulating the system behavior and characteristics. Since the diffusion flux dominates the convective flux and steady rate production of species in the mass transport equation, the accurate modeling and calculation of this diffusion coefficient is paramount to the accurate atomic hydrogen mole fraction solution.

Two previously referenced and analyzed atomic hydrogen diffusion coefficients were presented in Chapter 6 [35, 64]. However, simulation results using these approximated diffusion coefficients were not presented, but are now included in Fig. 7.3 through Fig. 7.5 for atomic hydrogen mole fraction and gas temperature.

Comparing Fig. 7.3 through Fig. 7.5, it is clear the atomic hydrogen diffusion coefficient is effected by the choice of diffusion coefficient representation. Moreover, since this mole fraction is closely related to the gas temperature, it too is changed slightly from its nominal value. More specifically, the maximum atomic hydrogen mole fraction is observed to decrease by more than 20% when going from the Hirschfelder atomic hydrogen diffusion coefficient to the Koldanov approximation. This also results in a roughly 0.25% change in maximum gas temperature. The atomic hydrogen distributions are also slightly altered when comparing those using different diffusion coefficients. For example, the solution associated with the Mankelevich approximation is more confined to the immediate region surrounding the reactor axis, while that using the Koldanov approximation is more diffuse. This suggests the approximated Koldanov diffusion coefficient is greater than that of both the Hirschfelder and Mankelevich coefficients.

It is also clear the choice of diffusion coefficient plays a large role in the final solution





Figure 7.3: (a) Atomic hydrogen mole fraction and (b) gas temperature (K) within the plasma region for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.





Figure 7.4: (a) Atomic hydrogen mole fraction and (b) gas temperature (K) calculated using the Mankelevich approximated atomic hydrogen diffusion coefficient within the plasma region for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.





Figure 7.5: (a) Atomic hydrogen mole fraction and (b) gas temperature (K) calculated using the Koldanov approximated atomic hydrogen diffusion coefficient within the plasma region for the MSU MPACVD Reactor B operating at 180 Torr and 2.2 kW.

for the atomic hydrogen mole fraction, and can even effect other physical quantities. While the stated approximations are often much easier to calculate, they are not suggested for future use, as they remain approximations to the much more rigorous Hirschfelder diffusion calculation. However, the future analysis of the present diffusion coefficient is suggested and even posited for experimental validation.

7.5 Conductivity

The electrical conductivity solution is important to analyze in terms of the different operating powers and pressures. For example, its maximum absolute value is observed to range between $0.02 \ S/m$ and $5 \ S/m$ in the given power and pressure ranges typically used in MPACVD systems.

The lower conductivity value of $0.02 \ S/m$ results in complete electromagnetic wave propagation through the entire plasma with little attenuation. Moreover, when realizing this maximum conductivity is only present at the very center of the plasma ball with diminishing values moving away, the electromagnetic wave attenuation is expected to decrease even further.

On the other hand, the maximum conductivity absolute value approaching 5 S/m represents a marked increase in electromagnetic wave attenuation at the particular frequencies often associated with MPACVD systems. For example, the attenuation coefficient corresponding to this conductivity value may be calculated in the following derivation. While the absolute conductivity value approaches 5 S/m, its imaginary component is often around 1 S/m and the real component likewise approaches 5 S/m. Taking these values, the attenua-

tion coefficient is calculated by first calculating the corresponding complex wavenumber

$$k = k' - jk''$$

= $k_0 \left(\sqrt{\epsilon' - j\sqrt{\epsilon''}} \right)$
= $k_0 \left(\sqrt{\epsilon' - \frac{\sigma''_e}{\omega\epsilon_0}} - j\sqrt{\epsilon'' + \frac{\sigma'_e}{\omega\epsilon_0}} \right)$ (7.2)

where ' and '' denote the real and imaginary components of the complex permittivity and conductivity, respectively. Assuming the permittivity in the plasma region in Eq. (7.2) is completely real (which is valid in this case assuming vacuum), the imaginary wavenumber within the plasma may be calculated as

$$k' = k_0 \sqrt{\frac{\sigma'_e}{\omega\epsilon_0}}$$
$$= \frac{2\pi f}{c} \sqrt{\frac{\sigma'_e}{\omega\epsilon_0}}$$
$$= \frac{\sqrt{2\pi f}}{c} \sqrt{\frac{\sigma'_e}{\epsilon_0}}$$
(7.3)

where f is the frequency of the electromagnetic excitation. Finally, the attenuation coefficient may be calculated by approximating a 2 cm thick plasma region via

$$\alpha = \exp\left(-\frac{\sqrt{2\pi f}}{c}\sqrt{\frac{\sigma'_e}{\epsilon_0}}r_p\right)$$
(7.4)

where r_p is the thickness of the plasma through which the plane wave propagates. Plugging in the values for this expression given in Eq. (7.4) results in an attenuation coefficient of $\sim 2 \times 10^{-3}$. This, of course, is a very small coefficient, suggesting the majority of the electromagnetic wave is attenuated by the time it reaches the center of the plasma. However, comparing this value to the numerical results at this extreme high pressure condition, the electromagnetic field only drops to slightly more than 10% of its intensity just outside the plasma region. The discrepancy between these two values is attributed to the unrealistic assumption of consistent conductivity within the plasma when calculating this attenuation. That is, the electrical conductivity magnitude within the plasma region is not homogeneous, and more closely resembles a Gaussian distribution. Due to this spatial variation, the attenuation of the electromagnetic fields is only maximized at the very center of the plasma, with little attenuation toward its outer region. As a result, the *effective* attenuation of the electromagnetic fields is much smaller than that given in the above derviation in Eq. (7.2) through Eq. (7.4). Moreover, with a maximum conductivity magnitude approaching 5 S/m even at the most extreme operating conditions, the electromagnetic fields, and thus microwave power, is expected to keep penetrating completely into the plasma within MPACVD reactors.

7.6 Stability

Stability refers to both the physical system in terms of the location of the plasma and its physical formation, and the numerical solution and convergence. These two different meanings of stability will be discussed in the following section.

The physical stability of the system is characterized by the consistent formation of the plasma above the substrate within the plasma region. Moreover, the plasma is considered stable if its location does not change significantly over several solution iterations. The combination of these two definitions excludes even a consistent plasma forming at the bell jar corner, its top surface, or below the substrate from being classified as stable. This definition agrees with the experimental observation of nominal system operation, where these conditions would be classified as unstable.

The physical stability of the system depends on several factors, including the reactor configuration, positions of the reactor height and substrate surface, and the operating conditions. For example, the operation of the MPACVD reactor at high power levels but low pressures often results in the formation of a plasma at the top bell jar surface. The very high electron and gas temperatures in close proximity to the top bell jar surface can cause its overheating and even lead to its mechanical failure.

Numerical stability is important to the accuracy and numerical efficiency of the simulation. This is characterized by the convergence toward a single numerical solution, often coinciding with the physical stability of the plasma at the same time. In this case, the divergence of any one solution variable would signal numerical instability.

The numerical stability of the simulation depends on many factors including the initial solution distributions, the system operation parameters, mesh resolution, and choice of solution procedures. The maximum number of updates to the physical parameters within the plasma fluid module SOR routine are of critical importance. The choice of these numerical parameters is important to an efficient numerical solution and thus must be chosen carefully to avoid long run times or inefficient solution methods.

The numerical stability of the complete simulation is not fully understood at this time and has not been rigorously characterized. Several factors influence this stability, including mesh resolution, numerical initial and physical operating conditions, and choice of SOR relaxation coefficients within the transport equations update. In light of this, the combination of reasonable physical operating conditions, the incorporation of a previous solution as the initial solution guess, and fewer inner and outer SOR iterations often leads to the most stable simulations. These choices are recommended for future simulations and the numerical stability analysis in future work.

7.7 Convergence

The numerical convergence of the solution within the coupled, multiphysics simulation is necessary to gauge its progress and finality. That is, without the tracking of solution convergence, it would never be known whether the simulation has finished. This trait is not typically reported along with results from previous simulations, and thus is difficult to gauge an appropriate or similar tolerance level for the solution. However, residual tolerance levels may be approximated and set according to visual observation of changes to the solution across iterations, and even inspection of the relative convergence rates themselves. These limits are typically chosen to correspond to levels of non-changing distributions or plots and range from 10^{-8} to 10^{-1} .

The convergence rate of the numerical solution depends on many factors within the simulation, and is often different between solution variables. This is evident from the error plots given in, for example Fig. 6.98. The smooth convergence of certain solution variables, such as the atomic hydrogen mole fraction and gas temperature, is attributed to the dominance of the diffusion and conduction fluxes over their source terms, respectively. On the other hand, the numerical residuals associated with the H_3^+ ion and the electron temperature appear to plateau after several hundred complete iteration cycles. This is expected, as the electron temperature is used in many physical parameter calculations, the set of which result in a nonlinear dependence on this variable.

The solution convergence depends primarily on the solution procedure associated with the plasma module update scheme. For the SOR scheme employed in the present simulation, the choice of inner and outer iteration limits is most important. In order to analyze these choices of iteration limits, the same reactor configuration and operating conditions are applied to the MSU MPACVD Reactor B configuration. Maintaining consistency with previous results, the operating pressure was set to 180 Torr with 2.2 kW of total absorbed power. Various combinations of iteration limits were chosen representing likely choices for these values are presented in Table 7.7 with resulting total residual error plot in Fig. 7.6.

The total summed plasma matrix equation residuals shown in Fig. 7.6 exhibit very different behavior from one another. Most importantly, the only combination of iteration limits that results in the actual convergence of the simulation toward a single solution is that corresponding to the smallest numbers of five inner and outer iterations. As a result, the total

Table 7.1: Maximum iteration limits imposed in plasma module solution to demonstrate convergence.

No.	Inner	Outer
1	5	5
2	10	5
3	20	5
4	10	10



Figure 7.6: Total residual in plasma matrix equations for differing allowed maximum iteration limits during Gauss-Seidel update.

plasma matrix equation residual in this case begins at roughly 1% and approaches 0.01%. On the other hand, the remaining combination of iteration limits correspond to divergent solutions, as interpreted by their seemingly stochastic behavior indicating no convergence. This interpretation is confirmed after observing the resultant plasma quantity data with either discontinuous or unreasonable solutions.

These data in Fig. 7.6 confirm the necessity to update the plasma physical quantities often and limit the allowed convergence of the related solution. Although these particular iteration limits are not necessarily required in all cases, at these higher pressures and with zero initial conditions, they appear sufficient and are recommended for future use. The convergence of the numerical solution is also heavily dependent on the initial conditions and choice of initial solution. This initial solution can either take on the form of an applied previous solution at slightly different operating conditions, or a *cold* or *zero* condition start. In the latter case, only the electrical conductivity profile is supplied to the electromagnetics solution module, with all related plasma solution variables remaining close to their lower limits. As a result, all non-molecular hydrogen mole fractions are set to their lower limits of 10^{-14} and the gas flow is set to zero everywhere outside the in- and outflow regions. The gas temperature resembles a parabolic function across the entire solution domain with a value of 1200 K at the substrate top surface and 600 K everywhere else. Likewise, the electron temperature is simply set to five times the gas temperature at every sample location. This choice of initial temperature distributions ensures solutions ensures temperature gradients which are important to future plasma updates. These initial *cold* temperature distributions are provided in Fig. 7.7.

This choice of electron temperature being five times that of the gas temperature is an approximation to the typical relationship between these two quantities over a wide range of operating conditions. The solution itself is an approximation to the temperature solution in the absence of any foreknowledge of the final solution. In this way, the *cold* initial solutions are used in the case of an unknown final solution distribution arising from the absence of a previous solution. This may be due to either changes in the physical reactor configuration, or to the mesh resolution of the solution domain. The numerical solution convergence rates associated with these two initial conditions are drastically different as shown in the total plasma residual data given in Fig. 7.8.

As can be seen from Fig. 7.8, the application of a previous solution at slightly different operating conditions to the initial solution of the present simulation results in a lower overall residual limit. This also leads to a much faster convergence rate at the onset of the solution procedure as seen in decrease of the residual in the first roughly 500 iterations. On the other hand, the choice of a *cold* initial solution results in a solution with an increasing plasma







Figure 7.7: Initial (a) electron and (b) gas temperature solutions during *cold* start conditions for plasma solution module. Units are given in K.



Figure 7.8: Total residual in plasma matrix equations for differing initial solutions provided to the plasma fluid module.

matrix equation residual over this same time, which only then stabilizes and approaches its residual limit. From Fig. 7.8, it is clear the application of a similar, previous solution as the choice of initial plasma solution is preferable over a *cold* start when available. However, even in the case of this cold start, convergence to a reasonable residual limit is achievable with the valid choice of iteration limits.

Finally, the choice of mesh resolution, or grid spacing, is addressed. The mesh resolution of any spatially sampled numerical simulation is important to the accuracy and numerical efficiency of the particular model. This is equally important in the present MPACVD simulation as discussed below. In order to highlight the affect mesh spacing has on the overall solution accuracy and numerical efficiency, the same reactor geometry configuration and physical operating conditions were supplied to simulations of varying mesh resolution within the plasma region. These grid spacings were defined as the width between opposite facing edges within each element, and ranged from approximately 0.5 mm to 1.2 mm. Four different grid spacings were used, and are calculated in terms of the electromagnetic free space wavelength as $\lambda_0/100$, $\lambda_0/150$, $\lambda_0/200$, and $\lambda_0/250$, corresponding to approximately 1.2 mm to 0.5 mm, respectively. These calculations assume the standard MSU MPACVD microwave excitation frequency of 2.45 GHz and are provided in the remaining chapter figures.

Little difference is observed between the electromagnetic field intensity solutions throughout the MPACVD reactor cavity as shown in Fig. 7.9. This is expected, as the mesh resolution outside the plasma region remained fixed at $\Delta x = \lambda_0/40$, while the change in electrical conductivity was not significant. As a result, the electromagnetic fields were captured sufficiently at the current grid spacing.

In contrast to the electric field intensities shown in Fig. 7.9, the absorbed power densities presented in Fig. 7.10 and Fig. 7.11 exhibit significant changes in both maximum values and overall distributions. For example, the maximum absorbed power density increases more than two fold when decreasing the mesh spacing from $1.2 \ mm$ to $0.5 \ mm$. This significant increase confirms the region of maximum absorbed power is very small and resides close to the substrate surface. Thus, a fine mesh spacing must be employed in order to accurately capture the power absorption profile close to the substrate. At the same time, the absorbed power distribution. As a result, the total absorbed power profile is shifted more toward the substrate, suggesting the unstable plasma and reflected power conditions are not as significant as indicated at the lower mesh resolution. The major observation associated with these results suggest a mesh spacing of *less than 0.5 mm* is required in order to accurately resolve the absorbed power density profile at higher pressures, perhaps approaching 250 μ m.

The atomic hydrogen mole fraction solutions presented in Fig. 7.12 and Fig. 7.13 suggest a mesh spacing of 0.5 mm is significant in capturing its physical solution. This is indicated by the decrease in maximum atomic hydrogen mole fraction solution at the smallest mesh spacing from its previous solution. Moreover, the fact that these solutions do not change significantly in shape or position also confirm a sufficient grid spacing. Similar results were also observed for the gas temperature solution.

Due to its close relationship with the absorbed power density profile, the electron mole



Figure 7.9: Plots of electric field intensities for (a) radial component at coarse grid spacing, (b) radial component at fine grid spacing, (c) vertical component at coarse grid spacing, and (d) vertical component at find grid spacing throughout the MSU MPACVD Reactor B at 180 Torr and 2.2 kW. All units are given in V/m.





Figure 7.10: Plots of absorbed power density in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 1.2 and (b) 0.8 mm. Units are given in W/m^3 .





Figure 7.11: Plots of absorbed power density in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 0.6 and (b) 0.5 mm. Units are given in W/m^3 .





Figure 7.12: Plots of atomic hydrogen mole fraction in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 1.2 and (b) 0.8 mm.



Figure 7.13: Plots of atomic hydrogen mole fraction in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 0.6 and (b) 0.5 mm.

(b)

0.000 0.020 0.040 0.060 r (m) -2.801e-13

0.02

0.00 +







Figure 7.14: Plots of electron mole fraction in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 1.2 and (b) 0.8 mm.






Figure 7.15: Plots of electron mole fraction in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 0.6 and (b) 0.5 mm.

fraction solutions given in Fig. 7.14 and Fig. 7.15 exhibit similarly large differences in both profiles and maximum values. The discontinuous solution at the lowest mesh resolution is quickly replaced by continuous solutions that steadily increase in maximum electron mole fraction. This suggests a grid spacing of less than approximately 1 mm is necessary in capturing a continuous electron mole fraction solution at the given operating conditions. Similar results to the electron mole fraction solutions were also observed in the electron number density solutions.

Like the electron mole fraction solutions, the electron temperature solutions provided in Fig. 7.16 and Fig. 7.17 move from a discontinuous solution at the largest mesh spacing toward continuous distributions as this numerical sampling rate is increased. Moreover, the maximum electron temperature also steadily increases. Finally, the electron temperature becomes more concentrated and elevated at the substrate surface as the mesh resolution is increased. This corresponds to the increased mesh resolution required to accurately capture the absorbed power density profile discussed in earlier paragraphs. Thus, the microwave power is more strongly absorbed and localized about the substrate top surface at higher pressures. This is likely an important indicator for the increased radical production and thus deposition rate at the substrate surface at higher pressures. The electron temperature solution is still changing significantly between the 0.5 and 0.6 mm solutions, thus suggesting a mesh resolution of at least 0.5 mm is required to accurately capture the electron temperature solution at higher pressures.

Finally, the effect of mesh resolution on the overall convergence rate of the plasma fluid module solution can be quantified through the related matrix equation residuals as given in Fig. 7.18.

The total plasma fluid module transport solution matrix residuals observed in Fig. 7.18 confirm better convergence as the mesh resolution is increased. This is expected, as smaller changes in the overall solution variable distributions are achieved with this increasing mesh resolution. This leads to a smaller matrix equation residual error between successive update



(a)



Figure 7.16: Plots of electron temperature in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 1.2 and (b) 0.8 mm. Units are given in K.





Figure 7.17: Plots of electron temperature in the plasma region of MSU MPACVD Reactor B at 180 Torr and 2.2 kW for mesh spacings of approximately (a) 0.6 and (b) 0.5 mm. Units are given in K.



Figure 7.18: Total plasma fluid module transport equation matrix residuals for four mesh resolutions corresponding to the MSU MPACVD Reactor B configuration at 180 Torr and 2.2 kW.

schemes, and thus better final convergence.

This numerical error or uncertainty can be quantified in the overall solution as well. That is, the final total residual computed between all iterative matrix equation solutions may be applied to the physical variable distributions. As a result, uncertainties may be associated with these values, with particular interest in their maximum values. For example, since the electron temperature typically comprises the bulk of the residual error in the solution of the plasma transport equations, its numerical uncertainty is expected to be the largest. This may be calculated from the minimum total electron temperature residual given at the most coarse grid spacing in Fig. 7.18. With a minimum residual of approximately 30% over 3600 total samples, this results in a estimated numerical uncertainty of roughly 0.0083%. This translates to an expected accuracy to the sixth decimal place.

However, the electron temperature rarely converges to the sixth decimal place. Instead, it will often oscillate about mean values in the fourth or even third decimal place. This numerical uncertainty and instability is attributed to the solution procedure required by the stiffness of the overall set of governing equations. The total numerical uncertainty associated with specifically the electron temperature, and thus the maximum uncertainty applied to the overall simulation, is thusly estimated at roughly 0.1% to 1%. This estimation is based upon numerical observation and experience with simulation results, and the resulting data plots.

It should be noted that a trade off of this lower convergence limit achieved with increasing mesh resolution also requires significantly greater simulation run time as indicated by Fig. 7.19.



Figure 7.19: Total simulation run times (in seconds) for four mesh resolutions corresponding to the MSU MPACVD Reactor B configuration at 180 Torr and 2.2 kW.

Given the results of Fig. 7.19, the choice of mesh resolution clearly has a significant impact on the numerical efficiency of the complete simulation. That is, although roughly an order of magnitude better total residual is achieved when decreasing the mesh spacing from 1.2 to 0.5 mm, the effective run time increases more than six fold. Moreover, the relationship between grid spacing and run time scales worse than linear, meaning a linear decrease in mesh spacing results in an exponential increase in run time. As a result, a sufficient balance between accuracy and run time must be achieved.

Combining these observations, a mesh resolution of $0.5 \ mm$ or less is suggested within the plasma region in order to accurately simulate hydrogen-based microwave discharges within MPACVD reactors at moderate pressures. Similar mesh spacings are typically used in similar moderate pressure simulations, and may contain even smaller grid spacings in the substrate region [34]. Thus, such grid spacings are recommended for use at these higher pressure operating conditions as well.

CHAPTER 8

SUMMARY

This work details the theory behind, solution of, and results produced from a multiphysics numerical simulation of hydrogen plasmas in MPACVD systems at moderate pressures. The simulation is composed of three primary physics modules which are coupled together to arrive at a single, multiphysics solution. These modules simulate the microwave energy propagation and absorption within the MPACVD reactor; the chemical, kinetic, and temperature behavior and properties of the hydrogen plasma; and the temperature distribution within the internal substrate structure. The electromagnetic fields are simulated within the MPACVD reactor using a finite-difference frequency domain (FDFD) formulation. The microwave power density is extracted and supplied to the plasma fluid module where it is used in the electron and total energy transport equations. The mass and momentum transport equations are also solved within the plasma fluid module via a Gauss-Seidel Successive Over-Relaxation scheme. The energy flux to the MPACVD reactor substrate is extracted from the plasma fluid module and passed to the substrate temperature module. The steady heat equation is solved within the substrate structure and coupled back to the plasma fluid module by forcing the gas temperature at the correct boundary. Finally, the complex electrical conductivity of the plasma is inserted into the electromagnetics module and used to recalculate the electromagnetic fields. This iterative solution process is strongly under-relaxed and continues until a specified tolerance in the overall system residual is reached.

This multiphysics MPACVD plasma model improves upon previous lower pressure models by including both the average gas flow and substrate temperature in the coupled solution. The incorporation of the average gas flow via the momentum transport equation update offers a more accurate solution at higher pressures where convective transport has been hypothesized to affect the plasma properties. The inclusion of the substrate temperature results in more accurate fluxes and capturing of the critical plasma behavior in the region immediately surrounding the substrate surface. On top of these new physical processes, a more efficient electromagnetic solution method was developed and included, significantly improving the numerical run time of the overall simulation. Finally, the simulation framework and nomenclature were carefully chosen and organized in an effort to make it easier to model a wider range of MPACVD reactor configurations, operating conditions, and physical processes.

Many insights into the behavior and properties related to hydrogen plasmas in MPACVD reactors at moderate pressure operating conditions were achieved. Most notable were the effective role of convective forces within the plasma at higher operating pressures, and the influence of the substrate temperature on fluxes at the deposition surface. The average gas flow throughout the plasma region at typical operating conditions within MPACVD reactors remains quite low, never rising above 15 cm/s at any point in the simulations. As a result, the related forces due to the gas flow acting upon the plasma remain too small to significantly influence its properties or location. This was evident regardless of operating conditions and reactor configuration.

The substrate temperature varies significantly across this structure, and is greatly affected by both the plasma properties and its internal material makeup. Simulation results suggest the heat flux to the substrate due to gas temperature gradient in the plasma dominates over the energy flux due to hydrogen collisions and recombination. These flux contributions are themselves significantly affected by the plasma properties in the immediate vicinity of the substrate. As a result, the substrate vertical position and even reactor configuration also significantly impact the steady substrate temperature distribution. Changes to the substrate position within the reactor of as little as 5 mm can alter the resulting substrate temperature by as much as 200 K. A pseudo-gas layer was inserted and its material properties adjusted in order to approximate imperfect heat conduction across substrate materials and match substrate temperature experimental data [5]. The diamond deposition rate may be estimated from the hydrogen flux to the substrate surface, but is left for future implementations of the simulation.

The coupled, multiphysics simulation of MPACVD systems and their hydrogen plasmas presented and discussed in this work is suggested for use in the future design and prediction of MPACVD reactors. It is the first known simulation that incorporates numerical solutions of the electromagnetic fields, plasma behavior, gas flow, and substrate temperature within MPACVD systems at moderate pressures into a single, coupled, multiphysical manner. As such, it is expected to be more accurate than previous multiphysics simulations including only some of these physical processes at lower pressures [16, 34, 35, 64, 76]. The code structure also makes it easy to analyze and predict the behavior of a wide range of MPACVD reactors at various operating conditions, and including numerous physical processes. Thus, the present simulation is recommended for the future prediction of, and insight into, the behavior of hydrogen plasmas in MPACVD systems.

8.1 Future work

Further improvements of the presented simulation are recommended in several areas as described in the paragraphs below. The majority of these improvements add or ensure numerical accuracy, or capture further physical processes within the MPACVD system.

8.1.1 Further physics modules

The incorporation of more physics modules would ensure a more accurate overall simulation while also providing further insight into the behavior and properties of MPACVD system plasmas. Some of these described below have been included in other MPACVD or separate simulations.

The decision to exclude hydrocarbon species in the present simulation is due in part to the resulting simplicity related to the reduced number of species and chemical reactions to track. Their inclusion is not uncommon in similar simulations and results in the capture of many more important chemical reactions [33, 34, 42, 64, 76]. Thus, the inclusion of hydrocarbon species and their related chemical reactions is recommended in future versions of the multiphysics simulation.

Another suggested improvement on the present simulation is the explicit inclusion of a plasma sheath model. This plasma sheath is currently approximated through the numerical boundary conditions and surface interaction rates. However, a separate model for this behavior would undoubtedly result in more accurate fluxes at the substrate surface, and perhaps the simulation as a whole. Due to its extremely narrow interaction zone at the plasma domain boundaries, a one-dimensional model is recommended.

Finally, a diamond deposition model is recommended for inclusion in future versions of the simulation. Plasma discharges within experimental MPACVD systems are currently used as more diagnostic tools for estimating the deposition rates associated with these systems. The development of a diamond deposition model would instead provide a direct prediction of the deposition rate prior to the experiment. It would likely remain a one-dimensional model, and could take on the form of previously developed models [87].

The above mentioned and briefly discussed physical modules are by no means the only physical processes that could be added to it to improve its accuracy and the capturing of more physical phenomena within MPACVD systems. Instead, these are recommended as the next foreseeable steps in future implementations of the present simulation.

Several improvements are also recommended with regards to the numerical solution scheme. Moving to more advanced relaxation coefficient update schemes in the plasma transport equations could improve the overall numerical efficiency., A new plasma transport equations solution method could also improve the numerical run time. Similarly, the parallelization of the numerical code would significantly improve the numerical efficiency and run time if parallel computer architectures are available. Parallelization of the code could be implemented in several areas, including the sparse solver architecture and method, the SOR routine over solution variables within the plasma fluid module, and the updating of physical constants and rate coefficients also in the plasma fluid module. Thus, several opportunities for this parallelization exist, which suggests the simulation may be capable of running much faster.

8.2 Recommendations for experiments

As a final remark, several recommendations are made for the gathering of experimental data. Experimental data served as the primary method for validating the present simulation. As such, much of this experimental data was only available at lower pressures and for several specific physical variables including substrate temperature, electron density, and gas temperature. However, important physical values including average gas speeds and diffusion coefficients were unavailable. Moreover, all of these variables except substrate temperature were unavailable at pressures exceeding 200 Torr. Thus, it is recommended that future experiments measure these data within the higher pressure regime to assist in the validation of future simulations.

APPENDICES

Appendix A: Collision Integrals

The calculation of the collision integral associated with the collision of species and various chemical reactions is vital to the accuracy of the self-consistent simulation. That is because this data is used to not only calculate the total effective mass diffusion coefficients, but also the thermal conductivities associated with each species and mode. The collision integrals must also be calculated in an efficient manner, as they are updated along with the plasma physical constants. To this end, they are often approximated by logarithmic fits to experimental data. The data associated with these fits is provided in the following section. Direct comparisons with experimental data are also provided where available.

Coefficients

The collision integrals in the present simulation take on the form

$$\Omega_{jk}^{(ii)} = T^{C_1} \exp\left(C^{(ii,N_p,j,k)}\right)$$
(1a)

$$C_1 = \sum_{i=1}^{N_p} C_{ii,i,j,k} \left[\ln \left(T \right) \right]^{N_p - i - 1}$$
(1b)

where the indices j and k represent the two species involved in the collision, ii is denotes the collision integral of either the first or second kind, T is the temperature associated with the collision, N_p is the number of coefficients associated with the numerical fit, and C is a numerical fit coefficient array. This constant is provided below in Table A.1.

Species 1	Species 2	Type	<i>C</i> ₁	<i>C</i> ₂	<i>C</i> ₃	<i>C</i> ₄
1	1	1	0.0	-5.0949e-2	0.47409	0.80454
		2	0.0	-5.889e-2	0.64142	0.18926
1	2	1	0.0	-3.3403e-2	0.13563	2.0844
		2	0.0	-3.1267e-2	0.12675	2.2555
1	3	1	0.0	-3.3403e-2	0.13563	2.0844
		2	0.0	-3.1267e-2	0.12675	2.2555
1	4	1	0.0	-3.3403e-2	0.13563	2.0844
		2	0.0	-3.1267e-2	0.12675	2.2555
1	5	1	0.0	0.0	-0.4	5.6096
		2	0.0	0.0	-0.4	5.6313
1	6	1	0.0	0.0	-0.4	5.6096
		2	0.0	0.0	-0.4	5.6313
1	7	1	0.0	0.0	-0.4	5.6096
		2	0.0	0.0	-0.4	5.6313
1	8	1	0.0	0.0	-0.4	5.6096
		2	0.0	0.0	-0.4	5.6313
1	9	1	-3.4122e-2	0.79562	-5.9754	15.8856
		2	-3.4122e-2	0.79562	-5.9754	15.8856
2	2	1	0.0	5.8478e-3	-0.42247	4.2854
		2	0.0	-8.1062e-3	-0.20755	3.6016
2	3	1	0.0	5.8478e-3	-0.42247	4.2854
		2	0.0	-8.1062e-3	-0.20755	3.6016
2	4	1	0.0	5.8478e-3	-0.42247	4.2854
		2	0.0	-8.1062e-3	-0.20755	3.6016

Table A.1: Collision integral polynomial fit coefficients.

Species 1	Species 2	Type	<i>C</i> ₁	C_2	C ₃	C_4
2	5	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
2	6	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
2	7	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
2	8	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
2	9	1	1.7253e-2	-0.47276	3.9085	-7.6063
		2	1.0911e-2	-0.32361	2.7619	-4.8733
3	3	1	0.0	5.8478e-3	-0.42247	4.2854
		2	0.0	-8.1062e-3	-0.20755	3.6016
3	4	1	0.0	5.8478e-3	-0.42247	4.2854
		2	0.0	-8.1062e-3	-0.20755	3.6016
3	5	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
3	6	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
3	7	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
3	8	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
3	9	1	1.7253e-2	-0.47276	3.9085	-7.6063
		2	1.0911e-2	-0.32361	2.7619	-4.8733
4	4	1	0.0	5.8478e-3	-0.42247	4.2854

Table A.1 (contd)

Species 1	Species 2	Type	C_1	C_2	C_3	C_4
		2	0.0	-8.1062e-3	-0.20755	3.6016
4	5	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
4	6	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
4	7	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
4	8	1	-7.372e-6	5.9999e-4	-2.1169e-2	3.4623
		2	0.0	0.0	-0.4	5.6313
4	9	1	1.7253e-2	-0.47276	3.9085	-7.6063
		2	1.0911e-2	-0.32361	2.7619	-4.8733
5	5	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
5	6	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
5	7	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
5	8	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
5	9	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
6	6	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
6	7	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154

Table A.1 (contd)

Species 1	Species 2	Type	<i>C</i> ₁	<i>C</i> ₂	<i>C</i> ₃	C_4
6	8	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
6	9	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
7	7	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
7	8	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
7	9	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
8	8	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
8	9	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.2154
9	9	1	0.0	0.0	-2.0	22.6789
		2	0.0	0.0	-2.0	23.1613

Table A.1 (contd)

Validation

Since these data provided in Table A.1 only represent a numerical fit to experimental data, some differences between these two data sets are expected. For reference, the calculated collision integrals based upon the above data for several interactions of hydrogen-based species are plotted against their corresponding experimental data in Fig. A.1 through Fig. A.11. The experimental data were extracted from [88].



Figure A.1: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the H - H+ interaction.



Figure A.2: Experimental data and corresponding numerical approximation for the collision integral of type 2 in the H - H+ interaction.



Figure A.3: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the H - e interaction.



Figure A.4: Experimental data and corresponding numerical approximation for the collision integral of type 2 in the H - e interaction.



Figure A.5: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the $H_2 - e$ interaction.



Figure A.6: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the H_2 self interaction.



Figure A.7: Experimental data and corresponding numerical approximation for the collision integral of type 2 in the H_2 self interaction.



Figure A.8: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the H self interaction.



Figure A.9: Experimental data and corresponding numerical approximation for the collision integral of type 2 in the H self interaction.



Figure A.10: Experimental data and corresponding numerical approximation for the collision integral of type 1 in the $H - H_2$ interaction.



Figure A.11: Experimental data and corresponding numerical approximation for the collision integral of type 2 in the $H - H_2$ interaction.

As can be seen from this series of data presented in Fig. A.1 through Fig. A.11, the approximated logarithmic to the experimental data is sufficient for most interactions. An exception is the collision integral of the first kind for the H - H+ interaction, which is significantly inaccurate for a majority of given temperatures. However, this interaction is not as significant as many of the others included in the simulation, and thus represents an acceptable fit.

Appendix B: List of Chemical Reactions

The list of chemical reactions used in the simulation are provided, with all falling into one of two categories. The first includes those whose rates follow the Arrhenius equation form, while the second is composed of those reactions which do not follow the Arrhenius equation. In order to accurately simulate the chemical reaction rates of the second category, an exponential polynomial fit is applied. The various coefficients corresponding to the chemical reaction rate calculations for each category are listed below in Table B.1 and Table B.2.

The recombination of chemical species at material surfaces are governed by seven surface reactions listed in Table B.3. These are given in qualitative form, with only species, stoichiometric, and recombination coefficient data given.

Reaction	$k_0 \ (m^3/s \ mol)$	η	$T_a(K)$	T_g, T_e
$\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H} + \mathrm{e^-}$	3.63×10^{25}	-4.0	0.0	T_e
$\rm H^+ + e^- \rightarrow \rm H$	1.46×10^{8}	-0.699	0.0	T_e
${\rm H}_2 + 2{\rm H} \rightarrow 2{\rm H}_2$	1.0×10^{5}	-0.6	0.0	Tg
$\rm 3H \rightarrow \rm H_2 + \rm H$	3.2×10^{3}	0.0	0.0	T_g
$\mathrm{H} + \mathrm{H}_2^+ \to \mathrm{H}_2 + \mathrm{H}^+$	3.85×10^8	0.0	0.0	T_g
$\mathrm{H}_2 + \mathrm{H}_2^+ \rightarrow \mathrm{H} + \mathrm{H}_3^+$	1.27×10^9	0.0	0.0	Tg
$2H_2 \rightarrow H_2 + 2H$	8.61×10^{11}	-0.7	5.253×10^4	T_g
$\rm H_2 + \rm H \rightarrow 3 \rm H$	2.7×10^{10}	-0.1	5.253×10^4	T_g
$\rm H + \rm H^- \rightarrow 2\rm H + e^-$	4.5×10^{2}	1.5	6.98×10^2	T_g
$\mathrm{H} + \mathrm{H}^- \rightarrow \mathrm{H}_2 + \mathrm{e}^-$	1.43×10^9	-0.15	8.15×10^2	Tg
$\mathrm{H}_2 + \mathrm{H}^+ \to \mathrm{H} + \mathrm{H}_2^+$	1.94×10^{8}	0.0	2.1856×10^4	T_g
$\mathrm{H^{+} + H^{-} \rightarrow 2H}$	1.78×10^{11}	0.0	1.768×10^{3}	T_g
$\mathrm{H}_{2}^{+} + 2\mathrm{e}^{-} \rightarrow 2\mathrm{H} + \mathrm{e}^{-}$	3.17×10^9	-4.5	0.0	T_e
$\mathrm{H}_{3}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} + \mathrm{H} + \mathrm{e}^{-}$	3.17×10^9	-4.5	0.0	T_g
$^{\circ}_{2\mathrm{H}_{2}} + \mathrm{H}^{+} \rightarrow \mathrm{H}_{2} + \mathrm{H}_{3}^{+}$	1.95×10^{8}	-4.5	0.0	T_g
$\mathrm{H}_2^+ + \mathrm{H}^- \to \mathrm{H}_2 + \mathrm{H}^\circ$	2.08×10^{12}	-0.5	0.0	T_g
$\tilde{H}_3^+ + H^- \rightarrow 2H_2$	2.08×10^{12}	-0.5	0.0	T_q
$H_2 + H(n=2) \rightarrow H_3^+ + e^-$	1.675×10^{7}	0.5	0.0	T_g
$\mathrm{H}_2 + \mathrm{H(n=3)} \rightarrow \mathrm{H}_3^{+} + \mathrm{e}^{-}$	1.675×10^{7}	0.5	0.0	T_g
$H(n=3) \rightarrow H(n=2) + \gamma$	6.58×10^7	0.0	0.0	T_g

Table B.1: List of Arrhenius chemical reactions.

Reaction	C_1	C_2	C_3	C_4	C_5	C ₆
$\mathrm{H}_2 + \mathrm{e}^- \to \mathrm{H}_2^+ + 2\mathrm{e}^-$	-2.37e3	3.95e2	-1.64e1	1.88e6	-6.78e9	6.74 e12
$\mathrm{H} + \mathrm{e}^{-} \to \mathrm{H}^{\mp} + 2\mathrm{e}^{-}$	-1.84e3	3.04e2	-1.25e1	1.54e6	-5.76e9	5.78e12
$\rm H_2 + e^- \rightarrow 2H + e^-$	-1.15e3	1.91e2	-7.77	1.03e6	-4.08e9	4.22e12
$\mathrm{H}_3^+ + \mathrm{e}^- \to 3\mathrm{H}$	-4.24e1	1.25e1	-6.1	2.58e4	-4.26e7	3.15e10
$\mathrm{H}_3^+ + \mathrm{e}^- \to \mathrm{H}_2 + \mathrm{H}$	3.30e1	-1.25	3.06e-2	-1.53e4	$4.03 e^{-7}$	-3.50e10
$\mathrm{H}_{3}^{+} + \mathrm{e}^{-} \rightarrow 2\mathrm{H} + \mathrm{H}^{+} + \mathrm{e}^{-}$	-2.42e3	4.09e2	-1.72e1	1.81e6	-6.28e9	6.20 e12
$H_2 + e^- \rightarrow H + H^-$	-1.70e2	3.32e1	-1.48	1.29e5	-5.07e8	5.04e12
$\mathrm{H}_{2}^{+} + \mathrm{e}^{-} \to \mathrm{H} + \mathrm{H}^{+} + \mathrm{e}^{-}$	-2.93	2.25	2.13e-2	8.02e4	-5.74e8	6.44e11
$H_2^+ + e^- \rightarrow 2H$	-2.20	4.61	-0.214	6.91e3	-9.08e6	$5.97\mathrm{e}9$
$\mathrm{H}^- + \mathrm{e}^- \to \mathrm{H} + 2\mathrm{e}^-$	$3.13\mathrm{e}1$	-0.963	4.70e-2	-5.05e4	1.25e8	-1.25e11
$\mathrm{H}_2 + \mathrm{e}^- \to \mathrm{H} + \mathrm{H}(\mathrm{n}{=}2) + \mathrm{e}^-$	-2.13e3	3.65e2	-1.56e1	1.28e6	-3.16e9	-2.41e12
$\mathrm{H}_2 + \mathrm{e}^- \rightarrow \mathrm{H} + \mathrm{H}(\mathrm{n=3}) + \mathrm{e}^-$	-2.57e3	4.43e2	-1.90e1	1.54e6	-3.81e9	-2.23e12
$H + e^- \rightarrow H(n=2) + e^-$	-1.40e3	2.44e2	-1.05e1	8.09e5	-1.78e9	-2.87e12
$H + e^- \rightarrow H(n=3) + e^-$	-1.60e3	2.77e2	-1.19e1	9.50e5	-2.21e9	-2.71e12

Table B.2: List of non-Arrhenius chemical reactions. All reactions depend on the electron temperature, T_e .

Table B.3: List of surface chemical reactions.

Surface Reaction	β
$2H \rightarrow H_2$	0.1
$H(n=2) \rightarrow H$	1.0
$H(n=3) \rightarrow H$	1.0
$\mathrm{H^+} \to \mathrm{H}$	1.0
$\mathrm{H}_2^+ \to \mathrm{H}_2$	1.0
$\mathrm{H}_3^+ \xrightarrow{-} \mathrm{H} + \mathrm{H}_2$	1.0
${}^{\circ}\mathrm{H}^{-} \to \mathrm{H}$	1.0

Appendix C: Physical Constants Calculations

The derivations of the numerous physical constants present in Eq. (3.18), Eq. (3.27), Eq. (3.33), and Eq. (3.39) and related terms are derived in the following paragraphs. Some of these constants are based upon empirical observations and data, while others are derived from quantum mechanical or classical kinetic theories. These are available with further details and citations in other works [63, 81].

Collision Integral

The interactions between the various chemical species within the plasma gas mixture are important to the plasma behavior and characteristics. In fact, these inter-atomic forces and interactions are the primary source of new species production and internal energy transfer within the plasma. This suggests the accurate capture of these interactions is important to the overall accuracy of the numerical model. Not surprisingly, collisions and their related physical quantities appear in several of the physical constants listed in the previously derived transport equations. Their characteristics are well documented and have been developed over several decades of research [81,88]. The various forces and considerations required to accurately resolve these interactions at the molecular level mark the starting point for the derivation of said physical constants. The majority of these derivations are available in other works, and are summarized here for convenience [63, 81, 88]. Collisions between electrons, ions, and neutrals may be calculated by estimating the collision integral between each species. Consider two particles moving along trajectories in the absence of external forces. If their trajectories are close enough, they will both influence the position and velocity of the other, resulting in an altered ending trajectory. This crude example is often referred to as a binary system, due to only two particles being present. Many physical constants may be extrapolated and calculated from this simple interaction system. It is used as the basis for the following derivations, and is an estimation of the weighted average of the cross sectional area of the target mass experienced by the projectile in plasma particle interactions. It has been shown that these collision integrals may be used in combinations to represent transport coefficients [81]. These coefficients are only referenced here, with more detailed descriptions available elsewhere [81]. The collision integral may be calculated analytically by performing the following integrations [63]

$$\pi \bar{\Omega}_{ij}^{(k,l)} = 4\pi \frac{\int_0^\infty \int_0^\pi \exp\left(-\gamma^2\right) \gamma^{2l+3} \left(1 - \cos^k \chi\right) \sigma_{ij} \sin \chi d\chi d\gamma}{\int_0^\infty \int_0^\pi \exp\left(-\gamma^2\right) \gamma^{2l+3} \left(1 - \cos^k \chi\right) \sin \chi d\chi d\gamma}$$
(2)

where $\pi \bar{\Omega}_{ij}^{(k,l)}$ represents the collision integral with units of area, σ_{ij} is the collision cross section for the pair of interaction species, i and j, χ is the scattering angle between the two interacting particles, and γ is their reduced velocity as calculated [63]

$$\gamma = v \left[\frac{m_i m_j}{2 \left(m_i + m_j \right) k_b T} \right]^{1/2} \tag{3}$$

where v is the relative velocity of the projectile particle taken with respect to the target particle at rest. This notation of $\pi \overline{\Omega}_{ij}^{(k,l)}$ follows the later works by Yos and Lee [63, 88]. It also represents the same collision integral derived by Hirschfelder, *et al.*, where it is instead represented by simply Ω_{ij}^{kl} with no leading π symbol [81]. This explicit notation used here is meant to avoid the confusion over this representation which has appeared in previous simulations.

The integral calculation from Eq. (2) can be quite difficult to calculate and requires prior knowledge of numerous physical properties including initial relative velocity between species and their respective trajectories. With collision frequencies in MPACVD systems often within the GHz to THz range, calculating these integrals for every collision is not feasible. Instead, experimental observations are used to estimate these collisions in the plasma under certain physical conditions related to pressure, species temperature, and its chemical makeup. These collision approximations were observed, with their data tabulated and summarized, for the case of hydrogen ions and electron collisions by Yos [88]. In this sense, the basic collision integral data used in the calculation of numerous physical transport coefficients is taken from experimental measurements. Polynomial fits to these data have been tabulated and are used here to approximate these experimental collision integral data [16]. These polynomial fits take the form

$$\pi \bar{\Omega}_{sr}^{(\gamma)} = T_g^{\beta\gamma} \exp\left(\alpha_{4,\gamma}\right) \tag{4a}$$

$$\beta_{\gamma} = \sum_{i=1}^{3} \alpha_{i,\gamma} \log \left(T_g \right)^{3-i} \tag{4b}$$

where α_i are coefficients used to approximate the polynomial fit to the empirical collision integral data, and γ represents the data associated with, and collision integral of, either the first or second kind. The later notation assumes that the final collision state as denoted by k, l in Eq. (2) requires k = l. This polynomial fit is essentially a log-polynomial fit, as is seen in Eq. (4). The result is a set of relatively accurate and continuous collision integral functions spanning the entire expected temperature range and for all unique interactions.

The modified collision integrals may then be tabulated once the collision integral functions themselves are known. These are also associated with collisions of the first and second kind, as given in Eq. (5) [63]

$$\Delta_{sr}^{(1)}(T) = \frac{8}{3} \pi \bar{\Omega}_{sr}^{(1,1)} \sqrt{\frac{2m_s m_r}{\pi k_b T (m_s + m_r)}}$$
(5a)

$$\Delta_{sr}^{(2)}(T) = \frac{16}{5} \pi \bar{\Omega}_{sr}^{(2,2)} \sqrt{\frac{2m_s m_r}{\pi k_b T (m_s + m_r)}}$$
(5b)

having units of $m \ s$.

Binary Diffusion Coefficient

The diffusion of particles from regions of high particle concentrations to lower concentration is a well-known phenomenon governed by Fick's Law. Although simple in the case of a single gas, this process can become complex and difficult to mathematically represent in the case of multicomponent plasmas. In order to better understand this process, a binary system of two types of interacting particles is assumed. Here, the binary diffusion coefficient governing the rate of particle flux through an arbitrary plane may be calculated. It is expressed for the two species, s and r, and is based upon the modified collision integral derived the previous paragraph as given in [63]

$$D_{sr} = \frac{k_b T_g}{p \Delta_{sr}^{(1)}(T_g)} \tag{6}$$

where D_{sr} is the binary diffusion coefficient and $\Delta_{sr}^{(1)}(T_g)$ is the modified collision integral of the first kind in calculated in terms of the gas temperature. The units of the binary diffusion coefficient are m^2/s , which may be thought of as representing the rate of flux of a unitless parameter through a fixed area.

Mass Density Diffusion

At this point, the binary diffusion coefficient has been stated for any two-component system. However, it is not the term present in the transport equations, which must be calculated for a multicomponent plasma. Instead, the diffusion coefficient for individual species must be stated, as given in Eq. (7) [16,63]

$$D_{s} = \frac{c_{tot}M_{s}\left(1 - \frac{M_{s}x_{s}}{M}\right)}{\sum_{\substack{r=1\\r \neq s}}^{N_{s}} \frac{x_{r}}{D_{sr}}}$$
(7)

where c_{tot} is the total molar concentration of the plasma, M_s is the molar mass of species s, and M is the total molar mass of the plasma. The diffusion coefficient in Eq. (7) represents the diffusion flux of the volumetric mass density. It may be expressed in terms of the standard diffusion coefficient as

$$D_s = \rho_s D_{s,0} \tag{8}$$

where D_s is the mass diffusion coefficient for species *s* present in the transport equations previously derived, and $D_{s,0}$ is the standard diffusion coefficient representing the flux of a unitless quantity related to species *s*. This mass density diffusion is substituted here in order to take advantage of its otherwise mass density product calculation present during each of its uses in the scalar transport equations. That is, the species diffusion coefficient present in the transport equations in each case is multiplied by the species mass density. This is common in MPACVD simulations [16].

Ambipolar Diffusion

Due to the presence of oppositely charged species, the ambipolar diffusion coefficient must be introduced. As was outlined earlier, the behavior of charged particles is influenced in the presence of electromagnetic fields. This behavior can be calculated through the Lorentz force law given in Eq. (3.11), resulting in positively charged particles accelerating along the electric field lines, while negatively charged particles move in the opposite direction.

MPACVD plasmas are known to remain electrically neutral over distances greater than

the deBye length suggesting the ion and electron densities are equal, with $n_e = n_i$. While the electron diffusion velocity in the presence of an external electric field is much greater than that of the ions, this does not lead to drastic changes in overall charge distribution. Instead, a static electric field forms between the rapidly diffusing electrons and more slowly diffusing ions. This electrostatic field acts to slow the diffusion velocity of electrons, while accelerating the ions. The effective rate of diffusion for these charged species is thus altered, and becomes the ambipolar diffusion coefficient. A detailed derivation of this ambipolar diffusion coefficient is provided elsewhere and is restated here for convenience as [67]

$$D_a = D_s \left(1 + \frac{T_e}{T_g}\right)^{q_s} \tag{9}$$

It is clear from Eq. (9) that the modifying factor multiplying the volumetric mass density diffusion coefficient is always greater than two, since $T_e > T_g$ for MPACVD system plasmas. In the present system, $|q_s/q_0| = 1$, meaning only singly-charged ions are included. This leads to a modified ion diffusion velocity that is at least twice the original ion diffusion velocity simply due to the presence of the more quickly diffusing electrons. The above ambipolar mass diffusion coefficient replaces all instances of the mass density diffusion coefficient for ion species in the transport equations. The electron mass density diffusion coefficient is calculated using an analytic function dependent on empirical data for hydrogen plasmas [16].

Viscosity

The viscosity of a multicomponent gas mixture is derived elsewhere and stated here for convenience [63]. It is used as the scalar kinematic viscosity term in Eq. (3.27) and given by

$$\mu = \frac{m_e x_e}{\sum_{r=1}^{N_s} x_r \Delta_{er}^{(2)}(T_e)} + \sum_{\substack{s=1\\s \neq e^-}}^{N_s} \frac{m_s x_s}{x_e \Delta_{se}^{(2)}(T_e) + \sum_{\substack{r=1\\r \neq e^-}} x_r \Delta_{sr}^{(2)}(T_g)}$$
(10)

where μ is the viscosity of the plasma, and $\Delta_{sr}^{(2)}$ is the modified collision integral of the second kind between species s and r. Note the separate treatment of electrons in Eq. (10) as referenced from the e^- terms.

Thermal Conductivities

The thermal conductivity terms present in both Eq. (3.33) and Eq. (3.39) are important for calculating the rate of energy transfer between species and the cavity surroundings. That is, their presence is related to the heat flux throughout the plasma region and is important for the accurate capturing of physical processes. Likewise, these conductivities will become even more important during the numerical solution procedure, where they will be used in updating of temperatures via matrix inversion. Thus, their derivation is important to the accuracy of the electron and total energy transport equations.

Heat conduction within the plasma occurs through both collisional processes and the diffusion of reacting chemical species [63]. The latter is explicitly treated and already present in the energy transport equations in Eq. (3.33) and Eq. (3.39). Thermal conduction via collisional processes is included by treating the contribution of the three kinematic hydrogen energy modes (translational, rotational, and vibrational) and electrons. They are functions of the collisional processes resulting in the excitation and filling of the various modes. These expressions become [63]

$$\lambda_t = \frac{15}{4} k_b \sum_{s=1, s \neq e}^{N_s} \frac{x_s}{\sum_{r=1, r \neq e}^{N_s} a_{sr} x_r \Delta_{sr}^{(2)}(T_g)}$$
(11a)

$$\lambda_r = k_b \sum_{s=mol} \frac{x_s}{\sum_{r=1}^{N_s} x_r \Delta_{sr}^{(1)}(T_g)}$$
(11b)

$$\lambda_{v} = k_{b} \sum_{s=mol} \frac{x_{s}}{\sum_{r=1}^{N_{s}} x_{r} \Delta_{sr}^{(1)}(T_{g})}$$
(11c)

$$\lambda_e = \frac{15}{4} k_b \sum_{s=1}^{N_s} \frac{x_s}{\sum_{r=1}^{N_s} x_r \Delta_{er}^{(2)}(T_e)}$$
(11d)

where

$$a_{ST} = 1 + \frac{\left(1 - (M_S/M_T)\right)\left(0.45 - 2.54(M_S/M_T)\right)}{\left(1 + (M_S/M_T)\right)^2} \tag{11e}$$

and λ_t , λ_r , and λ_v represent the thermal conductivities of the molecular hydrogen translational, rotational, and vibrational modes, respectively, λ_e is the thermal conductivity of electrons, and s = mol denotes the summation over only molecular species. It is clear from Eq. (11) that the rotational and vibrational thermal conductivity coefficients are identical [63].

Finally, the translational and rotational thermal conductivity terms are often combined to form the translational-rotational thermal conductivity of the hydrogen species, λ_{tr} via

$$\lambda_{tr} = \lambda_t + \lambda_r \tag{12}$$

This term is used in the updating of the neutral and ion species temperature in the total energy transport equation from Eq. (3.39).

Enthalpy

Before any plasma species can react, there must be sufficient energy for activation, as well as the energy to produce the space for the new species, with the latter being a measure of enthalpy. The enthalpy calculation is based upon the difference in stoichiometric coefficients both prior to and following the chemical reaction, and is extrapolated by a fifth-order polynomial fit with respect to species temperature [63]

$$h_s = \sum_i h_s^{(0)} \left(\eta_1^{(i)} - \eta_2^{(i)} \right)$$
(13a)

$$h_s^{(0)} = \sum_{i=1}^5 \frac{\alpha_i}{iT^i}$$
(13b)

where η_1 and η_2 are stoichiometric coefficients representing the species present prior to and following the chemical reaction, α_i is the smoothing coefficient for each species, and T is the governing temperature depending on the reaction.

Chemical Reactions

The chemical reactions ongoing between species represent the source of mass production and consumption within the plasma. Their rates are important to many other physical processes, as mass and density of the various species significantly influence many other plasma properties. The majority of the reaction rates for hydrogen-based plasmas within the temperature ranges common in MPACVD reactors are well known. These specific reactions are tabulated elsewhere [16, 33].

Chemical reaction rates often take the form of the modified Arrhenius equation as given by [45]

$$k = AT^{\eta} e^{-E_a/RT} \tag{14}$$

where k is the chemical reaction rate, A is the pre-exponential factor (or frequency factor), T is the inherent plasma temperature, η is the Stoichiometric coefficient, R is the gas constant, and E_a is the activation energy of the chemical reaction. Many of the chemical reactions tabulated for MPACVD plasmas take this form. However, some chemical reactions do not follow the Arrhenius form from Eq. (14). In these particular cases, a hybrid logarithmicpolynomial fit to experimental data is employed [16, 45]

$$k = \exp\left(k_{r0}\right) \tag{15a}$$

$$k_{r0} = \sum_{i=1}^{3} \kappa_i \log^{i-1}(RT) + \sum_{i=4}^{6} \frac{\kappa_i}{(RT)^{i-3}}$$
(15b)
where κ_i are the chemical reaction empirical fit coefficients. These chemical reaction rates will be used in the following paragraphs to calculate the net rate of mass production and consumption for each chemical species.

Rate of Mass Production

The volumetric rate of mass production represents the net rate of change in the mass of each species, and is the source term observed on the right side of Eq. (3.18). This volumetric rate of mass production may be calculated based on the net rate of species production via chemical reactions, its mass, and the stoichiometric coefficients associated with its final reaction products. Its general form is given as [45]

$$W_{s} = M_{s} \left[\sum_{r=1}^{N_{r}} k_{r} \Pi_{q=1}^{N_{s}} c_{q}^{\eta_{rq}^{(1)}} \left(\eta_{sr}^{(2)} - \eta_{sr}^{(1)} \right) \right]$$
(16)

where N_r is the total number of chemical reactions included in the plasma simulation, c_q is the molar concentration of species q, and k_r is the reaction rate constant for reaction r. Once the chemical reaction rates are calculated from the above derived expressions and fits to empirical data, the rate production of species in Eq. (16) becomes available. This rate of mass production is tabulated for all chemical species contained in the plasma.

Energy Exchange Rates

The final group of terms from the plasma transport equations left to calculate are the various volumetric rates of energy exchange found in the two energy transport equations, Eq. (3.33) and Eq. (3.39). These include the exchange of energy between the various molecular modes, electrons, chemical reactions, and loss due to electromagnetic radiation. They have been derived elsewhere in detail, and are listed here for convenience [63].

Electron-Vibrational Energy Exchange

The electron-vibrational energy exchange rate represents the rate of energy passed from electrons to the molecular hydrogen vibration mode. Molecular hydrogen is a diatomic molecule with allowed vibrational modes predicted by the quantum oscillator model. This means the theoretical number of possible vibration modes is infinite. However, this number is essentially limited by the energy of the system. Thus, only the first fourteen modes are allowed here, as keeping with previous simulations [16]. This number is expected to completely capture all vibrational modes based upon the energies typically present in MPACVD plasmas.

Energy passing from electrons to the molecular hydrogen vibration modes may occur along one of two pathways [32]. One method includes energy transformation from electron kinetic energy to the hydrogen vibrational mode [32]

$$H_2(v) + e^- \to H_2(w) + e^- \tag{17}$$

where $H_2(v)$ and $H_2(w)$ represent the prior and final molecular hydrogen vibration modes, with a net gain of energy being assumed. This energy rate may be calculated in generic form via the Landau-Teller relaxation equation as [32, 63]

$$\frac{\partial e_v}{\partial t} = \frac{e_v^{(2)}(T_e) - e_v}{\tau_{ev}}$$
(18a)

$$\tau_{ev} = \left[n_e \left(1 - \exp\left(-\theta_v/T_e\right) \right)^2 \frac{1}{2} \int k_{0j} j^2 dj \right]^{-1}$$
(18b)

where e_v is the vibrational energy per unit mass, $e_v^{(2)}(T_e)$ is the equilibrium vibrational energy at the electron temperature, τ_{ev} is the relaxation time for the electron-vibration energy exchange process, θ_v is the characteristic temperature of vibration, and $k_{0j}(j)$ is the rate coefficient for the vibrational mode to transition from the ground to the j^{th} vibrational state [63]. The rate coefficient for the ground state vibrational model transition may be calculated

by integrating over the Maxwellian EEDF for each transition [45]. However, this rate coefficient and thus electron-vibration relaxation time would be prohibitively costly to calculate at each update step. Instead, a polynomial fit to the impacting electron temperature is used to numerically approximate this term, as given by

$$\tau_{ev} = \left[n_e \left(1 - \exp\left(-\frac{\theta_v}{T_e}\right) \right)^2 \frac{1}{2} \int k_{0j}(j)^2 dj \right]^{-1} \\ \approx \frac{1}{n_e} \sum_{i=1}^{N_{ev}} \alpha_i \left[\log\left(T_e\right) \right]^{i-1}$$
(19)

where α_i are the polynomial fit coefficients associated with each polynomial order. As a result, the final expression for the numerical calculation of the energy exchange rate between the electrons and the molecular hydrogen vibrational modes due to direct excitation becomes

$$Q_{ev}^{(1)} = \frac{\sum_{s=mol}^{c_s M_s} \left(e_{v,s}^{(2)} - e_{v,s}\right)}{\frac{1}{n_e} \sum_{i=1}^{N_{ev}} \alpha_i \left[\log\left(T_e\right)\right]^{i-1}}$$
(20)

where the denominator in Eq. (20) is substituted from Eq. (19).

Energy transfer from the electrons to the molecular hydrogen vibrational modes may also occur through excitation of hydrogen singlets, which then radiate and return to previous or lower vibrational modes. The rate coefficients of this energy transfer are calculated dependent on hydrogen cross sections and the transition probabilities [45]. This results in the following exchange rate equation [45]

$$Q_{ev}^{1v} = n_{H_2} R\theta_v \left[k_{ev}^B(T_e) S_B(T_v) + k_{ev}^C(T_e) S_C(T_v) \right]$$

$$\tag{21}$$

where Q_{ev}^{1v} is the volumetric energy exchange rate density of energy transfer from electrons to the hydrogen vibration modes via an intermediate energy state, θ_v is the characteristic vibration energy, k_{ev} are the rate coefficients for electron excitation of the hydrogen singlets, and S_B and S_C are dimensionless probability functions [45]. These S functions may be calculated assuming an anharmonic oscillator model, yielding analytic vibrational energy levels [45]. Higher order polynomial fits of experimental data are used to approximate these functions taking on the form

$$S_{B,C}(T_v) = \sum_{i=0}^{2} a_i T_v^i$$
(22)

where a_i represent polynomial fitting coefficients to experimental data, and are provided elsewhere [45]. The electron-vibrational rate constants, $k_{ev}^{B,C}$, are similarly calculated from curve fits of cross sectional data from Buckman and Phelps[89].

The resultant rate of energy lost by electrons through their excitation of singlet vibrational modes may be calculated as

$$Q_{ev}^{1e} = n_e n_{H_2} \left(k_{ev}^B \epsilon_B + k_{ev}^C \epsilon_C \right) \tag{23}$$

where ϵ_B and ϵ_C are the dimensionless energies levels of the vibrational modes associated with the hydrogen B and C states.

From these three modes of energy exchange between electrons and vibrational modes, the net rate of energy transfer from the electron to molecular hydrogen vibrational modes may be calculated through their summation via

$$Q_{ev} = Q_{ev}^{(1)} + Q_{ev}^{1v} - Q_{ev}^{1e}$$
(24)

where Q_{ev} is the net rate of energy exchange between electrons and hydrogen vibrational modes as seen in Eq. (3.33). The net rate of energy radiated by electrons may also be computed as simply the difference between Q_{ev}^{1v} and Q_{ev}^{1e} becoming

$$Q_{rad} = Q_{ev}^{1e} - Q_{ev}^{1v} \tag{25}$$

where Q_{rad} is the rate of electron energy loss due to radiative processes present in Eq. (3.39).

Translational/Rotational-Electron Energy Exchange

The energy transfer rate between electrons and the translational-rotational kinetic states of the heavy particles is derived by Hassouni, *et al.* elsewhere [45]. However, it is restated here for convenience as

$$Q_{et} = 3Rn_e \left(T_e - T_g\right) \sqrt{\frac{8RT_e}{\pi m_e}} \sum_{s \neq e^-} \sigma_{se} \frac{n_s n}{m_s^2}$$
(26)

where σ_{se} is the momentum transfer collision cross section, and n is the total gas density for all present species.

Translational/Rotational-Vibrational Energy Exchange

Due to the relatively high pressure of operation for most MPACVD systems, the rotational, translation, and vibrational modes are all assumed to be in thermal equilibrium. This suggests that the vibrational temperature is equivalent to the gas temperature. As such the energy exchange rate between the translational-rotational and vibrational modes in molecular hydrogen is nominally zero in most MPACVD systems. Thus, its derivation and final expression are neglected.

Electron-Chemical Energy Exchange

Electrons also exchange energy through the activation of chemical reactions and the resultant mass production. This general process is again often derived from empirical data, but can be expressed in general form following external works as [45]

$$Q_{ec} = \sum_{r=1}^{N_r} \eta_{re} v_r \epsilon_{act,r} \tag{27}$$

where η_{re} is the electron stoichiometric coefficient for reaction r, v_r is the reaction rate, and $\epsilon_{act,r}$ the chemical reaction activation energy. This activation energy is tabulated from empirical observations of the included chemical reactions. This concludes the derivation and statement of all transport coefficients.

Macroscopic Observables

One further necessary derivation step is to define the remaining macroscopic observable calculations. These macroscopic variables are often just as important as the macroscopic solution variables in their influence of the plasma properties. Moreover, their forms may vary depending on definition and source. As such, many of the important macroscopic plasma quantities not already derived are provided in detail in the following paragraphs.

Molar Mass and Concentration

The plasma molar mass is calculated as a summation of all mole fractions and molar mass products

$$M = \sum_{i=1}^{N_S} x_S M_S \tag{28}$$

while the total and species molar concentrations are calculated

$$c_{tot} = \frac{p}{R\left[T_g\left(1 - x_e\right) + T_e x_e\right]}$$
(29a)

$$c_s = x_s c_{tot} \tag{29b}$$

where the pressure, p, is the local pressure distribution as calculated during the momentum transport equation.

Number Densities

Since both the pressure distribution and temperatures are known, the species and total volumetric number densities may be calculated as

$$n_s = N_{av} c_{tot} x_s \tag{30a}$$

$$n = N_{av}c_{tot} \tag{30b}$$

where n is the total volumetric number density of the plasma.

Mass Densities

Finally, the species and total volumetric mass densities are calculated as

$$\rho_S = c_S M_S \tag{31a}$$

$$\rho = c_{tot} M \tag{31b}$$

where ρ is the total volumetric mass density of the plasma.

The governing transport equations, transport coefficients, and macroscopic observable calculations have all been derived. The transport equations were derived from the distribution function and Boltzmann equation. This set of expressions, coefficients, and calculations represents a closed set of equations that may be solved numerically to update the plasma properties and behavior.

Appendix D: Finite Difference Stencil for Momentum Transport Equation

The finite-difference (FD) numerical stencil representing the discretized form of the viscous flow update to the momentum transport equation as stated in Eq. (4.49) is now derived. This represents the first implicit update step in the Chorin projection method. An implicit update is required since the time rate of change in the momentum depends on the velocity itself. Moreover, the two vector velocity components similarly depend on not only their own values, but also those with orthogonal orientation. As such, the numerical stencil will include both radial and vertical velocity components using the standard whole and half integer indexing scheme.

To begin, the point form of this viscous force implicit projection step is again stated for convenience in Eq. (32)

$$v_{r}^{\prime\prime} = v_{r}^{\prime} - \frac{\delta t}{\rho} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \left[-\mu \left(2 \frac{\partial v_{r}}{\partial r} - \frac{2}{3} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r v_{r} \right) + \frac{\partial v_{z}}{\partial z} \right] \right) \right] \right) \right] + \frac{\delta t}{\rho} \left[\frac{\partial}{\partial z} \left(-\mu \left[\frac{\partial v_{r}}{\partial z} + \frac{\partial v_{z}}{\partial r} \right] \right) \right]$$
(32a)

$$v_{z}^{\prime\prime} = v_{z}^{\prime} - \frac{\delta t}{\rho} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \left[-\mu \left(\frac{\partial v_{r}}{\partial z} + \frac{\partial v_{z}}{\partial r} \right) \right] \right) \right] + \frac{\delta t}{\rho} \left(\frac{\partial}{\partial z} \left[-\mu \left(2 \frac{\partial v_{z}}{\partial z} - \frac{2}{3} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r v_{r} \right) + \frac{\partial v_{z}}{\partial z} \right] \right) \right] \right)$$
(32b)

Both compressive and shear forces are present in both the radial and vertical components of the velocity update equations provided in Eq. (32) as evident from the presence of radial and vertical derivatives in both terms. The compressive force calculations (as represented by derivatives lying parallel to the flow component direction) are easily calculated from the neighboring two sample points. However, the shear forces in both cases are not naturally represented at the given sampling locations as defined by the numerical mesh. Instead, their values must be approximated from likewise neighboring edges. Similarly, due to the location of the velocity components along the edges of each mesh element, the gas density must likewise be translated to the element edge. Finally, this also requires the gas kinetic viscosity to be calculated at the mesh nodes, which is calculated prior to the iterative update scheme and based upon a two-dimensional bilinear interpolation scheme.

In order to present the complete discrete form of the viscous force projection step update of the momentum transport equation, it is decomposed into its four primary terms. These represent both the compressive and shear force terms present in both velocity components. As a result, a simplified viscous force projection step update is provided in Eq. (33).

$$v_r'' = v_r' + \frac{\delta t}{\rho} \left[-\tau_{rr} + \tau_{rz} \right]$$
(33a)

$$v_z'' = v_z' + \frac{\delta t}{\rho} \left[+\tau_{zr} - \tau_{zz} \right]$$
(33b)

The four viscosity tensor terms in Eq. (33) are now presented in discrete form. Thus, these equations do not represent complete equations themselves, but instead simply discrete forms of numerical terms to be substituted back into Eq. (33). This decreases confusion with regards to the lengthy derivation, and also mimics the numerical code structure, with each viscosity tensor term being calculated and filled in a separate subroutine. As usual, these terms are derived and centered about an arbitrary mesh index location.

The compressive tensor term corresponding to the radial velocity component update may be expressed in point form as

$$\tau_{rr} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \left[-\mu \left(2 \frac{\partial v_r}{\partial r} - \frac{2}{3} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r v_r \right) + \frac{\partial v_z}{\partial z} \right] \right) \right] \right)$$
(34)

which may be expanded and simplified as

$$\tau_{rr} = \frac{2}{r} \frac{\partial}{\partial r} \left(\mu r \frac{\partial v_r}{\partial r} \right) + \frac{2}{3r} \frac{\partial}{\partial r} \left(\mu \frac{\partial}{\partial r} \left(r v_r \right) \right) + \frac{2}{3r} \frac{\partial}{\partial r} \left(\mu r \frac{\partial v_z}{\partial z} \right)$$
(35)

which is now discretized about the generic vertical edge with corresponding index $i, j + \frac{1}{2}$ as

$$\begin{aligned} \tau_{rr,i,j+\frac{1}{2}} &= \frac{2}{r_i} \frac{\mu_{i+\frac{1}{2},j+\frac{1}{2}}r_{i+\frac{1}{2}}\left(v_{r,i+1,j+\frac{1}{2}}-v_{r,i,j+\frac{1}{2}}\right)}{(r_{i+1}-r_i)\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \\ &+ \frac{2}{r_i} \frac{\mu_{i-\frac{1}{2},j+\frac{1}{2}}r_{i-\frac{1}{2}}\left(v_{r,i,j+\frac{1}{2}}-v_{r,i-1,j+\frac{1}{2}}\right)}{(r_i-r_{i-1})\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \\ &+ \frac{2}{3r_i} \frac{\mu_{i+\frac{1}{2},j+\frac{1}{2}}\left(r_{i+1}v_{r,i+1,j+\frac{1}{2}}-r_{i}v_{r,i,j+\frac{1}{2}}\right)}{(r_{i+1}-r_i)\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \\ &+ \frac{2}{3r_i} \frac{\mu_{i-\frac{1}{2},j+\frac{1}{2}}\left(r_iv_{r,i,j+\frac{1}{2}}-r_{i-1}v_{r,i-1,j+\frac{1}{2}}\right)}{(r_i-r_{i-1})\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \\ &+ \frac{2}{3r_i} \frac{\mu_{i+\frac{1}{2},j+\frac{1}{2}}r_{i+\frac{1}{2}}\left(v_{z,i+\frac{1}{2},j+1}-v_{z,i+\frac{1}{2},j\right)}{(z_{j+1}-z_j)\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \\ &+ \frac{2}{3r_i} \frac{\mu_{i-\frac{1}{2},j+\frac{1}{2}}r_{i-\frac{1}{2}}\left(v_{z,i-\frac{1}{2},j+1}-v_{z,i-\frac{1}{2},j\right)}}{(z_{j+1}-z_j)\left(r_{i+\frac{1}{2}}-r_{i-\frac{1}{2}}\right)} \end{aligned}$$
(36)

The compressive tensor term corresponding to the vertical flow vector component may be expanded and simplified as given in the following

$$\tau_{zz} = \frac{4}{3} \frac{\partial}{\partial z} \left(\mu \frac{\partial v_z}{\partial z} \right) - \frac{2}{3} \frac{\partial}{\partial z} \left(\frac{\mu}{r} \frac{\partial}{\partial r} \left(r v_r \right) \right)$$
(37)

In discretized form, centered about the generic horizontal mesh edge with index pair $i + \frac{1}{2}, j$, this becomes

$$\tau_{zz,i+\frac{1}{2},j} = \frac{4}{3} \frac{\mu_{i+\frac{1}{2},j+\frac{1}{2}} \left(v_{z,i+\frac{1}{2},j+1} - v_{z,i+\frac{1}{2},j} \right)}{\left(z_{j+1} - z_{j} \right) \left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}} \right)} \\ - \frac{4}{3} \frac{\mu_{i+\frac{1}{2},j-\frac{1}{2}} \left(v_{z,i+\frac{1}{2},j} - v_{z,i+\frac{1}{2},j-1} \right)}{\left(z_{j} - z_{j-1} \right) \left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}} \right)} \\ - \frac{2}{3} \frac{\mu_{i+\frac{1}{2},j+\frac{1}{2}} \left(v_{r,i+1,j+\frac{1}{2}} - v_{r,i,j+\frac{1}{2}} \right)}{r_{i+\frac{1}{2}} \left(r_{i+1} - r_{i} \right) \left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}} \right)} \\ + \frac{2}{3} \frac{\mu_{i+\frac{1}{2},j-\frac{1}{2}} \left(v_{r,i,j+\frac{1}{2}} - v_{r,i-1,j+\frac{1}{2}} \right)}{r_{i+\frac{1}{2}} \left(r_{i+1} - r_{i} \right) \left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}} \right)}$$
(38)

 τ_{rz}

The radial gas flow component shear force term is significantly simpler in form than the previous compression force expressions given in the preceding sections. However, due to the orthogonal orientation terms, an averaging of velocity components must be used. Once again, the τ_{rz} term is expanded from that given in Eq. (32) to become

$$\tau_{rz} = -\frac{\partial}{\partial z} \left(\mu \frac{\partial v_r}{\partial z} \right) - \frac{\partial}{\partial z} \left(\mu \frac{\partial v_z}{\partial r} \right)$$
(39)

which may be written in discrete form for the index pair $i, j + \frac{1}{2}$ as

$$\tau_{rz,i,j+\frac{1}{2}} = -\frac{\mu_{i,j+1}\left(v_{r,i,j+\frac{3}{2}} - v_{r,i,j+\frac{1}{2}}\right)}{\left(z_{j+\frac{3}{2}} - z_{j+\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)} + \frac{\mu_{i,j}\left(v_{r,i,j+\frac{1}{2}} - v_{r,i,j-\frac{1}{2}}\right)}{\left(z_{j+1} - z_{j}\right)\left(z_{j+1} - z_{j}\right)} - \frac{\mu_{i,j+1}\left(v_{z,i+\frac{1}{2},j+1} - v_{z,i-\frac{1}{2},j+1}\right)}{\left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)} + \frac{\mu_{i,j}\left(v_{z,i+\frac{1}{2},j} - v_{z,i-\frac{1}{2},j}\right)}{\left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}\right)\left(z_{j+1} - z_{j}\right)}$$
(40)

 au_{zr}

Finally, the shear force associated with the vertical gas flow vector component follows is a similar form as that of τ_{rz} . Only now, instead of the reference edge being vertical in orientation, it is now horizontal. Moreover, a more complicated radial derivative is present due to the cylindrical coordinate frame. As a result, the expanded τ_{zr} term becomes

$$\tau_{zr} = -\frac{1}{r}\frac{\partial}{\partial r}\left[\mu r\left(\frac{\partial v_r}{\partial z}\right)\right] - \frac{1}{r}\frac{\partial}{\partial r}\left[\mu r\left(\frac{\partial v_z}{\partial r}\right)\right] \tag{41}$$

Once again, in discrete form the above expression centered at the generic horizontal edge with index pair $i + \frac{1}{2}, j$ becomes

$$\tau_{zr,i+\frac{1}{2},j} = -\frac{1}{r_{i+\frac{1}{2}}} \frac{\mu_{i+1,j}r_{i+1}\left(v_{r,i+1,j+\frac{1}{2}} - v_{r,i+1,j-\frac{1}{2}}\right)}{(r_{i+1} - r_i)\left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}\right)} \\ + \frac{1}{r_{i+\frac{1}{2}}} \frac{\mu_{i,j}r_i\left(v_{r,i,j+\frac{1}{2}} - v_{r,i-1,j-\frac{1}{2}}\right)}{(r_i - r_{i-1})\left(z_{j+\frac{1}{2}} - z_{j-\frac{1}{2}}\right)} \\ - \frac{1}{r_{i+\frac{1}{2}}} \frac{\mu_{i+1,j}r_{i+1}\left(v_{z,i+\frac{3}{2},j} - v_{z,i+\frac{1}{2},j}\right)}{\left(r_{i+\frac{3}{2}} - r_{i+\frac{1}{2}}\right)(r_{i+1} - r_i)} \\ + \frac{1}{r_{i+\frac{1}{2}}} \frac{\mu_{i,j}r_i\left(v_{z,i+\frac{1}{2},j} - v_{z,i-\frac{1}{2},j}\right)}{\left(r_{i+\frac{1}{2}} - r_{i-\frac{1}{2}}\right)(r_{i+1} - r_i)}$$
(42)

Substituting Eq. (36) through Eq. (42) into Eq. (33) results in a $N_e \times N_e$ matrix structure, where N_e is the total number of edges in the simulation domain (horizontal plus vertical). Moreover, the structure of this matrix is block-diagonal in a 2×2 fashion. Solving the resulting implicit matrix equation with the previous solution provided as the generic right hand side solution vector results in the first implicit projection method update to the momentum transport equation.

Appendix E: FORTRAN files

master.f90

```
program master
! master program file for e/m-plasma simulation
use indices
use constants
use modtimer
use plasmadata
use mesh
use geometry
use em
use geometrydeallocate
use plasma
use thermal
implicit none
save
character*100 :: time
double precision :: time1, time2
! write starting time out to file
call systime(time);
open(unit=8, file='../status/time.out', status='unknown')
write(8,*) 'Starting time:'; write(8,*) trim(time);
! first, initialize physical constants
if (verbose.ge.2) then
print*, 'Calling [initialize_constants] module...'
```

```
end if
call initialize_constants
! if necessary, allocate timer values
if (Ctimer.gt.0) then
call initialize_timer
end if
! start multi-physics solution algorithm
if (Csolveplasma.eq.1) then
! initialize global counter
itt=0
! read in plasma data
if (verbose.ge.2) then
print*, 'Calling [plasma_data] module...'
end if
call plasma_data
! generate mesh (if applicable)
if (Cgenmesh.gt.0) then
call generate_mesh
end if
! next, process simulation geometry
if (verbose.ge.2) then
print*, 'Calling [process_geometry] module...'
end if
call process_geometry
! open status files (to be appended during simulation)
call master_status_open
! ** MAIN SOLUTION LOOP **
rplas=2.d0*Cmaxerr
do while ((itt.lt.Cnitermax+1).and.(Cresmaxflag.eq.0))
! step global counter forward
itt=itt+1
! initialize power minimization on/off flag
Crefpowminon=0; Crefpowminfinish=0;
! print status
```

```
write(*, '(a10, i4, a8, i4, a)'), 'Iteration ', itt,' of max ', Cnitermax, '...'
! write global counter to file
open(unit=10,file='../status/itt.out', status='unknown')
write(10,*) itt; close(10);
! update e/m solution (if necessary)
if (Csolveem.eq.1) then
if (verbose.ge.2) then
print*, 'Calling [solve_em] module...'
end if
call cpu_time(time1)
if ((Crefpowminflag.gt.0).and.(mod(itt,Cnrefpowmin).eq.0)) then
Crefpowminon=1
call geometry_deallocate
call refpowmin
Crefpowminon=0
else
call solve_em
end if
call cpu_time(time2)
if (Ctimer.gt.0) then
timer(1,1)=timer(1,1)+time2-time1
end if
end if
! solve plasma flow module
if (verbose.ge.2) then
print*, 'Calling [solve_plasma] module...'
end if
! ** MAIN PLASMA LOOP **
itp=0; call cpu_time(time1)
do while (itp.lt.Cniterpmax)
itp=itp+1
call solve_plasma
end do
call cpu_time(time2)
if (Ctimer.gt.0) then
timer(1,2)=timer(1,2)+time2-time1
end if
! update substrate temperature model
if (Ctempsubsolve.eq.1) then
call cpu_time(time1)
```

```
call solve_thermal
call cpu_time(time2)
if (Ctimer.gt.0) then
timer(1,3)=timer(1,3)+time2-time1
end if
end if
! write to timer file for comparison
call master_timer_write(itt,timer)
end do
! close status files
call master_status_close
else if (Csolveplasma.eq.0) then
! if ONLY e/m solution is desired
if (Csolveem.eq.1) then
! initialize reflected power minimization flag
Crefpowminon=0
! write first iteration to file
open(unit=10, file='../status/itt.out', status='unknown')
itt=1; write(10,*) itt; close(10);
! reflected power minimization loop
if (Crefpowminflag.gt.0) then
Crefpowminon=1
call refpowmin
Crefpowminon=0
else
if (Cgenmesh.gt.0) then
call generate_mesh
end if
call process_geometry
call solve_em
call geometry_deallocate
end if
end if
! if ONLY substrate thermal solution is desired
if (Ctempsubsolve.eq.1) then
```

```
! write first iteration to file
open(unit=10, file='../status/itt.out', status='unknown')
itt=1; write(10,*) itt; close(10);
! check for mesh generation
if (Cgenmesh.gt.0) then
call generate_mesh
end if
call process_geometry
call solve_thermal
call geometry_deallocate
end if
end if
! write starting time out to file
call systime(time);
write(8,*) 'Ending time:'; write(8,*) trim(time); close(8);
end program master
subroutine master_status_open
! open status files for appending during simulation
open(unit=1001, file='../status/residual.out', status='unknown')
open(unit=1002, file='../status/powref.out', status='unknown')
if (Ctempsubsolve.gt.0) then
open(unit=1003, file='../status/tsuberror.out', status='unknown')
end if
open(unit=3333, file='../status/l2errtg.out', status='unknown')
end subroutine master_status_open
subroutine master_status_close
! close status files
close(1001)
close(1002)
if (Ctempsubsolve.gt.0) then
close(1003)
end if
close(3333)
end subroutine master_status_close
```

```
subroutine master_timer_write(itt,timer)
! write master timings to file
integer :: itt
double precision :: timesum, timer(1,3)
! calculate total time
timesum=0.d0
do i=1,3
timesum=timesum+timer(1,i)
end do
! write timings to file
if (Ctimer.gt.0) then
open(unit=10, file='../status/timer.out', status='unknown')
write(10,*) 'Time required for E/M calculations:'
write(10,*) timer(1,1)/float(itt), timer(1,1)/timesum
write(10,*) 'Time required for plasma calculations:'
write(10,*) timer(1,2)/float(itt), timer(1,2)/timesum
write(10,*) 'Time required for thermal calculations:'
write(10,*) timer(1,3)/float(itt), timer(1,3)/timesum
close(10)
end if
end subroutine master_timer_write
em.f90
module em
! solve electromagnetics model
use indices
use constants
use modtimer
use geometry
use emconductivity
use emsolve
use empower
use empoynting
```

```
use emreflected
use emqvalue
use emsubstrate
use emplot
use emdeallocate
implicit none
save
double precision :: timeem1, timeem2
contains
subroutine solve_em
if (verbose.ge.3) then
print*, 'Running [solve_em] module...'
end if
if (verbose.ge.4) then
print*, 'Calling [em_conductivity]...'
end if
call em_conductivity
if (verbose.ge.4) then
print*, 'Calling [em_pml]...'
end if
call em_pml
if (verbose.ge.4) then
print*, 'Calling [em_curlcurl]...'
end if
call cpu_time(timeem1)
call em_curlcurl
call cpu_time(timeem2)
if (Ctimer.gt.0) then
timer(2,1)=timer(2,1)+timeem2-timeem1
end if
if (verbose.ge.4) then
print*, 'Calling [em_source]...'
end if
call em_source
if (verbose.ge.4) then
```

```
print*, 'Calling [em_solve]...'
end if
call cpu_time(timeem1)
call em_solve
call cpu_time(timeem2)
if (Ctimer.gt.0) then
timer(2,2)=timer(2,2)+timeem2-timeem1
end if
if (Cpoyntsub.gt.0) then
if (verbose.ge.4) then
print*, 'Calling [em_poynting]...'
end if
call em_poynting
end if
if (Crefpow.gt.0) then
if (verbose.ge.4) then
print*, 'Calling [em_reflected]...'
end if
call em_reflected
end if
if (Cemqvalue.gt.0) then
if (verbose.ge.4) then
print*, 'Calling [em_qvalue]...'
end if
call em_qvalue
end if
if (Cemsubstrate.gt.0) then
if (verbose.ge.4) then
print*, 'Calling [em_substrate]...'
end if
call em_substrate
end if
if (verbose.ge.4) then
print*, 'Calling [em_power]...'
end if
call em_power
if ((itt.eq.1).or.(mod(itt,Cplotem).eq.0)) then
if (verbose.ge.4) then
print*, 'Calling [em_plot]...'
```

```
end if
call cpu_time(timeem1)
call em_plot
call cpu_time(timeem2)
if (Ctimer.gt.0) then
timer(2,3)=timer(2,3)+timeem2-timeem1
end if
end if
if (verbose.ge.4) then
print*, 'Calling [em_deallocate]...'
end if
call em_deallocate
if (verbose.ge.4) then
print*, 'Calling [em_solve_write]...'
end if
call solve_em_write
end subroutine solve_em
subroutine solve_em_write
! write em timer values to file
if (Ctimer.gt.0) then
open(unit=10, file='../status/timerem.out', status='unknown')
write(10,*) 'Time required for curl x curl calculation:'
write(10,*) timer(2,1)/itt, timer(2,1)/sum(timer(2,1:3))
write(10,*) 'Time required for e/m solve:'
write(10,*) timer(2,2)/itt, timer(2,2)/sum(timer(2,1:3))
write(10,*) 'Time required for e/m plot:'
write(10,*) timer(2,3)/itt, timer(2,3)/sum(timer(2,1:3))
close(10)
end if
end subroutine solve_em_write
end module em
```

plasma.f90

module plasma

```
! update plasma model
  use indices
  use constants
  use modtimer
  use geometry
  use plasmaallocate
  use plasmainitialize
  use plasmaphysics
  use plasmatransport
  use plasmaupdate
  use plasmarelax
  use plasmaconductivity
  use plasmapass
  use plasmasize
  use plasmabeam
  use plasmafluxsub
  use plasmaplot
  use plasmadeallocate
  implicit none
  save
  double precision :: timeplas1, timeplas2, rcompare
contains
  subroutine solve_plasma
    if (verbose.ge.3) then
       print*, 'Running [solve_plasma] module...'
    end if
    ! read in global iteration number from file
    open(unit=10, file='../status/itt.out', status='old')
    read(10,*) itt; close(10)
    if (verbose.ge.4) then
```

```
print*, 'Calling [plasma_allocate] module...'
    end if
    call plasma_allocate
    if (verbose.ge.4) then
       print*, 'Calling [plasma_initialize] module...'
    end if
    call plasma_initialize
    if (Ctimer.gt.0) then
    timer(3,1:2)=0.d0
    end if
    ! update flows via momentum transport
    if (Cvel.gt.0) then
      ! update physical quantities
      if (verbose.ge.4) then
         print*, 'Calling [plasma_physics] module...'
      end if
      call plasma_physics
      if (verbose.ge.4) then
        print*, 'Calling [plasma_momentum] module...'
      end if
      call cpu_time(timeplas1)
      call plasma_momentum
      call cpu_time(timeplas2)
      if (Ctimer.gt.0) then
       timer(3,1)=timer(3,1)+timeplas2-timeplas1
      end if
    end if
    ! outer plasma loop
    iouter=0
    do while (((iouter.lt.Cniteromin).or.(plaserrcond.lt.Cmaxerrcond)) &
1 .and.(iouter.lt.Cniteromax))
       ! step outer counter forward
       iouter=iouter+1
       ! update physical quantities
       if (verbose.ge.4) then
          print*, 'Calling [plasma_physics] module...'
       end if
       call plasma_physics
```

```
if ((itt.eq.1).and.(iouter.eq.1)) then
   iinmax=Cniterimax0
else
   iinmax=Cniterimax
end if
! step total counter forward
itotal=itotal+1
! reset maxerrplas
maxerrplas=1.d-1*Cmaxerrplas
! print starting iteration
call solve_plasma_iouter
! inner plasma loop
iinner=0; call cpu_time(timeplas1)
do while (iinner.lt.iinmax)
   ! step inner counter forward
   iinner=iinner+1
   if (verbose.ge.4) then
      print*, 'Calling [plasma_relax_coefficients]...'
   end if
   call plasma_relax_coefficients
   if (verbose.ge.4) then
      print*, 'Calling [plasma_transport] module...'
   end if
   call plasma_transport
   if (verbose.ge.4) then
      print*, 'Calling [plasma_update] module...'
   end if
   call plasma_update
   if (verbose.ge.4) then
      print*, 'Calling [plasma_relax_convergence]...'
   end if
   call plasma_relax_convergence
   if (verbose.ge.4) then
      print*, 'Calling [plasma_relax_error]...'
   end if
```

```
call plasma_relax_error
      ! print relaxation rates
      write(*,100) frxs(2:nspec-1), frte, frtg
   end do
   call cpu_time(timeplas2)
   if (Ctimer.gt.0) then
   timer(3,2)=timer(3,2)+timeplas2-timeplas1
   end if
   if (verbose.ge.4) then
      print*, 'Calling [plasma_conductivity] module...'
   end if
   call plasma_conductivity
   ! calculate residuals
   call plasma_relax_residuals
   call plasma_relax_convergence_total
   print*, 'Residual summation = ',rplas
end do
! check for maximum residual condition
call solve_plasma_resmax
! write residuals to file
if (itt.gt.1) then
   write(1001,101) itt, rplas, rxs(2), rxs(7), rte, rtg, velerr
end if
if (verbose.ge.4) then
  print*, 'Calling [plasma_pass] module...'
end if
call plasma_pass
if (verbose.ge.4) then
  print*, 'Calling [plasma_size] module...'
end if
call plasma_size
if (Cpbeam.gt.0) then
if (verbose.ge.4) then
print*, 'Calling [plasma_beam] module...'
end if
```

```
call plasma_beam
   end if
   if (Cpfluxsub.gt.0) then
   if (verbose.ge.4) then
      print*, 'Calling [plamsa_fluxsub] module...'
   end if
   call plasma_fluxsub
   end if
   if ((itt.eq.1).or.(mod(itt,Cplotplasma).eq.0)) then
      if (verbose.ge.4) then
         print*, 'Calling [plasma_plot] module...'
      end if
      call cpu_time(timeplas1)
      call plasma_plot
      call cpu_time(timeplas2)
      if (Ctimer.gt.0) then
              timer(3,3)=timer(3,3)+timeplas2-timeplas1
      end if
   end if
   if (verbose.ge.4) then
      print*, 'Calling [plasma_deallocate] module...'
   end if
   call plasma_deallocate
    ! write timings to file
   call solve_plasma_timer
100 format(8e9.2,e8.1)
101 format(i4,6e12.4)
 end subroutine solve_plasma
 subroutine solve_plasma_iouter
      print*, '-----'
      print*, '-----'
      print*, 'Starting outer iteration ',iouter,' ...'
      print*, '-----'
 end subroutine solve_plasma_iouter
```

```
subroutine solve_plasma_resmax
```

```
! check for maximum residual error reached
    ! if so, set flag for simulation termination
    ! ensure residual error flag is zero
    Cresmaxflag=0
    ! check for condition
    do i=1,Cnresmax
    if (Ciresmax(i).le.nspec) then
    rcompare=rxs(Ciresmax(i))
    else if (Ciresmax(i).eq.nspec+2) then
    rcompare=rte
    else if (Ciresmax(i).eq.nspec+3) then
    rcompare=rtg
    end if
    if (rcompare.ge.Cresmax(i)) then
    Cresmaxflag=Cresmaxflag+1
    end if
    end do
    if (rplas.ge.Cresmaxtot) then
    Cresmaxflag=Cresmaxflag+1
    end if
    ! change sign on flag
    if (Cresmaxflag.eq.0) then
    Cresmaxflag=1
    else
    Cresmaxflag=0
    end if
 end subroutine solve_plasma_resmax
 subroutine solve_plasma_timer
    ! write plasma timings to file
    if (Ctimer.gt.0) then
open(unit=10, file='../status/timerplas.out', status='unknown')
write(10,*) 'Time required for momentum update:'
write(10,*) timer(3,1)/iouter, timer(3,1)/sum(timer(3,1:3))
write(10,*) 'Time required for transport updates:'
write(10,*) timer(3,2)/iouter, timer(3,2)/sum(timer(3,1:3))
write(10,*) 'Time required for plasma plot:'
write(10,*) timer(3,3)/itt, timer(3,3)/sum(timer(3,1:3))
close(10)
```

```
end if
```

end subroutine solve_plasma_timer

end module plasma

thermal.f90

```
module thermal
! module for updating substrate thermal model
use indices
use constants
use geometry
implicit none
save
integer :: ntlhss, ntsub
double precision, dimension(:), allocatable :: fluxxh0, fluxxh
double precision, dimension(:), allocatable :: fluxtg0, fluxtg
double precision, dimension(:), allocatable :: fluxsub
double precision, dimension(:), allocatable :: trhs, tsoln
double precision, dimension(:), allocatable :: tsoln0, alphat
double precision, dimension(:,:), allocatable :: tlhss
contains
subroutine solve_thermal
if (verbose.ge.3) then
print*, 'Running [thermal] module...'
end if
if (verbose.ge.4) then
print*, 'Calling [thermal_allocate]...'
end if
call thermal_allocate
if (verbose.ge.4) then
```

```
print*, 'Calling [thermal_diffusivity]...'
end if
call thermal_diffusivity
if (verbose.ge.4) then
print*, 'Calling [thermal_left]...'
end if
call thermal_left
if (verbose.ge.4) then
print*, 'Calling [thermal_read]...'
end if
call thermal_read
if (verbose.ge.4) then
print*, 'Calling [thermal_right]...'
end if
call thermal_right
if (verbose.ge.4) then
print*, 'Calling [thermal_solve]...'
end if
call thermal_solve
call thermal_relax
if (verbose.ge.4) then
print*, 'Calling [thermal_error]...'
end if
call thermal_error
if (verbose.ge.4) then
print*, 'Calling [thermal_pass]...'
end if
call thermal_pass
if ((itt.eq.1).or.(mod(itt,Cplotthermal).eq.0)) then
if (verbose.ge.4) then
print*, 'Calling [thermal_plot]...'
end if
call thermal_plot
end if
if (verbose.ge.4) then
print*, 'Calling [thermal_deallocate]...'
```

```
end if
call thermal_deallocate
end subroutine solve_thermal
subroutine thermal_allocate
! allocate substrate thermal model arrays
allocate(tlhss(3,5*ntel))
allocate(trhs(ntel))
allocate(tsoln0(ntel))
allocate(tsoln(ntel))
allocate(alphat(ntel))
tlhss=0.d0
trhs=0.d0
tsoln0=0.d0
tsoln=0.d0
alphat=0.d0
end subroutine thermal_allocate
subroutine thermal_diffusivity
! update thermal diffusivity array
integer :: nlamtype
double precision :: cpt(ntel), rhot(ntel)
double precision :: lamtype(10)
! set specific heats and mass densities at
! each element in substrate
lamtype=0.d0; lamtype(1)=lambdasub(1); nlamtype=1;
do i=2,ntel
flag=0
do j=1,nlamtype
if (lambdasub(i).eq.lamtype(j)) then
flag=flag+1
end if
end do
if (flag.eq.0) then
nlamtype=nlamtype+1
lamtype(nlamtype)=lambdasub(i)
end if
end do
```

```
! fill specific heat and mass density vectors
do i=1,ntel
! lambda > 10 (METAL)
if (lambdasub(i).gt.1.d1) then
cpt(i)=5.d2
rhot(i)=1.d4
! lambda < 0.1 (GAS)
else if (lambdasub(i).lt.1.d-1) then
cpt(i)=1.43d4
rhot(i)=1.d-2
! else (SILICA)
else
cpt(i)=7.d2
rhot(i)=2.d3
end if
alphat(i)=lambdasub(i)/(cpt(i)*rhot(i))
end do
end subroutine thermal_diffusivity
subroutine thermal_left
! fill sparse left-hand-side array
double precision :: r0, rm1, r1, rp1, r2, dr0, dr1, dr2
double precision :: z0, zm1, z1, zp1, z2, dz0, dz1, dz2
double precision, dimension(:,:), allocatable :: tlhss0
double precision :: drdzterm, alphatavg, coef, tlhssd
! fill sparse left-hand-side array
k=0
do i=1,ntel
! check for otherwise bordering elements
flag=0
do j=1,4
if (tel4tel(j,i).eq.0) then
flag=flag+1
end if
end do
if ((tforced(i).gt.0).and.(flag.eq.0)) then
! inner forced (water-cooled)
k=k+1
tlhss(1,k)=i
tlhss(2,k)=i
```

```
tlhss(3,k)=1.d0
else if ((flag.gt.0).and.(tforced(i).eq.0)) then
! domain borders
! main diagonal
k=k+1
tlhss(1,k)=i
tlhss(2,k)=i
if ((tel4tel(1,i).eq.0).or.(tel4tel(2,i).eq.0)) then
tlhss(3,k)=1.d0
end if
if (tel4tel(3,i).eq.0) then
tlhss(3,k)=alphat(i)/abs(telCoords(1,i)-telCoords(1,tel4tel(2,i)))
end if
if (tel4tel(4,i).eq.0) then
tlhss(3,k)=alphat(i)/abs(telCoords(2,i)-telCoords(2,tel4tel(1,i)))
end if
! off-diagonal
k=k+1
tlhss(1,k)=i
if (tel4tel(1,i).eq.0) then
tlhss(2,k)=tel4tel(4,i)
end if
if ((tel4tel(2,i).eq.0).and.(tel4tel(3,i).ne.0)) then
tlhss(2,k)=tel4tel(3,i)
end if
if (tel4tel(3,i).eq.0) then
tlhss(2,k)=tel4tel(2,i)
end if
if (tel4tel(4,i).eq.0) then
tlhss(2,k)=tel4tel(1,i)
end if
if ((tel4tel(1,i).eq.0).or.(tel4tel(2,i).eq.0)) then
tlhss(3,k)=-1.d0
end if
if (tel4tel(3,i).eq.0) then
tlhss(3,k)=-alphat(i)/abs(telCoords(1,i)-telCoords(1,tel4tel(2,i)))
end if
if (tel4tel(4,i).eq.0) then
tlhss(3,k)=-alphat(i)/abs(telCoords(2,i)-telCoords(2,tel4tel(1,i)))
end if
else if ((tforced(i).gt.0).and.(flag.ne.0)) then
! bordering, but still forced
k=k+1
tlhss(1,k)=i
tlhss(2,k)=i
```

```
tlhss(3,k)=1.d0
else if ((flag.eq.0).and.(tforced(i).eq.0)) then
! all other non-boundary locations
! spatial terms
r0=telCoords(1,i)
rm1=tnodeCoords(1,tel2tnode(1,i))
r1=telCoords(1,tel4tel(2,i))
rp1=tnodeCoords(1,tel2tnode(2,i))
r2=telCoords(1,tel4tel(3,i))
dr0=abs(rp1-rm1)
dr1=abs(r0-r1)
dr2=abs(r0-r2)
z0=telCoords(2,i)
zm1=tnodeCoords(2,tel2tnode(1,i))
z1=telCoords(2,tel4tel(1,i))
zp1=tnodeCoords(2,tel2tnode(4,i))
z2=telCoords(2,tel4tel(4,i))
dz0=abs(zp1-zm1)
dz1=abs(z0-z1)
dz2=abs(z0-z2)
! fill sparse array
tlhssd=0.d0
do j=1,4
ii=tel4tel(j,i)
if (j.eq.1) then
drdzterm=1.d0/(dz0*dz1)
else if (j.eq.2) then
drdzterm=rm1/(r0*dr0*dr1)
else if (j.eq.3) then
drdzterm=rp1/(r0*dr0*dr2)
else if (j.eq.4) then
drdzterm=1.d0/(dz0*dz2)
end if
! off diagonal terms first
if (ii.ne.0) then
alphatavg=(alphat(i)+alphat(ii))/2.d0
coef=alphatavg*drdzterm
k=k+1; tlhss(1,k)=i; tlhss(2,k)=ii
tlhss(3,k)=coef; tlhssd=tlhssd-coef
end if
end do
! main diagonal
k=k+1; tlhss(1,k)=i; tlhss(2,k)=i; tlhss(3,k)=tlhssd
end if
end do
```

```
ntlhss=k
! contract sparse lhs array
allocate(tlhss0(3,5*ntel))
tlhss0=tlhss
deallocate(tlhss)
allocate(tlhss(3,ntlhss))
tlhss=tlhss0(:,1:ntlhss)
deallocate(tlhss0)
end subroutine thermal_left
subroutine thermal_read
! read in flux data from file
! count number of total substrate bounds
ntsub=0
do i=1,ntel
if (tel4tel(3,i).eq.0) then
ntsub=ntsub+1
end if
end do
do i=1,ntel
if (tel4tel(4,i).eq.0) then
ntsub=ntsub+1
end if
end do
! allocate data arrays
allocate(fluxxh0(ntsub)); fluxxh0=0.d0
allocate(fluxtg0(ntsub)); fluxtg0=0.d0
allocate(fluxxh(ntsub)); fluxxh=0.d0
allocate(fluxtg(ntsub)); fluxtg=0.d0
allocate(fluxsub(ntsub)); fluxsub=0.d0
! read in temperature flux at substrate
! boundaries from files as calculated
! in plasma module
! if (itt.eq.1) then
! fluxxh0=0.d0; fluxtg0=0.d0
! else
! open(unit=10, file='../plasma/fluxxhtot0.out', status='unknown')
! open(unit=11, file='../plasma/fluxtgtot0.out', status='unknown')
! do i=1,ntsub
```
```
! read(10,*) fluxxh0(i)
! read(11,*) fluxtg0(i)
! end do
! close(10); close(11)
! end if
open(unit=12, file='../plasma/fluxxhtot.out', status='old')
open(unit=13, file='../plasma/fluxtgtot.out', status='old')
do i=1,ntsub
read(12,*) fluxxh(i)
read(13,*) fluxtg(i)
end do
close(12)
close(13)
! calculate total flux at boundary elements
do i=1,ntsub
! if (itt.eq.1) then
fluxsub(i)=(fluxxh(i)+fluxtg(i))
! else
! fluxsub(i)=(1.d0-Ctempsubrelax)*(fluxxh0(i)+fluxtg0(i)) &
! 1 +Ctempsubrelax*(fluxxh(i)+fluxtg(i))
! end if
end do
end subroutine thermal_read
subroutine thermal_right
! fill right-hand-side vector
! check for r=0 or forced region
do i=1,ntel
! zeroed neumann on r=0
if (tel4tel(2,i).eq.0) then
trhs(i)=0.d0
end if
! force room temperature (300 K) in bulk
if (tforced(i).gt.0) then
trhs(i)=3.d2
end if
end do
! initialize flux edge counter
j=0
```

```
! vertical edges
do i=1,ntel
if (tel4tel(3,i).eq.0) then
j=j+1
trhs(i)=fluxsub(j)
end if
end do
! horizontal edges
do i=1,ntel
if (tel4tel(4,i).eq.0) then
j=j+1
trhs(i)=fluxsub(j)
end if
end do
end subroutine thermal_right
subroutine thermal_solve
! solve substrate thermal model
call axbdmumps(ntlhss,tlhss,ntel,trhs)
tsoln=trhs
! check for NaN
do i=1,ntel
if (tsoln(i).ne.tsoln(i)) then
tsoln(i)=0.d0
end if
end do
end subroutine thermal_solve
subroutine thermal_relax
! relax substrate temperature update
! update solution
do i=1,ntel
if (tforced(i).eq.0) then
tsoln(i)=(1.d0-Ctempsubrelax)*tsoln0(i)+Ctempsubrelax*tsoln(i)
end if
end do
end subroutine thermal_relax
```

```
subroutine thermal_error
! calculate error between current solution
! and previous temperatures at substrate
double precision :: tsuberror
! retrieve old temperature values
if (itt.eq.1) then
! initialize temperature to zero
tsoln0=0.d0
else
! read in tsolnO from file
open(unit=10, file='../plasma/tgsub.out', status='old')
do i=1,ntel
if (tel4tel(3,i).eq.0) then
read(10,*) tsoln0(i)
end if
end do
do i=1,ntel
if (tel4tel(4,i).eq.0) then
read(10,*) tsoln0(i)
end if
end do
close(10)
end if
! calculate L2Norm between current
! gas temperatures on boundaries
! and new solution
tsuberror=0.d0
do i=1,ntel
if (tel4tel(3,i).eq.0) then
tsuberror=tsuberror+(tsoln(i)-tsoln0(i))**2
end if
end do
do i=1,ntel
if (tel4tel(4,i).eq.0) then
tsuberror=tsuberror+(tsoln(i)-tsoln0(i))**2
end if
end do
tsuberror=sqrt(tsuberror)
! write out error to file
```

```
write(1003,*) itt, tsuberror
end subroutine thermal_error
subroutine thermal_pass
! pass substrate temperature solution
! to plasma module (gas temperature)
! open file
open(unit=10, file='.../plasma/tgsub.out', status='unknown')
! write substrate outer wall to file
do i=1,ntel
! check for element bounding plasma domain
if (tel4tel(3,i).eq.0) then
write(10,*) tsoln(i)
end if
end do
! write substrate top surface to file
do i=1,ntel
if (tel4tel(4,i).eq.0) then
write(10,*) tsoln(i)
end if
end do
! close file
close(10)
! ! pass current flux to old files
! open(unit=10, file='../plasma/fluxxhtot0.out', status='unknown')
! open(unit=11, file='../plasma/fluxtgtot0.out', status='unknown')
! do i=1,ntsub
! write(10,*) fluxxh(i)
! write(11,*) fluxtg(i)
! end do
! close(10); close(11)
end subroutine thermal_pass
subroutine thermal_plot
! plot substrate thermal solution
if (Cplotplasma.gt.0) then
```

```
! call plotvtk(ntel,lambdasub,'lambdasub')
! call plotvtk(ntel,tsoln,'tsub')
! open(unit=10, file='../plot/lambdasub.3d', status='unknown')
! write(10,*) 'r z phi lambdasub'
! do i=1,ntel
! write(10,'(2e16.8,i4,e16.8)') telCoords(:,i), 0, lambdasub(i)
! end do
! close(10)
open(unit=10, file='../plot/alphat.3d', status='unknown')
write(10,*) 'r z phi alphat'
do i=1,ntel
write(10,'(2e16.8,i4,e16.8)') telCoords(:,i), 0, alphat(i)
end do
close(10)
open(unit=10, file='../plot/tsub.3d', status='unknown')
write(10,*) 'r z phi tsub'
do i=1,ntel
write(10,'(2e16.8,i4,e16.8)') telCoords(:,i), 0, tsoln(i)
end do
close(10)
end if
end subroutine thermal_plot
subroutine thermal_deallocate
! deallocate substrate thermal model arrays
deallocate(fluxxh0,fluxxh,fluxtg0,fluxtg)
deallocate(fluxsub)
deallocate(tlhss)
deallocate(trhs)
deallocate(tsoln0)
deallocate(tsoln)
deallocate(alphat)
end subroutine thermal_deallocate
end module thermal
```

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