# A GLOBAL MODELING FRAMEWORK FOR PLASMA KINETICS: DEVELOPMENT AND APPLICATIONS

By

Guy Morland Parsey

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#### ABSTRACT

# A GLOBAL MODELING FRAMEWORK FOR PLASMA KINETICS: DEVELOPMENT AND APPLICATIONS

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The modern study of plasmas, and applications thereof, has developed synchronously with computer capabilities since the mid-1950s. Complexities inherent to these charged-particle, manybody, systems have resulted in the development of multiple simulation methods (particle-in-cell, fluid, global modeling, etc.) in order to both explain observed phenomena and predict outcomes of plasma applications. Recognizing that different algorithms are chosen to best address specific topics of interest, this thesis centers around the development of an open-source global model framework for the focused study of non-equilibrium plasma kinetics. After verification and validation of the framework, it was used to study two physical phenomena: plasma-assisted combustion and the recently proposed optically-pumped rare gas metastable laser.

Global models permeate chemistry and plasma science, relying on spatial averaging to focus attention on the dynamics of reaction networks. Defined by a set of species continuity and energy conservation equations, the required data and constructed systems are conceptually similar across most applications, providing a light platform for exploratory and result-search parameter scanning. Unfortunately, it is common practice for custom code to be developed for each application— an enormous duplication of effort which negatively affects the quality of the software produced. Presented herein, the Python-based Kinetic Global Modeling framework (KGMf) was designed to support all modeling phases: collection and analysis of reaction data, construction of an exportable system of model ODEs, and a platform for interactive evaluation and post-processing analysis. A symbolic ODE system is constructed for interactive manipulation and generation of a Jacobian, both of which are compiled as operation-optimized C-code.

Plasma-assisted combustion and ignition (PAC/PAI) embody the modernization of burning fuel by opening up new avenues of control and optimization. With applications ranging from engine efficiency and pollution control to stabilized operation of scramjet technology in hypersonic flows, developing an understanding of the underlying plasma chemistry is of the utmost importance. While the use of equilibrium (thermal) plasmas in the combustion process extends back to the advent of the spark-ignition engine, works from the last few decades have demonstrated fundamental differences between PAC and classical combustion theory. The KGMf is applied to nanosecond-discharge systems in order to analyze the effects of electron energy distribution assumptions on reaction kinetics and highlight the usefulness of 0D modeling in systems defined by coupled and complex physics.

With fundamentally different principles involved, the concept of optically-pumped rare gas metastable lasing (RGL) presents a novel opportunity for scalable high-powered lasers by taking advantage of similarities in the electronic structure of elements while traversing the periodic table. Building from the proven concept of diode-pumped alkali vapor lasers (DPAL), RGL systems demonstrate remarkably similar spectral characteristics without problems associated with heated caustic vapors. First introduced in 2012, numerical studies on the latent kinetics remain immature. This work couples an analytic model developed for DPAL with KGMf plasma chemistry to better understand the interaction of a non-equilibrium plasma with the induced laser processes and determine if optical pumping could be avoided through careful discharge selection.

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#### **CHAPTER 1**

#### **INTRODUCTION**

Plasma, described as the fourth state of matter or a charge-balanced gas of ions and electrons, makes up the majority of the known visible universe. This profusion of matter has a broad range of defining characteristics due to the combined effects of the underlying mechanical, electrical and quantum forces and atomic and molecular collisions. Existing both naturally (e.g. astrophysical plasma) and in man-made forms, plasmas have been a focus of study since before the term was coined by Irving Langmuir in 1928 [98]. The complex nature of the driving forces limits analytical solutions to most phenomena of interest, which restricted this field to experimental research until the advent of computational methods of numerical simulation. The first numerical studies were performed using simplified models by the plasma simulation pioneers in the 1950s [162, 23] and 60s [17, 37]. The evolution of computational hardware since has led to an exponential growth in the field, resulting in a wide range of applications and simulation methods.

Though the forces involved in plasma are relatively well defined at a fundamental level, the sheer number of particles leads to an impossibility of simulating all forces involved in an *ab initio* manner. Each method of simulation is reliant on a certain set of imposed assumptions in order to balance accuracy and computational evaluation time. The wide range in the types of plasmas results in overlaps between physical behavior and assumptions built into computational methods. These overlaps are used to choose simulation methods given a specific system of interest and, with advancing computational hardware, motivated the development of hybrid methods combining beneficial aspects. The majority of development has focused on understanding the physical dynamics of plasma systems, commonly resulting in simplifying assumptions placed on the underlying chemistry involved in gas-plasma interactions. To be fair, modeling this chemistry is still unfortunately restricted by the availability of experimental and numerical fundamental data as opposed to operating on fundamental principles.

This chapter provides an overview of plasma fundamentals and the main types of simulation



Figure 1.1 Types of plasma relative to electron density and temperature [118].

methods, followed by motivations to develop a plasma-chemistry simulation platform with features differing from available tools. The key capabilities and limitations of each method are described along with examples of available software implementations. With the realization of plasma applicability to a wide range of scenarios, commercial and academic software exist for each method, designed to tailor towards specific regimes. Emerging interest in regimes requiring integration of involved plasma-chemistry motivates a simulation platform with a wide acceptance of data and an intrinsic flexibility to quickly incorporate different physics. If designed in a manner to rapidly evaluate different parameters, a quick chemistry engine could be included in a hybrid modeling method for higher fidelity simulation.

## **1.1 Plasma Fundamentals**

Langmuir described plasma as the "region containing balanced charges of ions and electrons," found in between the electrodes of an RF discharge encased by "sheaths" containing predominantly ions [98]. This description has been expanded to define plasma as a combination of free electrons with ionized and excited molecular, or atomic, species interacting with each other and external forces [19]. The set of charged species in a given plasma exhibits collective behavior due to long-range electrical forces and yet remains macroscopically neutral in a large number of cases. In the same manner that a solid or liquid undergoes a phase transition with the introduction of enough thermal kinetic energy, a plasma is formed through a system absorbing enough kinetic energy to exceed the binding energies of both gaseous molecules and orbital-bound electrons. The kinetic energy transfered by inelastic collisions results in the production of electrons and ions along with rotational, vibrational, and electrical excitations of atomic and molecular species. As the reaction dynamics can differ widely between ground and excited species, the introduction of electron impact processes can dramatically alter chemical kinetics with high electron energies and/or densities.

Aside from the plethora of possible excited species depending on the reaction network of a given system, plasmas can be further classified by their ionization fraction, whether or not they exhibit thermal behavior, and if the electrons are in equilibrium with their own ensemble. With the ionization fraction defined as the ratio of heavy particles that are ionized, the classification of thermal vs. non-thermal plasmas corresponds to the difference between electron and heavy species temperatures. Thermal plasmas are characterized as having approximately equal electron, heavy excited/ionized and ground species temperatures,  $T_e \gtrsim T_i \simeq T_g$ , and obeying the laws of thermodynamic equilibrium. In these cases, gas temperatures have increased to the order of 1 eV  $\approx$  10,000 K or greater from joule heating through electron-neutral collisions [50]. Lightning is a natural example of a thermal spark discharge, with local temperatures increasing to above 24,000 K [165]. Non-thermal plasma are characterized by electron and excited species temperatures differing from the ground state temperatures,  $T_e \gg T_i \gtrsim T_g$ , resulting in a dominance of excited species and elec-

tron impact reactions as opposed to equilibrium gas-phase reactions. The expression for energy exchange under elastic collisions between two gas species is written as, [6],

$$\frac{dU}{dt} = -3n_1 \frac{m_1 m_2}{(m_1 + m_2)^2} k(T_1 - T_2) n_2 < (v_1 - v_2) \sigma_m >$$
(1.1)

with cross section  $\sigma$ , <> denoting averaging with the velocity distribution, and mass *m*, density *n*, temperature *T* and velocity *v* for each species. The mass difference between electrons and heavy species results in an inefficient momentum transfer to heavy species, meaning a large portion of electron energy resides in excited states and electrons do not thermalize well with heavy species. An increasingly common example is a medical atmospheric plasma jets, where, in the discharge region, gas temperatures can approach 2000 K and electron temperatures are estimated to be in excess of 10 eV [88]. Paired with a difference in temperature, electron velocity distributions may not follow a Maxwell-Boltzmann, or equilibrium, distribution. This is primarily driven by the lack of thermodynamic equilibrium between forward and reverse inelastic collisions [54]. Consider a gas discharge system where fast electrons are generated in order to ionize and excite the gas in the bulk volume and the primary loss of electrons and radiation are to the wall. With reasonable gas pressures, the electron-electron collisions support a Maxwellian distribution in general, a comparably high inelastic collision frequency will perpetuate a non-equilibrium, or kinetic, electron energy distribution.

The utilization of plasma has spread across a wide range of technologies; to name a few: medical applications of sterilization and tissue regrowth [174], semiconductor manufacturing [96], hypersonic jet engines [74], thrusters [25], fusion [40, 51] and material modification [68]. Alterations in pressure, temperature, gas mixtures, and the type of electrical discharge all contribute to physical behavior of the plasma due to the underlying dominant forces, fig. 1.1. Selection of the best simulation method for a numerical study depends on the primary physics of interest and the computational resources and time available.

### **1.2** Plasma Simulation

A complete numerical description of a plasma requires resolving a number of underlying physical forces and reaction processes. As a system of neutral and charged species, the particle motion must be represented in a manner which responds to electromagnetic and thermal effects. This requires a solution of Maxwell's or Poisson's equations for the forces acting on species described as either particles or fluids. A description of the different species' kinetic and potential energies then dictates collisional processes when paired with reaction probabilities. Reaction probabilities are used as the addition of quantum processes for electron impact reactions would make simulation intractable regardless of the method used. Simulation methods are categorized into one of two methods: kinetic or fluid descriptions. However, interest in different physics, while factoring in computational run time, has also lead to the development of hybrid and reduced methods.

#### 1.2.1 Kinetic

A kinetic description of the electrons and heavy particle motion inherently implies moving individual, or clustered, particles around a domain as a response to electromagnetic, collisional, and boundary forces. Using a predominantly fundamental description retains very good physics; numerical solutions to the coupled Newton-Lorentz and Maxwell's equations (or Poisson's equation in the electrostatic case) are found with very few approximations [86], resulting in a self-consistent evaluation of the particle velocity distributions,  $f(\mathbf{x}, \mathbf{v}, t)$ . This high-fidelity method comes with a cost of computational intensity with regards to the total number of simulated particles. Due to memory limitations, it is not possible to set up a 1:1 relationship between plasma and computer particles for most plasma pressure regimes. To resolve this issue, the majority of current kinetic methods applied to plasmas rely on the particle-in-cell (PIC) scheme. Formalized in the 1970s by Birdsall and Langdon [18] and Hockney and Eastwood [43], the PIC scheme takes advantage of the collective behavior existing between charged particle species to simulate macro-particles as a statistical representation of  $10^{5-7}$  real particles. The typical solution scheme in PIC is reliant on the particles existing in continuum velocity and position space. With the macro-particles initialized to some set of positions and velocities, fields from both external forces and charged particles are found at discrete locations in space, at the nodes of some imposed grid, and then interpolated into collective forces acting on simulated macro-particles. Since both fields and particle data are known at discrete time intervals, their respective solutions are temporally separated by half of a time step  $\Delta t/2$  allowing for leapfrog, center-difference, integration of the equations of motion [169],

$$\frac{\mathbf{u}^{t+\Delta t/2} - \mathbf{u}^{t-\Delta t/2}}{\Delta t} = \frac{q}{m} \left[ \mathbf{E}^t + \frac{\mathbf{u}^{t+\Delta t/2} + \mathbf{u}^{t-\Delta t/2}}{2\gamma^t} \times \mathbf{B}^t \right]$$
$$\frac{\mathbf{x}^{t+\Delta t} - \mathbf{x}^t}{\Delta t} = \frac{\mathbf{u}^{t+\Delta t/2}}{\gamma^{t+\Delta t/2}} \tag{1.2}$$

for each macro-particle. Once the particles have been moved to their next configuration in time, boundary conditions and collisional process schemes are used to transfer energy and mass into different species states. The new set of particles at distinct positions and velocities then starts the cycle again until the total time of interest has been resolved. Selection of the weighting scheme used to transmit forces back to particles requires a balance of computational efficiency, physical accuracy, and simulation noise in the system [28] with the latter often suppressed actively or passively. Although short-range Coulomb forces between macro-particles in the same grid cell are underestimated [169], the simulations are fully kinetic and and take significantly less time than a numerical evaluation of direct Coulomb's law between all particles as the operations performed are  $O(N \log N)$  and  $O(N^2)$  respectively. Collisions are typically handled using a Monte Carlo collision scheme which determines particle interaction results from statistical probabilities. Further speeding up simulation time, a fictitious null-collision is used such that the total collision frequency of each species is independent of incident particle energy and uniform in space. This allows for collisional processes to be calculated on a random subset of macro-particles as opposed to performing multiple operations on each one. Considerations can also be made to fix certain species such that their full dynamics are ignored; heavy species can be fixed to the background accounting for relative immobility compared to electron motion, or, a background fluid of electrons can be assumed when ion and heavy particle behavior is of interest.

Though representing the highest-fidelity modeling of plasmas, PIC methods are not without stability requirements and evaluation limitations. The discrete nature of particle kinetics brings numerical fluctuations which converge proportionally to  $\sqrt{N}^{-1}$  for N macro-particles, requiring large numbers of macro-particles for a given simulations. Grid spacing  $\Delta x$ , is limited to being smaller than the smallest characteristic length scale of the system to be resolved (e.g. Debye length, sheath length, or Larmor radius). Time steps  $\Delta t$ , must be chosen to satisfy a number of conditions: resolving the shortest characteristic time scale (e.g. inverses of plasma frequency, driving frequencies, or maximum collision frequency), satisfying the particle Courant condition,  $v\Delta t < \Delta x$ , with particle velocity, v, and restricting particles to a single collision per time step. The major limitation of PIC simulations lies in the computational time required for large simulations, controlled predominantly by the number of macro particles and selection of  $\Delta t$  and  $\Delta x$ . Attempts to reduce the computational intensity relative to a a fully-kinetic molecular dynamics simulation induces numerical issues. Noise in the system from finite-particle numerical fluctuations is only reduced through increasing particle count, higher-order algorithms, or filtering high-frequency effects in plasma, the latter of which can also filter out certain physics of interest. The noise in the system further causes artificial cumulative heating which can dramatically effect the behavior of macro-particles confined for long periods of time. Finally, the number of particles must be large enough to adequately describe a statistical representation of particle velocity distributions which can range in several orders of relative magnitude.

In the context of plasma simulation, PIC is commonly used when high-fidelity modeling is required or the system is either at low-pressure or demonstrating non-equilibrium behavior. Lowpressure systems have the advantage of needing fewer particles to adequately describe the kinetics. The self-consistent description of the particle distribution is capable of demonstrating nonequilibrium effects accurately. Finally, the minimal number of assumptions made results in PIC methods being the most accurate description if particle count, grid size, and time steps are chosen correctly. The largest constraint on PIC simulations is simply the computational resources and clock time required for attaining a solution.

Several simulation packages exist for PIC simulation, ranging from open-source academic codes to commercial applications. Some of the first examples came from the Plasma Theory Simulation Group (PTSG) (e.g. XES1, XPD[P,C][1,2] and XOOPIC) [18, 170, 166, 171], laying the foundation for almost any PIC implementation. The desire for application-specific considerations led to the development of a number of simulation platforms for the study of plasma physics, such as: WARP for modeling particle beams with high-space charge intensities [58] and PICCANTE, as an effort towards massively parallel fully-relativistic PIC [137] extending from ALaDyn [14]. There also exist a number of commercial options, such as TechX's VSim (formally VORPAL) [33] and Orbital ATK's MAGIC Tool Suite [5], originally designed for microwave engineering applications.

#### 1.2.2 Fluid

Reducing computational intensity relative to kinetic methods, a fluid description describes the evolution of macroscopic quantities coming from velocity moments of the Boltzmann equation. The first three moments become the species continuity, momentum transfer and heat transfer equations. As with PIC, these equations are coupled with Maxwell's equations (or Poisson's equation) for self-consistent electric and magnetic fields [86]. The Boltzmann equation is defined as

$$\widetilde{\mathbb{B}} = \left[\frac{\partial}{\partial t} + \vec{\mathbf{v}} \cdot \nabla + \vec{a} \cdot \nabla_{\mathbf{v}}\right] f(\vec{x}, \vec{\mathbf{v}}, t) = \left(\frac{\partial f}{\partial t}\right)_{col}$$
(1.3)

where  $f(\vec{x}, \vec{v}, t)$  is the particle distribution,  $(\partial f / \partial t)$  is the collision term,  $\vec{a}$  and  $\vec{v}$  are particle accelerations and velocities, and  $\nabla$  and  $\nabla_v$  are del operators acting in position and velocity space respectively [19]. The zeroth velocity moment,  $\int (\widetilde{\mathbb{B}}) d^3v$ , defines the continuity equation for each species

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\vec{u}) = \frac{S_m}{m} = \int \left(\frac{\partial f}{\partial t}\right)_{col} d^3v$$
(1.4)

with species density  $n = \int f(v) d^3 v$ , average velocity  $\vec{u} = \frac{1}{n} \int \vec{v} f(v) d^3 v$ , and collisional mass source term  $S_m$ . In a similar fashion, the momentum and heat transport equations are found from the first,  $m \int (\vec{v} \widetilde{\mathbb{B}}) d^3 v$ , and second,  $\frac{1}{2} m \int (v^2 \widetilde{\mathbb{B}}) d^3 v$ , velocity moments respectively,

$$mn\frac{\partial(\vec{u})}{\partial t} + mn(\vec{u}\cdot\nabla)\vec{u} + \nabla\vec{\vec{P}} - nq(\vec{E}+\vec{u}\times\vec{B}) = \vec{S}_p = m\int(\vec{v}-\vec{u})\left(\frac{\partial f}{\partial t}\right)_{col}d^3v \qquad (1.5)$$

$$\frac{1}{\gamma - 1} \left( \frac{\partial p}{\partial t} + \nabla \cdot (p\vec{u}) \right) + (\vec{\vec{P}} \cdot \nabla)\vec{u} + \nabla \cdot \vec{L} = S_{\mathcal{E}} = \frac{1}{2}m \int (\vec{v} - \vec{u})^2 \left( \frac{\partial f}{\partial t} \right)_{col} d^3v \qquad (1.6)$$

after substituting the equations into each other. Analogous to  $S_m$ , the collisional momentum transfer  $\vec{S}_p$  and collisional heat transfer  $S_{\varepsilon}$  are found from velocity moments of the distribution time derivative with respect to collisions. Completing the equation, the pressure tensor  $\vec{P}$  and heat flux  $\vec{L}$  are defined as

$$\vec{P} = m \int (\vec{v} - \vec{u})(\vec{v} - \vec{u})f(v) d^{3}v \qquad \vec{L} = \frac{1}{2}m \int (\vec{v} - \vec{u})(\vec{v} - \vec{u})^{2}f(v) d^{3}v \qquad (1.7)$$

with scalar pressure defined through  $p\delta_{ij} = P_{ij}$  and  $\gamma$  is the ratio of specific heats. Energy is related to other macroscopic quantities through  $2\varepsilon = mn\vec{u}^2 + 2/(\gamma - 1)p$ . It should be noted that the use of macroscopic quantities averaged over the distribution implicitly assumes local thermodynamic equilibrium [139].

Unlike the kinetic formulation, the general fluid equations are not closed and the distribution is not found self-consistently. Demonstrating the closure problem, determining  $\vec{L}$  requires the third velocity moment of the Boltzmann equation. This problem lies in the inability to describe both momentum  $\vec{P}$  and heat  $\vec{L}$  fluxes in general and only in terms of macroscopic quantities; instead they require a prescription dependent on the physical regime and effects of interest [38]. Though higher-order closure methods exist, and are required for descriptions of turbulence [109], solution methods commonly rely on the first two or three moments, a declaration of distribution function, and approximative methods. Closure relations come from taking a hydrodynamic limit of the Boltzmann equation, commonly in the form of the Navier-Stokes equation by using Fourier's law for treating heat flux. These approximations and imposed distribution result in a loss of information relative to kinetic methods.

Depending on the regime of interest, approximations to terms in eqs. 1.4, 1.5 and 1.6 can drastically simplify simulation evaluation. The selection of which approximations, and hence forces to exclude, directly relates to both the accuracy and computational intensity of the simulation. As with PIC methods, species do not need to be declared in the same manner, neglecting small terms relative to differences in energy, mass, and reactive frequencies. A good set of relevant approximations can result in high-accuracy solutions at a considerably lower computational cost than kinetic methods. Approximations range from treatments of dimensionally-coupled force terms to reduction of the total number of PDEs required for simulating the system. Depending on the regime considered, the dynamics of some species can be neglected altogether. While the general equations above apply to all species, a two-fluid plasma model can be made when only considering electrons and ions [140]. This assumption forms the basis for the magnetohydrodynamic formulation [48].

Except in certain plasma regimes, such as for strongly magnetized systems such as in tokamaks [124], shear and viscous forces can be neglected [19]. The pressure tensor,  $\vec{P}$ , is then reduced to purely diagonal elements representing an anisotropy in the random velocities of species. Further neglecting any dependence on thermal conductivity, this combination results in an ideal compressible Eulerian system for closure relations. If the momentum transfer collision frequency is larger than the electric driving frequency, the drift-diffusion approximation can be made. This requires that inertia of the particles are neglected and assumes they respond instantaneously to external fields. Reducing the time derivative of the distribution to a relaxation time from an equilibrium,  $(\partial f/\partial t) \approx (f_{eq} - f)/\tau$ , introducing species mobility,  $\mu = q\tau/m$ , neglecting the magnetic field, and replacing the square velocity average with the equilibrium value,  $\frac{1}{n}\int \vec{v}^2 f(v) d^3v = e^{\frac{k_BT}{m}}$ , results in the simplified drift-diffusion formulation of eqs. 1.4 and 1.5 such that species and flux are defined as

$$\frac{\partial n_k}{\partial t} + \nabla \cdot \vec{\Gamma}_k = \frac{S_m}{m} \tag{1.8}$$

$$\vec{\Gamma}_k = \mu_k n_k \vec{E} - \nabla (D_k n_k) \tag{1.9}$$

for each species  $n_k$ , where the diffusion coefficient,  $D_k = \mu_k k_B T/q$ , comes from the Einstein relation [55]. These equations can provide analytic solutions and insight into complicated behavior when considered in reduced dimensions (e.g. ambipolar-diffusion from the drift diffusion formulation). Though these derivations do not assume an equilibrium distribution, the use of equilibrium velocity limits validity to small perturbations of the distribution from equilibrium.

The limits of fluid methods come from the approximations used to close the governing equations along with the methods used to solve them. Solutions to these PDEs are commonly found through the use of finite difference, finite element, or finite volume methods. Finite difference methods rely on representing derivatives through truncated Taylor expansions and allow the simplest implementation [67]. A variety of implicit (e.g. Crank-Nicholson) and explicit (e.g. Runge-Kutta) numerical methods can be used, each carrying their own limitations/restrictions [172]. Solving a major limitation of finite difference methods, finite element and volume methods are capable of complicated geometries from using unstructured grids. Finite element relies on the assumption of an approximate solution to the discretized problem with the method looking for a solution to the integral form of the PDEs through residual calculations [145]. Finite volume methods instead discretizes the integral forms of the equations, which becomes advantageous when the conservation laws can only be described in integral form [67]. While advantageous in situations with discontinuities, finite volume methods run into trouble when describing derivatives, limiting use to when viscosity terms can be neglected.

The wide range of approximations that can be made results in a surplus of fluid simulation packages for plasma applications. The general applicability of computational fluid dynamics has resulted in a number of general platforms which have been adapted to include plasma physics. Though a good number of codes remain in-house, a growing number have become available as open-source packages: plasmaFOAM [168] built from the openFOAM fluid dynamics framework for low temperature plasmas, BOUT++ [42] designed for curvilinear systems using computer architecture parallelization and ITM-TF [89], built on the open workflow system Kepler [36] and intended for analysis of ITER. Commercial applications include the COMSOL Plasma Toolkit [70], Tech-X's USim [32], and ESI's CFD-ACE+ [59].

#### 1.2.3 Hybrid

Expanding upon both methods above, hybrid simulation methods are made by combining kinetic and fluid methods. The intention is to get methods which have both accurate particle kinetics and the evaluation speed of fluid methods. As with fluid methods, the physics of interest dictates the pairing of particle species with solution method, with completely different overall descriptions. Electrons can be considered using PIC while considering a background ion fluid [146]. By comparison, studies on the ion energy distribution can treat ions with a PIC scheme and electrons as a background Maxwellian fluid [131]. Aside from the particle and fluid method limitations of each hybrid component, communication between the two methods must be given consideration, as reducing the time step size to the smallest requirement results in excessively long simulation times. The built in assumptions of hybrid models limits the ability for general-application software, however a number of codes are available such as Pegasus [95], designed for multi-fluid quasi-neutral astronomical plasmas, HPEM [97], designed for low-pressure plasma processing reactors, and HPHall-2 [125], designed for Hall-effect thrusters.

#### 1.2.4 Global/Chemistry

Volume-averaged global models represent the simplest forms of the plasma fluid description. Neglecting spatial variation requires a sizable number of approximation models and physical data to account for relevant physics while greatly reducing the computational intensity of evaluation. The simple description allows for emphasis on the scalar mass and energy flux terms,  $S_m$  and  $S_{\varepsilon}$ respectively. In order to speed up PIC and fluid methods, limited reaction chemistry is typically considered. This is not a problem when the dynamics of particle motion are the main interest, however applications in higher pressure gas mixtures depend on a non-linear collection of reactions which are not easily simplified *a priori*. With a minimal increase of computational intensity, continuity equations can be written for each considered species, coupled with one or more energy equations, to describe a complete picture of the plasma-chemistry interaction. Due to their inherent simplicity relative to other methods, global models are used for: fundamental studies of collisional effects on species populations, determining dominant reaction pathways to use in higher-fidelity solution methods, and analysis of reaction data sensitivity.

It is the emphasis on plasma-chemistry which makes global models ideal for exploratory analysis of low-temperature, high-pressure, nearly-homogeneous plasma systems. In these regimes, reactions between heavy species and electron-impact reactions both play an important role in system evolution. The number of distinct species required limits the applicability of a multi-fluid approach. Similarly, the number of reactions required for a complete picture would dramatically slow down kinetic methods. Not without their own caveats, global models require a large amount of reaction chemistry data paired with declaration of the energy distribution function. Along with continuity equations, energy equations can be derived for both electrons and heavy species. The energy distribution of heavy particles is commonly assumed to be in equilibrium, while the implementation of the electron energy distribution tends to separate global model platforms. Explicit selection of the electron energy distribution allows for algebraic electron impact rate coefficients, allowing for plasma global models using the chemical kinetics package CHEMKIN-III [85]. Codes such as ZD-PlasKin [123] and GlobalKin [41] represent some of the higher-fidelity global modeling softwares, coupling a Boltzmann equation solver for a self-consistent description of the electron distribution along with databases for electron impact reactions. Larger packages, such as PLASIMO [76] and COMSOL [70], are able to generate global models by reducing higher-dimensional descriptions. In many cases, the data used is restricted to pre-confirmed sets compiled by the code developers.

## **1.3 Kinetic Global Modeling Framework Motivation**

In the context of modeling systems with complicated plasma chemistry, global models are the best platform for developing an understanding of the species and reaction chain details of the underlying chemistry. The simplicity of the implementation further allows for the addition of new physics modules with relative ease. These modules are combined with the set of approximate spatial contributions which close the system of equations. The variable nature of approximations leads to a requirement of understanding implemented terms and the effect they impose on final solutions. What was found to be lacking in available software was the ability to modify reaction data, analytic approximation terms, and electron energy distributions along with easy avenues for dissecting contributing terms.

The data dependence of global models motivates the study of reaction data validity and system sensitivity. Multiple databases exist with different data describing the same process, differing by acquisition method or regime considered. The speed of global models should allow for quick replacement of data to quickly compare relative effects.

Analytic approximations have the capability of drastically altering simulation results. The assumptions built into these approximations tend to be extremely regime specific, requiring modification or replacement under different scenarios. Extending to the context of academic research, the incorporated models should be made transparent through open-source code. Even with the correct selection of approximations, the inclusion of new physics through additional terms should be made possible with minimal code alteration.

Finally, treatment of the electron energy distribution can dramatically change the underlying chemistry. While examples exist of global model software coupled to Boltzmann equation solvers, the approximations made to solve for the distribution are not always valid in considered regimes. For example, the common two-term approximation for the Boltzmann equation breaks down in systems with a large collisional mass flux (e.g. combustion). Even without a self-consistent description of the EEDF, sensitivity to energy distributions should be regularly considered, especially in systems with non-equilibrium chemistry.

Bringing all of these considerations to fruition required the development of a new generalpurpose global model platform with an emphasis on variation of assumptions and interactive usage.

#### **CHAPTER 2**

#### KINETIC GLOBAL MODELING FRAMEWORK

# 2.1 Introduction

In the last few decades, advances in computer architecture and scaling have drastically pushed the boundaries of what can be simulated of known physics. The study of plasma in particular requires the combination of electromagnetics, fluid dynamics, atomic and molecular collisions, and statistical mechanics in order to begin describing a physical model. There are three main components to a computational description of a plasma system: the environment and external forces, dynamics of the particles in response to their surroundings, and composition of the particle ensemble. Due to the high number of particles found even in a low pressure system, plasma simulations are performed using some type of approximating method to reduce the computational complexity as direct solve molecular dynamics simulations are usually not feasible. Fluid and Particle-in-Cell (PIC) methods remain the most common, for macroscopic plasmas, by simplifying the dynamics of individual particles into 'groups' while maintaining the complexity of transport and spatial variation.

Taking the extreme of low spatial resolution, global (volume-averaged) models reduce all spatial dependence to analytic approximations and provide a focused platform for studying reaction kinetics. Though the lack of spatial variations can lead to inaccurate results with regard to parameters of a specific simulated system, the intention is to study physical trends across variations of inputs. With the greatly reduced computational intensity of these simulations, global models can be used to map out a system's parameter space either in an exploratory manner or retroactively matching experimental results by iterating through possible input changes. An example of the latter is a "collisional radiative model" [141], wherein parameters of the global model are adjusted until a simulated spectrum matches that of an experiment. In the context of interest in high fidelity simulations, such as PIC, global models can be used to reduce the included reaction set to a minimized configuration maintaining relevant behavior.

The reaction kinetics of a given system describe the overall changes in particle densities and temperatures as a result of various forms of energy transfer. In the context of classical chemistry, this typically involves decomposition, displacement, and synthesis reactions involving molecular and atomic species. Plasma chemistry then expands the number of tracked species to include excited species created through processes such as electron impact ionization and excitation. Reactions involving electrons are herein referred to as 'plasma phase' whereas reactions between only heavy species are referred to as 'gas phase.' Further effects, such as diffusion or charge species absorption by sheaths, are treated through the use of approximate models. A reaction mechanism is then created by compiling a collection of all relevant reactions and effects involving species of interest, represented by a global model in the form of a coupled set of ordinary differential equations (ODE). While the simplest of models can include a handful of species and reactions, certain systems require hundreds of species and thousands of reactions for an accurate description.

#### 2.1.1 Overview of available software for global modeling of plasmas

Defined by a set of species continuity and energy conservation equations, required data and constructed global models are conceptually similar across most applications [78]. Due to the relative simplicity of smaller reaction mechanisms, it is common practice for custom code to be developed for each application; this results in a duplication of efforts which can negatively affect quality control and code maintenance. There otherwise exists a few published softwares for generating and evaluating plasma-chemistry global models; research codes such as PLASIMO [76], ZDPlasKin [123], and PLASMAKIN [128] and commercial options, such as COMSOL [70] and Quantemol-P [132] (based on GLOBALKIN [41]).

Global models have a rich history of use for studying the chemical kinetics of applications ranging from plasma-reactor etching/deposition systems employing different reactive discharges (e.g. radio frequency [100], inductively coupled plasmas [161], high power impulse magnetron sputtering [133]) to plasma assisted combustion [177] and Hall-effect thrusters [27]. With growing

interest in applying plasmas in biomedical, technological, and environmental applications, global models present an excellent opportunity for better understanding complex plasma chemistry interactions. While used for direct simulation of systems, the relative computational simplicity, as compared to spatially resolving codes, allows for quick sensitivity analysis [164] and experiment-matching iterative operation. Not only useful for research purposes, global models can be an invaluable tool for teaching chemical kinetics and building intuition about reaction network behavior. With a generality of application, access must be provided to both examine sub-components of underlying equations and to experiment with features and physics beyond the original design considerations. Closed-source codes, no matter how complex, do not offer enough flexibility due to an inability to modify methods. The use of global models as both a research tool and an educational platform calls for an open-source code written in an interactive language.

#### 2.1.2 Design

It should be evident that global models obfuscate quickly as the number of species and reactions increases. In order to handle these complexities, the Kinetic Global Modeling framework (KGMf) was developed with two primary goals in mind: 1) minimize confusion when trying to gather and compare data for a given reaction network and 2) provide a symbolic description of the global model allowing for data exchange, tuning, and the ability to incorporate custom effects into user modules. These two goals call for the creation of a local and self-checking database of reaction and species data, to be paired with multi-level symbolic equation generation. Secondary considerations during KGMf development were to: maintain as much operational flexibility as possible, allow for on-the-fly user interaction, and avoid redundant calculations.

The framework is written in Python, using Numerical Python (NumPy) [167], Scientific Python (SciPy) [79], Symbolic Python (SymPy) [117], Cython [12], and H5py [31]. The usage can be broken up into four stages:

1. importing of data into the local KGMf database for reference

- 2. gathering the set of relevant reactions and processes
- 3. generating symbolic and numerical forms of the global model equations
- 4. evaluation of the global model and post-processing.

In principle the first stage is only done with initial installation or with the addition of new data for the database. The second stage is initially performed automatically with regards to internal databases, generating two humanly-readable input files for model setup (herein referred to as reaction and simulation input files) and allowing for user truncation of the rate mechanism, addition of non-imported reaction data, selection of non-rate dependent options. The third stage is largely automatic; input files define everything from physics assumptions and pre-processing steps to the logic of the reaction network, allowing the KGMf to generate all symbolic equations and terms within an interactive Python instance followed by compilation into a callable form from generated C-code. The fourth stage involves integrating the system of ODEs in time, likely being performed multiple times with variations on inputs (from integration time to data used), and post-processing analysis by decomposing the ODE system into evolved components or collecting results from multiple integrations.

Taking advantage of the nature of Python, each user stage can be performed as a script or interactively via command line. While scripted usage has obvious benefits with regards to repetitive tasks, interactive use exposes KGMf subroutines, data, and results for plotting, symbolic manipulation and extraction (post-processing), and user additions beyond those natively supported by the KGMf. To bridge the gap between the two methods, each stage can be completed with a single function call or split into sections for analysis or tweaking.

# 2.2 Global Model Equations

Global models are composed of a set of coupled non-linear ODEs representing species continuity and energy conservation equations. Using the notation of the system state vector, *Y*, containing all evolving species densities, temperatures, and additional terms for which a differential equation is included, the global model system of ODEs, *F*, and corresponding Jacobian, *J*, are defined as

$$F(t,Y) = \frac{dY}{dt}$$
 and  $J(t,Y) = \frac{dF}{dY}$  (2.1)

By using a symbolic representation of F and all functions therein, the Jacobian is found using the standard derivative functions included in the SymPy library. Of increasing importance with the stiffness of F, J greatly improves integrator performance and is found by default in the KGMf routines.

#### 2.2.1 Continuity and Energy Conservation Equations

From a given species set and reaction network, a governing set of equations can be defined to describe the propagation of energy in a system. Evolution of each tracked species density,  $n_k$ , is described by a continuity equation of the form:

$$\dot{n}_k = \frac{dn_k}{dt} = \sum_i v_i^k K_i \prod_j n_j + (G - L)_k$$
(2.2)

where *i* sums over all reactions including species  $n_k$ ,  $K_i$  is the reaction rate for a given process, *j* creates a product of reactant species for reaction *i*,  $v_i^k$  is the integer growth or loss factor for species  $n_k$  from reaction  $K_i$ , and  $(G-L)_k$  represents gain and loss terms independent of the reaction network. If relevant to given system, the imposition of quasi-neutrality allows for electrons to be defined as the charged weighted sum of all ionized species, removing the need for an additional ODE.

Depending on the system being modeled, energy conservation equations are implemented to maintain physicality. From the assumption of thermodynamic equilibrium, all massive species are assumed to have the same rotational and translational temperatures. The energy conservation equation for this shared gas temperature is defined as:

$$\frac{dT_g}{dt} = \frac{-T_g \sum_{k=1} \left( \hat{H}_k(T_g) - 1 \right) \dot{n}_k + \dot{Q} + \dot{P}_{\text{proc}}}{\sum_{k=1}^N \left( \hat{C}_{p_k}(T_g) - 1 \right) n_k}$$
(2.3)

where  $T_g$  is the gas temperature in kelvin, k sums over all tracked species,  $\hat{H}_k = H_k/RT_g$  and  $\hat{C}_{p_k} = C_{p_k}/R$  are the species specific enthalpy and specific heat in normalized NASA polynomial format [24],  $\dot{Q}$  represents external heat flux, and  $\dot{P}_{proc}$  represents heat flux from thermodynamic process (e.g adiabatic) energy transfer. It should be noted that  $\dot{n}_k$ , in eqs. 2.2 and 2.3, represents the full continuity equation for species  $n_k$ , resulting in a large expression as the number of species increases. This equation is derived in appendix A.1. Though appropriate for massive species, electrons usually have a different temperature from the background gas and can be far from having a Maxwellian distribution. Completing the energy picture is a description of the effective electron temperature,  $T_e$ , from the electron energy equation,

$$\frac{d}{dt} \left[ \frac{3}{2} n_e T_e \right] = \frac{P_{abs}}{V} - n_e \sum_i n_i K_i \Delta E_{ij} + \dot{Q}_e \tag{2.4}$$

defined as the sum of absorbed power,  $P_{abs}$  (in power density units with volume, V), the kinetic energy lost during electron impact reactions, and kinetic energy lost to the system from electron absorption,  $\dot{Q}_e$ . The second term is defined as the sum over all electron impact reactions of the product between larger species' potential energy flux,  $\Delta E_{ij}$ , and average reaction frequency, from the product of reaction rate,  $K_i$ , and involved reactant electron,  $n_e$ , and large species,  $n_i$ , densities. In the case of momentum transfer reactions, a modified form of  $K_i\Delta E_{ij}$  is constructed from reaction cross section and involved electron energy. This equation is solved for  $dT_e/dt$  using the product rule, resulting in the electron continuity equation,  $dn_e/dt$ , appearing on the RHS as in eq. 2.3. The inclusive repetition of ODE equations is used for function optimization prior to compilation.

It should be noted that terms such as  $\dot{Q}$  in eq. 2.3 and  $P_{abs}$  in eq. 2.4 are not restricted to a constant value and can instead be defined as functions of time and/or the state vector Y. While there are included methods to provide time dependent pulsing terms (square, gaussian, etc.) and other known forms of external effects (e.g. microwave power absorption dependent on both electron density and electron-neutral collision frequencies [120]), any analytic expression can be used through symbolic substitution.

#### 2.2.2 Reaction Rates

By their construction, global models are entirely data driven with regards to the reaction rates making up the majority of the continuity equations. These rates represent a wide range of processes, with defining data found through both empirical fitting and theoretical calculation, resulting in multiple forms of mathematical expressions. Data for these expressions ranges from constant values and parameterization to numerical function convolution with an excited species energy distribution function. Relying on data availability, the KGMf was designed to keep as much flexibility and variability as possible for both physical accuracy and integration error handling.

The range of both gas and plasma phase chemistry covers a large number of different uni-, bi-, and termolecular processes. Gas phase chemistry is largely responsible for mass transfer between species, either through synthesis or decomposition reactions, potentially affecting the gas temperature. Plasma phase reactions diversify gas species into ionized, electronic, and vibrationally excited levels resulting in spontaneous emission and charged species accumulation. Though data for reactions can be stored in a multitude of forms, they can all be thought of as either expressions of system parameters/terms or cross section convolution with an energy distribution function.

#### 2.2.2.1 Rates as Symbolic Expressions

The more directly handled rates are those that follow a specific analytic form with the ability to differentiate symbolically. The majority of empirically found rates, both in gas and plasma phase, are fitted with the modified Arrhenius temperature dependence equation:

$$K_i(T_a) = A_i T_a^{\beta_i} \exp\left\{\left(\frac{-E_i}{R_c T_a}\right)\right\}$$
(2.5)

where  $A_i$ ,  $\beta_i$ , and  $E_i$  are fitted numerical values,  $T_a$  is the temperature (either  $T_g$  or  $T_e$ ), and  $R_c$  is either the universal gas constant, R, or Boltzmann constant,  $k_B$ , depending on the unit balancing required. The simplest usage of eq. 2.5 is for constant rates, setting all but  $A_i$  to zero, while more complex terms can be used depending on data availability. If changes in enthalpy,  $\Delta H$  and entropy,  $\Delta S$ , are known for involved ground state species, the reverse reaction rate,  $K_{ri}$ , is defined as:

$$K_{ri} = \frac{K_i}{K_{c_l}} = K_i \left[ \exp\left\{ \left( \frac{\Delta S_l^0}{R} - \frac{\Delta H_l^0}{RT} \right) \right\} \left( \frac{P_{atm}}{RT} \right)^{\sum_{k=1}^{N} v_{k_i}} \right]^{-1}$$
(2.6)

using the change in the Gibbs free energy for the reaction, where  $K_{c_l}$  is the equilibrium rate, R is the universal gas constant,  $P_{atm}$  is the pressure at one atmosphere, and  $\Delta S_l^0$  and  $\Delta H_l^0$  represent changes in entropy and enthalpy respectively [52]. Recombination reactions are considered as a collision of two reactants, the high-pressure limit  $k_{\infty}$ , or as a three-body reaction with another species participating as a collisional partner, the low-pressure limit  $k_0$ . The arbitrary pressure reaction rate is defined using the Lindemann approach [105]:

$$K = k_{\infty} \left[ \frac{P_r}{1 + P_r} \right] F \quad \text{with} \quad P_r = \frac{k_0 [M]}{k_{\infty}}$$
(2.7)

where the Arrhenius rates for each limit are related to the reduced pressure  $P_r$ , and equivalently the gas mixture density. In the Lindemann form, F is set to unity, however increased flexibility can be achieved with the addition of Troe [163] and SRI International [156] forms of F as data dependent parameterizations of gas temperature and reduced pressure.

To account for other parameterizations existing in the literature, the KGMf supports expression parsing from the reaction input file or the addition of symbolic rate expressions composed of system variables prior to compilation. All expressions used within the KGMf retain their variable dependence in order to generate a system Jacobian and to be accessible for post-processing analysis as functions.

#### 2.2.2.2 Reaction Rates Computed from Cross Section Data

When cross section data is available for a given process and the impact particle energy distribution is known, the rate is defined as a convolution of the impact velocity  $v(\varepsilon)$ , reaction cross section  $\sigma(\varepsilon)$ , and energy distribution function (EDF)  $f(\varepsilon, \tilde{Y})$ :

$$K_{i}(\tilde{Y}) = \int_{0}^{\infty} \mathrm{d}\varepsilon \, \mathrm{v}_{\alpha}(\varepsilon) \sigma_{i}(\varepsilon) f_{\alpha}(\varepsilon, \tilde{Y})$$
(2.8)
where  $\varepsilon$  is the relative impact kinetic energy approximated as the absolute impact species energy and  $\tilde{Y}$  can represent any expression composed of state vector components (e.g.  $T_e$  or the ionization fraction,  $n_e/n_{total}$ ). Though most commonly used with electrons as the energetic impact species, the KGMf supports cross section defined ion impact reactions through EDF declaration for any charged impact species. Since electron impact reactions are prevalent in global model reaction networks and the effective electron energy evolves with a conservation equation, the rest of this work will discuss convolved rates as being functions of the electron energy distribution function (EEDF), however it all applies to any rate defined through a cross section and an associated EDF. Cross sections can be defined either numerically or analytically and, analogously to eq. 2.6, cross sections for reverse inelastic excitation processes can be calculated using the principle of detailed balance [112].

The largest present caveat with the KGMf is the lack of a Boltzmann equation solver for a self-consistent evaluation of the EEDF. Though presently fixed with regards to a given system, the KGMf supports dynamic EEDFs through parameterization of one evolving system term. Without extra parameterization of the EEDF beyond  $\varepsilon$ , the convolved rate reduces to a constant value. An external Boltzmann solver, such as BOLOS [110] or BOLSIG+ [60], can be used to generate numerical EEDFs. Multiple generated EEDFs can be a function of some variable, such as  $T_e$  or the ionization fraction, or analytic expressions can be used, such as the generic form [120]:

$$f_e(\varepsilon, T_e, x) = \frac{x\varepsilon^{\frac{1}{2}}}{(\frac{3}{2}T_e)^{\frac{3}{2}}} \frac{(\Gamma(\frac{5}{2x}))^{\frac{3}{2}}}{(\Gamma(\frac{3}{2x}))^{\frac{5}{2}}} \exp\left[-\left(\frac{\Gamma(\frac{5}{2x})}{\Gamma(\frac{3}{2x})}\frac{\varepsilon}{\frac{3}{2}T_e}\right)^x\right]$$
(2.9)

where  $T_e$  is used as the evolving parameter, x is a fixed shape parameter (x = 1 corresponds to a Maxwell-Boltzmann distribution, x = 2 yields a Druyvesteyn distribution, etc.), and  $\Gamma$  is the gamma function. In either case, reaction rate convolutions are performed for a range of values of the parametrized variable as a pre-processing step. These convolution results are then converted into either third order b-splines or PCHIP-splines, as functions of the parameterization. These splines are used to maintain continuous derivatives, using the Cox de-Boor recursion formula [20], for use within the system Jacobian. Though not entirely self-consistent, this method is accurate assuming the EEDF does not evolve beyond the scope of the chosen parameterization.

#### 2.2.3 Additional Physics Effects

Extending beyond reaction rates, the KGMf contains a few different modules for including terms for pseudo-spatial effects and non-standard processes. In the simplest form these contribute to the (G - L) terms in eq. 2.2, however, they can extend with the addition of new species in the state vector, Y, and corresponding continuity equations into the ODE system, F and J. Aside from whatever methods are used to acquire reaction data, these modules encapsulate the majority of assumptions found within the global model reaction network. Though the modules discussed below are incorporated into the KGMf source code, methods exist for a user to use custom modules through specification in the simulation input file without requiring source code modification.

#### 2.2.3.1 Pseudo-spatial Effects

Since global models are inherently independent of spatial characterization, effects due to geometrical configuration, gradients, and gas flow must be approximated. Two such native examples are the flow and sheath/diffusion modules. The flow module adds rates corresponding to inflow of sourced species and outflow of all species from the system with assumed flow rates and a linear flow progression across the global model system. Excited neutral species diffusion is treated as a function of mass, gas temperature, neutral collision cross section, and a characteristic diffusion length of the assumed geometry. If a plasma sheath profile can be derived analytically or fit to an experiment or spatial simulation, losses of charged particles  $n_c$  due to a plasma sheath can be described as:

$$L_{sheath} = u_B n_c g(h_{cS}, A, V) \tag{2.10}$$

where  $u_B = \sqrt{(eT_e/M_c)}$  is the Bohm velocity,  $h_{cS}$  is the edge-to-center density ratio of species  $n_c$ , *g* is a function of area *A*, volume *V*, and sheath density ratio [53].

The form of *G* largely depends on the system and the method of determining the sheath profile. Analytical expressions are typically found assuming constant ionization of a single species without electron-ion recombination. Though this assumption breaks down with higher gas pressures, higher pressures also result in the charged species flux terms becoming negligible, countering the inaccuracy. For example, Godyak and Maximov [53] derived analytical expressions for  $h_{cS}$  and *g* as functions of length, radius, and ion-neutral mean free path in the context of a low-pressure discharge and cylindrical geometry.

#### 2.2.3.2 Non-standard Processes

Unlike the relatively simple spatial terms, the inclusion of some effect modules requires the treatment of new evolved species along with their corresponding equations. A simple example is the specification of plasma voltage and current,  $dV_p/dt$  and  $dI_p/dt$  respectively, when the system is powered with a circuit model. A more complicated example is the module for optical pumping and stimulated emission. Following the derivation of a two-way averaged plane-wave model [179] for a three-level laser system, the intracavity intensity,  $\Psi$ , is tracked as an evolved species with its corresponding continuity equation:

$$\frac{d\Psi(t)}{dt} = (t_L R_m \exp\{[2\beta]\} - 1)\frac{\Psi}{\tau_{rt}} + n_2 \frac{\sigma_{21}c^2 h v_{21}}{l_g}$$
(2.11)

where  $\tau_{rt}$  is the residence time,  $t_L$  is the transmission coefficient,  $R_m$  is the mirror reflectivity,  $l_g$ is the gain length,  $\sigma_{21}$  is the optical emission cross section between states  $n_2$  and  $n_1$ , and  $\beta = l_g \sigma_{21} (n_2 - \frac{g_2}{g_1} n_1)$  is the laser gain. In this notation,  $n_1$  is the bottom level,  $n_3$  is the pumped level, and  $n_2$  is the lasing level with tracked output for the  $n_2 \rightarrow n_1$  transition.

# 2.3 Process of Operation

As mentioned before, usage of the KGMf can be broken into two pre-processing stages, a system setup stage, and an evaluation stage. The creation of the local KGMf database and generation of

model input files are the two large pre-processing steps for using the framework. Both attempt to simplify the process of building confidence in a reaction set by using automated selection methods, human confirmation, and computer sanity checking. The local KGMf database provides a foundation of trusted species and reaction data which can be accumulated from a wide variety of data sources. Due to potential differences in formatting, syntax, methods, and data type provided from each data source, the KGMf database uses (automated) methods to map related data for quickly gathering everything of relevance or detailing similarities and differences between overlapping datasets. Not only does this reduce the number of data-mismatch mistakes, the mapping is used to generate reaction and simulation input files with self-consistent checking. After user modification of the model input files, the third stage of setting up the system of equations for the global model is largely automatic relative to the user. Finally, the last stage incorporates evaluating the system of equations and post-processing of terms and results.

#### 2.3.1 Data Acquisition and local database

At the core level, the KGMf is designed for simulating a reaction network between a set of species. Though extra modules are considered for approximating external effects and spatial variance (e.g. flow diffusion, wall/sheath losses, etc), almost all data usage corresponds to the rates, or frequency of effect, for reactions involving one or more species as reactants and products. Regardless of project scale, physically realistic simulations depend on multiple types of data usually found from different sources. Adding the prospect of comparing data from multiple sources and varying chemical species makes for complicated bookkeeping. A benefit of the KGMf is the ability to maintain a local database of species and reaction data by combining generic datafile parsing routines and consistency checking into a file-and-forget reference of trusted species and reaction data.

With regards to plasma phase reaction data, generic parsing routines are used to import and convert data regardless of source database format. Routines are selected based on expected data type, known keywords, and formatting similarities to industry standards (NIST, LXcat, and CHEMKIN) and output is saved into a known internal format in standard units. This is predominantly composed of reference data from the NIST ASD/MSD database [92] being compared against cross section database files. This process eliminates manual entry error and guarantees unit consistency when using data from multiple sources. Data is organized and stored by major species, element or molecule, allowing for overlapping/redundant data from different sources and compressed dictionary accessing. For each major species, a reference dataset is created from the energy structure of excited levels to which all other datasets will be mapped (First half of listing 2.2). The reference dataset is used to check parsed-in rates when values are missing (e.g. threshold reaction energy for an inelastic collision) and to determine group state reactions (e.g. inelastic excitation to an entire orbital level, requiring degeneracy splitting between individual excited species).

Though accumulation of data into the KGMf database is largely automated and only needs to be performed once for a given database file, user confirmation that all data has been loaded correctly is recommended before first use. Aside from checking saved data and mapping files, plotting routines are used to show data truncation, grouped states, and possible gaps in the overall description (fig. 2.1 generated by the later half of listing 2.2).

#### 2.3.2 Model Source Generation

In the context of the KGMf, a given model is a combination of two model input files (simulation and reaction files) and relevant data. The reaction input file is composed of three listings: species involved in reactions, species variable mapping (e.g. pseudo species representing a combination of ODE species), and reactions involving species with explicit or referenced unique rate data. Defining only the reaction network, the reaction input file is completely independent of geometry and physical approximations to be used. The simulation input file provides configuration for KGMf modules, such as incorporating sheath losses or lasing, ODE parameters (e.g. fixed or free species declaration, initial conditions, etc.), and reference data overwriting (e.g. substituting values for energy levels). Both of these files are human readable and possible to create from scratch, however automatic generation methods are included for convenience and to reduce human error. Examples of input files are explained in Appendix A.2.



Figure 2.1 Cross section data for Ar excitation from the LXCat IST Lisbon [71] database. Horizontal lines are species energy levels, vertical lines are electron excitation reactions, dashed lines are radiative reactions, and red boxes highlight incomplete orbitals or orbitals constructed from grouped excitation.

```
import src
# Species mapping
mapper = src.KGM_exe.mapping_species.SpeciesMapping.MappingPureKGMdata()
savename = 'Cross_LXcat__LX_IST_Lisbon_all.txt_Ar.npz'
mapper.MapSpecies('Ar',savename)
# Plotting of DB mapping
data_plot = src.KGM_visualize.PlotMapping.PlotPureSpeciesMapping()
layout_dat = data_plot.All2PrepPlot('Ar',savename)
flat_data = [subelem for elem in layout_data for subelem in elem]
handle = data_plot.PlotLayout(flat_data,tit='LXcat IST Lisbon Ar Data')
```

Figure 2.2 Single data mapping for Ar with Biagi data

```
import src
# Model generation
generator = src.KGM_exe.model_gen.SpeciesModeling.GeneratePlasModelFiles()
generator.AllPLASProcessing(['Ar'],DBstyle='Biagi',Save=True)
# Inner access for debugging
#maplist = generator.LocateDataSources(['Ar'],DBstyle='Biagi89')
#gatdat = generator.GatherSpeciesData(maplist)
#out = generator.GeneratePlasModelFile2(gatdat,maplist,save=False)
```

Figure 2.3 Model generation for Ar with Biagi database [16].

Taking advantage of the KGMf database of previously mapped species data, generic model input files can be generated automatically. In the purely plasma phase case, a user specifies which major species are used and from which mapped source to pull reaction data, listing 2.3. This results in input files incorporating every relevant reaction from the KGMf database, which takes into account species decomposition and the expansion of the excited states. The inclusion of gas phase reactions is done by parsing CHEMKIN-like mechanism and thermo files [85], which are then mapped on the fly to the excited species in the local KGMf database. More advanced methods can be used to: truncate energy levels of interest, use multiple data sources to fill reaction gaps, and alter mapping between gas-phase and plasma-phase species. These automatic methods extract the relevant data from the KGMf database and compress them into a reaction data file, which no longer needs reference to the main database and can be packaged with the input files for portability across multiple machines.

The input files can then be easily edited to alter species of interest, ignore certain reactions, or add reactions which were not included in the KGMf database. In the same manner as would be done when not using the KGMf database, extra reaction data files can be created and linked to reactions in the reaction input file.

## 2.3.3 Preparing for Evaluation

As was alluded to previously, the system of equations defining the global model is first set up symbolically and then rendered into a callable function. Resulting in a compiled version of the

ODE system, this setup only needs to be done once for a given reaction mechanism and can otherwise be referenced during later evaluation. First a generic system of equations is created which is dependent solely on the reaction network being used, equivalently expanding continuity equations with symbolic place holders for each term. This generic system creates the symbolic skeleton from which a data dependent symbolic system is created. Rates which are defined via expressions are simply substituted for their placeholder symbol while rates defined by convolution are wrapped as SymPy generic symbolic functions. These symbolic forms are created to: generate a symbolic Jacobian for the extremely stiff system of ODEs, take advantage of existing functions in SymPy to generate Cython wrapped c-code and to use as reference during post-processing. Since any collection of symbols and terms is accessible as a function, the user is able to follow the symbol substitutions to look at how any term evolved within ODE integration.

In order to speed up both compilation and evaluation time, the KGMf takes advantage of the known symbolic structure to optimize the generated C-code. Since nearly every reaction will appear in multiple continuity equations, and some continuity equations contain others in their entirety, the symbolic system is recursively processed for common-sub-expressions to be evaluated separately. This implies that no collection of operations is ever performed multiple times in a single function call to either the ODE system or the Jacobian. Reducing the operation count by over an order of magnitude, paired with optimization flags for the compiled C-code, results in a significantly faster evaluation time than remaining in pure Python.

Finally, the ODE system and Jacobian are each wrapped into Python functions broken into two steps that occur with every call. For a given set of parameter values at some time step, all of the spline rate coefficients are evaluated in a vectorized form. These rate values, paired with the parameter values, are then passed to the compiled code to yield the differential change for each tracked species.



Figure 2.4 KGMf flow chart of the latter three user stages. Standard usage involves modifying control text files for extra reactions and system parameters, while every section is accessible for modification in a Python instance. Red dashed lines mark the future work of incorporating a Boltzmann equation solver.

#### 2.3.4 Evaluation and Usage

Acknowledging the potential stiffness of the equations, the Python wrapped ODE system and Jacobian are integrated in time to describe the overall evolution of species densities and energies. Presently native KGMf functions exist for using SciPy's various integrators under *odeint* and *ode* (see listing 2.5), however the functions can be passed by reference to any integrator library. While the default is to use *odeint* for convenience, usage of the *ode* class allows for on-the-fly analysis (e.g. termination upon reaching steady state) and dynamic time-stepping for handling extremely stiff problems.

Figure 2.5 Basic KGMf integrator usage.

## 2.3.4.1 Interactive Usage

Since the symbolic versions of the species continuity and energy equations are created from the reaction input file, references to symbols, and symbolic expressions, can be used for post-processing. In a similar manner as to how the system of symbolic ODEs can be converted into a callable numeric function, any expression composed using the same symbols can be rendered callable. This allows for visualization of numeric and analytic rates, along with rate terms (including the product of reactant species), being compared to the overall system evolution. This capability is invaluable to both developing an understanding of dominant reactions and determining if reaction data is correct.

#### 2.3.4.2 Batch Operation

Aside from being able to access the symbolic equations of the global model, at various points during the middle two stages, hash values are generated corresponding to macroscopic (e.g. full reaction input file) and microscopic (e.g. selection of EEDF) quantities in order to determine recovery points. During cases when a simulation is running multiple times with varying inputs, the integer hash values are used to quickly determine which of the previously saved data can be reused. This could be as simple as a change in initial condition, which would result in the same final Python wrapper being evaluated, or as involved as redefining the EEDF, which results in new numerical reaction rates being found and wrapped with the previously compiled C-code. Due to the reduced evaluation time from pre- processed reaction rates and recovery points, batch parameter scanning

and target value search methods can be used over relatively large search spaces.

## 2.4 Example Usage with Verification

In order to instill confidence in the KGMf and to demonstrate functional capabilities, a few example models are included with the KGMf for tutorial and verification purposes. In the simplest configuration, these models provide a sandbox for familiarization with input files and interactive usage, while packaged input files attempt to cover the range of possible inputs and called modules. Two systems in particular are used as verification of the plasma and gas phase chemistry methods: a recreation of the argon plasma global model presented by Ashida, Lee, and Lieberman [4] and an example of classical combustion using the validated GRI-Mech 2.11 reaction set [143] recreating an original validation case [29].

A script within the main KGMf directory, "quick\_rebuild.py" is used to populate a local database, with packaged data files from NIST [92], the Biagi v8.97 dataset hosted on LXCat [16], and to generate models for demonstrating code capabilities and verification. Example scripts and supplemented control files are located within the examples sub-directory "data/Example\_Source/".

#### 2.4.1 Plasma Verification

The work by Ashida et al. focused on studying "*the behavior of argon plasmas being driven by time modulated power*" using a global model. With an emphasis on plasma reactors, a cylindrical geometry is assumed with a microwave-driven plasma composed of argon in the ground, ionized, and electronically excited states truncated to include the 4p level. With a constant gas temperature, this system is used to verify implementations of plasma chemistry components and eq. 2.4. Published with two modeled species representing the grouped four 4s and ten 4p energy levels, KGMf comparison is performed with a faithful-recreation model and a model having distinct species for each energy level. In the first case, Arrhenius fitted reaction rates are used from the original work, while in the latter case, cross sections from the LXcat-hosted Biagi v8.97 database [16] are used

in conjunction with an assumed EEDF for each electron-impact reaction.

Example files are included in the KGMf to completely recreate the original work using both models; control files for each model along with scripts demonstrating generation of a base model, interactive usage, batch running configuration, and access of batch saved data compressed with H5Py. With a pressure of 5mTorr, gas temperature of  $T_g$ =600 K, and reactor with dimensions of R=15.25cm and L=7.5cm, four different absorbed power assumptions are tested: continuous wave to steady state, square wave, smooth change (square with coupled sinusoid segments to soften edges), and square with nonzero"off". In the latter three cases, multiple runs are performed using differing duty ratios and periods while maintaining the same total absorbed power. First looking at the transient behavior of the plasma, fig. 2.6 shows the originally published results (fig. 1.b) along with the faithful recreation and model with cross section data and an assumed Maxwellian EEDF. Though in very good agreement, differences between the original and faithful recreation can be attributed to rounding differences on reaction threshold energies and initial conditions passed to the integrator.

Exactly the same reaction pathways are allowed between the faithful recreation and the model using cross section data, the reaction rates differ due to both cross section data and functional representation. Ashida et al. used rates from the work by Kannari et al. [83] which relied on modified Arrhenius rate fitting of semi-empirical and experimental cross sections, from the 1960s and 70s, being convolved with a Maxwellian EEDF. By comparison, the second model relies on cross section data updated in 2002. The difference between rate implementations is highlighted in fig. 2.7 which plots the reaction rate for argon ionization from ground versus the effective electron temperature. For the pressure and temperature considered in the original work, a Maxwellian EEDF is a valid assumption, but for the purposes of better understanding the effects of the assumed EEDF, examples include batch runs with both Maxwellian and Druyvestyn distributions, with square wave time averaged results compared in fig. 2.8. As opposed to needing to find new rates in the literature which assume a specific EEDF, rates are convolved using the same cross section data, guaranteeing consistency.



Figure 2.6 Transient square wave behavior for a period of  $\tau = 100\mu s$ , duty ratio of 25%, and 500W of total absorbed power from: the original paper (x markers), faithful model with guessed unreported parameters (dotted) and tuned parameters (solid), and recreation with cross section dependent rates (dashed).

Example scripts relating to recreating the work by Ashida et al. are denoted with "\*VV\_ALL.py". Control files are located within the "BASIC\_PLAS\_\_Ar" generated model directory with "\*control\*" and "\*reALL\*" denoting the faithful model and KGMf recreation respectively.

## 2.4.2 Gas Phase Verification

Verifying the implementation of gas-phase chemistry components and eq. 2.3, example models for classical  $CH_4$ - $H_2$ - $O_2$ -Ar combustion are generated from the GRI-Mech 2.11 mechanism. Though more modern mechanisms exist, such as GRI-Mech 3.0 and NUI Galway [126], GRI-Mech 2.11 is small enough for quick validation while demonstrating caveats of an incomplete mechanism relative to pressure and temperature regimes. Due to the mass exchanging reactions (between major species), the defining system of ODEs for a given gas-phase model can be extremely stiff and require special care to integrate in a stable manner. Especially when the gas temperature equation is coupled with species continuity equations, values of the ODE state vector can range by



Figure 2.7 Argon ionization rates defined with: Arrhenius rate used by Ashida et al. (solid black) and KGMf spline implementations for convolutions of an assumed Maxwellian EEDF with cross sections from: the LXcat Biagi database (solid blue) and estimates of the cross section extracted from a figure in the Arrhenius rate source [127].



Figure 2.8 Comparison between results from different assumed EEDFs. With duty ratios of  $10\% \le \alpha \le 50\%$ , the faithful model is plotted in black while the cross section dependent model for a Maxwellian (*x* = 1) and Druyvestyn (*x* = 2) EEDFs are in blue and green respectively.



Figure 2.9 Example output a  $CH_4$ - $O_2$ -Ar mechanism with 90% argon and a stoichiometric fuel/oxidizer mixture initiated at a pressure of 1 atm and temperature of 1400 K.

over twenty orders of magnitude, as can be seen from fig. 2.9, resulting in a sensitivity to integrator parameters, time steps, and initial conditions.

The first gas phase model to be considered is a replication of the experimental work by Cheng et. al [29] which was used by the GRI-Mech group for mechanism validation. Using a shock tube, autoignition induction times (ignition times) were found for a variety of gas mixtures covering pressures of 1 to 3 atm and temperatures of 800 to 2400 K. An induction time correlation formula was fitted with dependence on fuel and oxidizer densities, ratio of H<sub>2</sub> and CH<sub>4</sub>,  $\zeta$ , and equivalence ratio,  $\phi$ 

$$\tau[\mathrm{CH}_4]^{0.48(\zeta-1)}[\mathrm{H}_2]^{-0.14\zeta}[\mathrm{O}_2]^{1.94-1.38\zeta} = (1.19e - 12)^{(1-\zeta)}(1.54e - 4)^{\zeta} e^{\frac{46.4 - 29.2\zeta}{\mathrm{RT}_g}}$$
(2.12)

where *R* is the universal gas constant and [\*] denotes species density in units of mole/cc. While example scripts generate models which compare against each of the eleven different gas ratios used by Cheng et al. and recreate the four published induction time plots, herein we present a recreation of the case with fuel defined as 66%CH<sub>4</sub>-33%H<sub>2</sub> ( $\zeta = 1/3$ , denoted as mixture number 3 in the original work). Fig. 2.10 plots the original experimental data, fitting function eq. 2.12, and scaled



Figure 2.10 Density-scaled ignition delay times for a mixture of CH<sub>4</sub>-O<sub>2</sub>-Ar combustion with  $\zeta = 1/3$ . Experimental data points were extracted from figure 5 in [29], the black line is the reported fitting function, and the blue line represents scaled estimates from the KGMf recreation model.

ignition times from the KGMf model for a range of initial temperatures and initial pressure of 1 atm. Since pressures were not defined for each point in the original work, the y-axis is scaled with species densities matching fig. 5 presented by Cheng et al. The deviation of the fitting function from the experimental data points can be explained by both their extraction from the original work and the fitting originally done with two different gas mixtures.

Similarly to the plasma model, a script is provided to integrate multiple conditions and generate curves for ignition delay times to compare with original mechanism validation work [29]. Example scripts for the GRI-Mech 2.11 validation models are denoted with "\*VV\_GRI.py". Control files are located within the "GP\_GRI\_Ar\_CO2\_CH4" generated model directory with "\*cheng\*" denoting original validation tests.

## 2.5 Conclusion

Due to interest in using global models for the study of kinetic plasma systems, the KGMf was developed for analysis of mixed-phase chemistry as both a tool for research and an educational platform. Implementation in Python allows for both scripted and interactive usage while remaining open-source allows for user contribution to development and guaranteed reproducibility. In using a symbolic description, the KGMf is able to: import user-defined analytic terms, automatically calculate global model Jacobians, minimize the operation count of evaluation, and provide access to sub-components of the numerical system. With the largest caveat of global models being data dependence, the KGMf was designed to quickly compare the effects of different data sources and assumptions. The design of KGMf allows for the addition of new physics, as demonstrated by the laser model. While operable in nearly a fully automatic manner, treatment of global models as initial value problems requires system specific tuning with regards to integrator parameters and initial conditions.

Examples are included to demonstrate KGMf features and both verification and validation of generated models in two contexts. Verifying species continuity and electron temperature equations, the modeling work by Ashida et. al [4] was recreated with originally published data as well as with cross section and EEDF declaration. This tested the implementation of conservation equations and time-dependent power absorption envelopes (constant, square, and smooth square) using an argon gas at 5mTorr. Requiring tuning for unpublished parameters, KGMf matched the published global model well aside from integration equilibration from incorrect species initialization. Using different data sources and explicit representation of states demonstrated variation in results from disagreement between experimental and analytical data. Agreeing with mechanism validation efforts by GRI Mech [143], the KGMf was used to model methane combustion at atmospheric pressure as reported by Cheng et. al [29]. Modeling results agreed with experimental results in systems with high initial hydrogen concentrations; methane systems agreed qualitatively however, demonstrated longer ignition times than originally reported. This is attributed to low chain branch-

ing rates associated with hydrogen radical generation.

# 2.6 Acknowledgments

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#### **CHAPTER 3**

## PLASMA-ASSISTED COMBUSTION WITH KGMF

# 3.1 Introduction

The study of plasma-assisted combustion (PAC) and plasma-assisted ignition (PAI) is motivated by the goal of optimizing combustion characteristics for novel engine concepts. The generality of this statement lies with the different characteristics of interest for different applications, while developing a better understanding of the underlying chemistry applies to every scenario. For over a century, spark-ignition internal combustion engines have use thermal-equilibrium plasmas in the form of arc discharges; however, these discharges rely on localized gas heating to initiate and propagate combustion, and provide limited options for control of ignition process [115]. Starting in the 20<sup>th</sup> century, the use of non-equilibrium plasma for ignition and combustion has received interest due to possibilities for modified ignition pathways, flame stabilization, and byproduct control. The seminal work of Haselfoot and Kirkby [66] introduced the concept of electrical interaction with the combustion process, resulting in an explosion of work to study the physics involved and potential applications. More recently in the 1980s, the effect of non-equilibrium plasma discharges on combustion kinetics was demonstrated by the pioneering experimental works by Kimura et. al [87] and Behbahani et. al [11] with plasma jet applications to high speed propulsion and NO<sub>x</sub> destruction respectively.

A plethora of experimental studies have demonstrated characteristics of different discharges with different gas mixtures in different regimes, however, even with a growing list of methods that can be shown to benefit the combustion process, it remains unclear which plasmas are optimal for specific applications. While the literature contains multiple review papers on PAC/PAI studies and applications [152, 129, 153, 149, 1, 81], the largest gap in PAC/PAI theory that remains is an understanding of the intricacies of plasma-combustion chemistry. Numerical modeling presents an opportunity to dissect components of the PAC/PAI processes while neglecting or approximating

complexities which arise from completely coupled systems.

This work provides an overview of PAC fundamentals in the context of volume-averaged global modeling followed by an analysis of the kinetic reaction chemistry effects resulting from non-equilibrium plasma discharges. Starting with an introduction to classical combustion theory, this chapter then continues into the general motivation and fundamentals of PAC/PAI. Nanosecond discharges are chosen for modeling following the progression of experimental works highlighting the focused study of non-equilibrium plasma chemistry in the ignition process. Numerical modeling results follow a description of the specifics of the global model formulation and systems used.

# **3.2** Classical Combustion

Prior to the end of the 18<sup>th</sup> century, the concept of combustion relied heavily on the legacy of Greek philosophers to whom fire was a classical element. Developed formally by Georg Ernest Stahl (following the works of Johann Joachim Becher) phlogiston theory attempted to explain oxidation as the release of a fire-like element through the process of dephlogistication [175]. The lack of an explanation for reaction products having a larger mass than the original reactants, such as in the creation of metal oxides from heating metals in air, seeded doubt and eventually led to the theory's abandonment. While supporters attempted to define a negative mass of phlogiston in their defense, the root of the problem was in not knowing the composition of the air.

Starting with experiments in the 1770s attempting to explain the results of phlogiston-supporter Joseph Priestly, Antoine-Laurent Lavoisier determined that the composition of air contained a mixture of at least two gases: an inert gas and one on which combustion was reliant. The latter, found in most acids and supporting both respiration and combustion, he named "oxygène," from the Greek words for acid generator. With his public attack on phlogiston theory beginning in 1783 based in a demand for strict involvement of the scientific method, Lavoisier presented the modern foundations of combustion in his book *Traité élémentaire de Chemie* [99]. Though Lavoisier proposed empirical arguments, the development of a kinetic theory of gases, by James Clerk Maxwell and Ludwig Boltzmann in the 19th century, led to an explanation of the heat and energy involved in combustion.

Combustion is an exothermic chemical reaction incorporating both a *fuel* and *oxidizer*, complicated by a dependence on both mechanical and chemical processes. While a complete picture of the combustion process requires mechanical processes , such as mass and heat transfer, the scope of this work aims to develop an understanding of the chemical processes and demonstrate how plasmas might provide augmentation of combustion characteristics. In the context of volume-averaged modeling, these mechanical processes are handled with approximations (e.g. loss of particle density due to gas flow) as opposed to having fully-resolved dynamics (e.g. turbulent mixing of fuel and oxidizer). With the implementation of mechanical approximations discussed later, this section will provide a brief introduction to chain branching and explosion limits.

#### 3.2.1 Chain Reactions

Prior to delving into the methods by which plasma can affect a combustion process, it is important to first understand how these processes evolve in a classical context. Consider, for example, the stoichiometric global reaction describing the interaction between molecular hydrogen and oxygen:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

While descriptive of the overall process, this reaction does not exist as a single step. Instead, the combustion process relies on radical species, such as H, O, and OH, to propagate energy release. Describing the system adequately, independent of pressure regimes, requires eight species and sixteen elementary reactions. The inclusion of radical species, or chain carriers, in the reaction mechanism provides the dynamics of the combustion process. These elementary reactions support an equilibrium composition of reactants and products at a given temperature and pressure, allowing for a reverse rate to be calculated from the change in Gibb's free energy. In the limiting case of low pressure, a simplified mechanism of seven reactions adequately describes the system and

introduces the concept of chain reactions:

$$H_2 \xrightarrow{k_0} 2H$$
 (R.1)

$$O_2 \xrightarrow{k_0} 2O$$
 (R.2)

$$O_2 + H \xrightarrow{k_1} OH + O$$
 (R.3)

$$H_2 + O \xrightarrow{K_2} OH + H$$
 (R.4)

$$H_2 + OH \xrightarrow{K_3} H_2O + H \tag{R.5}$$

$$H + wall \xrightarrow{K4} 0.5 H_2 \tag{R.6}$$

$$H + O_2 + M \xrightarrow{\kappa_3} HO_2 + M$$
 (R.7)

where M is a collision partner representing any major species, therefore directly related to the overall system pressure, and  $k_*$  represent reaction rates. Without some amount of chain carrier species, the reaction mechanism would not progress through a combustion process due to a lack of used elementary reactions. These reactions fall into one of four categories with regards to progression through the chain reaction. Triggering the mechanism, *chain initiation* reactions, R.1 and R.2, providing an initial concentration of radical species. Reactions R.3 and R.4, classified as *chain branching*, further produce radical species for accelerating the mechanism. Classified as *chain propagation*, reaction R.5 produces the final product, H<sub>2</sub>O. Finally, *chain termination* reactions, R.6 and R.7, remove carrier species from the system.

When comparing the rates of the chain branching and propagation reactions, R.3 progresses significantly slower than both R.4 and R.5, resulting in O and OH radicals being consumed faster than H species. This means that H production determines the majority of the combustion mechanism propagation in the low-pressure regime. Other species become limiting factors as pressure increases due to different sets of reactions which become dominant.

#### **3.2.2** Explosion Limits

The asymptotic behavior of radical species production directly defines the transition between deflagration and detonation, or the explosion limits, of a given system. While difficult to perform with a complete reaction mechanism, explosion limits determined analytically come from considering regime specific simplified mechanisms and assumptions of steady state behavior. First, writing the species continuity equation for each species, using  $n_{\alpha}$  to represent concentrations of species  $\alpha$ ,

$$\frac{dn_{\rm H}}{dt} = 2k_0n_{\rm H_2} - k_1n_{\rm O_2}n_{\rm H} + k_2n_{\rm H_2}n_{\rm O} + k_3n_{\rm H_2}n_{\rm OH} - k_4n_{\rm H} - k_5n_{\rm H}n_{\rm O_2}n_{\rm M}$$
$$\frac{dn_{\rm O}}{dt} = 2k_0n_{\rm O_2} + k_1n_{\rm O_2}n_{\rm H} - k_2n_{\rm H_2}n_{\rm O}$$
$$\frac{dn_{\rm OH}}{dt} = k_1n_{\rm O_2}n_{\rm H} + k_2n_{\rm H_2}n_{\rm O} - k_3n_{\rm H_2}n_{\rm OH}$$

Imposing the assumption of steady-state behavior of O and OH species relative to H, by setting their continuity equations to zero, results in steady-state values of

$$n_{\rm O}|_{\rm ss} = \frac{2k_0n_{\rm O_2} + k_1n_{\rm O_2}n_{\rm H}}{k_2n_{\rm H_2}}$$
 and  $n_{\rm OH}|_{\rm ss} = \frac{2k_1n_{\rm O_2}n_{\rm H} + 2k_0n_{\rm O_2}}{k_3n_{\rm H_2}}$ 

where  $n_{O}|_{ss}$  has been substituted into  $n_{OH}|_{ss}$  in order to remove all dependence on O and OH species. Plugging the two steady-state forms into the continuity equation for H and simplifying the result

$$\frac{dn_{\rm H}}{dt} = \underbrace{2k_0(n_{\rm H_2} + 2n_{\rm O_2})}_{s} + \underbrace{(2k_1n_{\rm O_2}}_{b} - \underbrace{(k_4 + k_5n_{\rm O_2}n_{\rm M})}_{t})n_{\rm H}$$

where *s* represents a general source term, *b* denotes chain branching and *t* chain termination. The behavior of H production reduces to two cases, depending on the relationship between *b* and *t*, when analyzing the analytic solution of

$$n_{\rm H} = \frac{s}{t-b} \left[ 1 - e^{-(t-b)t} \right]$$

In the case of t > s, the H concentration grows to an asymptotic value of s/(t - b) limiting the overall speed of the mechanism. While in the case of s > t, H species experiences exponential growth which in turn further increases the mechanism velocity resulting in an explosion as opposed to a slow and incomplete burn.

Not only does this analysis use a simplified mechanism neglecting reactions dominant at higher pressures, but the relationship between s and t depends on both total system pressure, through M collision partners, and O<sub>2</sub> concentration, resulting in extremely different behavior under different

pressure regimes. Repeated asymptotic analysis in each of the pressure regimes, using subsets of the 16 reactions (Appendix B.1) corresponding to their dominance at different pressures, results in the explosion limits shown in fig. 3.1. Here, the first limit occurs as chain carrier production exceeds wall termination due to pressure increasing. As pressure increases, the relatively-inert  $HO_2$  production, R.5, consumes carrier species and impedes run-off behavior, resulting in the second limit. Further increasing the pressure, heat release from the exothermic reactions cannot be dissipated, resulting in higher rates of endothermic reactions dissociating  $HO_2$  and  $H_2O_2$  to produce more carrier species and an explosion.

While asymptotic analysis provides analytical solutions, the effect of simplifying reactions mechanisms alters the exact locations of the explosion limits. The dotted line in fig. 3.1 corresponds to the second explosion limit in a stoichiometric mixture, where  $2k_2 = k_5 n_M$ , if all other reactions considering dissociation of HO<sub>2</sub> are neglected. Without analytical solutions to complete combustion mechanisms, the determination of the explosion limits requires the use of numerical integration or experimental studies.

## **3.3** Plasma Assisted Combustion

While understood for the last two centuries, humanity's methods of implementing classical combustion processes has not drastically changed since the patents of Nikolaus Otto and Rudolf Diesel in the late 19<sup>th</sup> century. Until recently, relying on thermal effects to drive the combustion process has not limited the ability to optimize designs of modern combustion platforms with regards to environmental, economic, and performance characteristics. Modern technologies and emissions regulations have created demands beyond the capabilities of classical combustion [111]. Of growing social and governmental importance is the control of harmful emissions with regards to both climate warming and air quality. With our present infrastructure and the energy density provided by hydrocarbons, synthetic and fossil fuel combustion will remain a dominant energy source well into the 21<sup>st</sup> century [121], though present methods result in the production and release of greenhouse



Figure 3.1 Experimental explosion limits of stoichiometric H<sub>2</sub>-O<sub>2</sub> combustion in a spherical KClcoated vessel from [30] with original data credited to [103]. Dotted line corresponds to where  $2k_2 = k_5 n_{\rm M}$ .



Figure 3.2 Schematic of plasma assisted combustion enhancement pathways taken from [80].

gases (e.g  $CO_2$ ) and pollutants (e.g.  $NO_x$ ). The prevalence of internal combustion car engines and gas turbines for both aircraft propulsion and electricity generation paired with increasing fuel costs have also driven a demand for better operating efficiency. The quest for efficiency and emission control has resulted in modern designs that push the boundaries of classical combustion lean and low-temperature flammability limits.

Beyond efficiency and emission control, interest in hypersonic propulsion calls for ignition control in extremely difficult conditions. At or near Mach 5 flight, the flow residence time in a combustor is significantly shorter than ignition time offered by spark sources [35] resulting in an incomplete burn. The use of specialized cavity geometries initially showed promise with regards to ignition and flame holding; however, thermoacoustic instabilities result in unstable operation risking blowout and the altered geometries induced stagnation pressure hampering engine efficiency [13]. As with fuel efficiency and by-product control, this further motivates a search for new methods of reliable, fast, and robust ignition and flame holding methods.

## 3.3.1 PAC Fundamentals

In the context of using a discharge to initiate combustion or maintain a flame, multiple mechanisms exist through which the generation of a plasma can affect the gas. Two thermal effects come from an (nearly-) equilibrium plasma in the form of: 1) local gas heating as a result of energy release increases chemical reaction rates, and 2) flow perturbations generated from inhomogeneous gas heating causing turbulence and mixing. In turn, the formation of a non-equilibrium plasma results in three new mechanisms for combustion modification: 1) excitation, dissociation, and ionization through electron impact leading to non-equilibrium radical species production, 2) momentum transfer from the electric field to the gas through interaction with space charge (ionic wind), and 3) ion and electron drift can lead to modified radical fluxes along gas flow gradients [153]. No obvious ways of separating these effects exist due to their inherent coupling, fig. 3.2, in turn requiring special considerations for systems attempting to analyze a single mechanism.

Of primary interest to this work is the generation of radical species from non-equilibrium plasma chemistry. Considering the set of reactions presented in the previous section, the introduction of electron impact driven or initiated chain initiation, branching, and propagation pathways has the potential to completely alter asymptotic behavior. An extremum case would be the bypassing of the extinction limit resulting in a completely monotonic explosion limit curve. Three types of species excitations are involved in the non-equilibrium generation of radicals: vibrationally and electronically excited species as well as ions. Unlike the short lived rotational states, vibrational-translational relaxation of vibrationally excited states of N<sub>2</sub> and O<sub>2</sub> occurs over 10-100  $\mu$ s, though inversely proportional to hydrocarbon density [129]. This allows for an accumulation of vibrational states which undergo reactions with other vibrationally excited molecules such as

$$H_2(v) + O \xrightarrow{k(v)} H + OH(w)$$
 (R.8)

Multiple reaction mechanisms exist using a *vibrational temperature* which assumes a Boltzmann distribution over the vibrational levels, however, their validity comes into question in non-equilibrium conditions [26]. Instead, a state-to-state model employs tracking of individual densities of vibra-



Figure 3.3 Comparison of chain propagation reactions with electron impact dissociation rates from [149] using an EEDF found using a two term Boltzmann solver assuming different field strengths, E/N, and a fixed gas composition.

tionally excited states [151]. As shown in [104], rate constants can vary by several orders of magnitude for different vibrational levels of both reactants and products, requiring a description of individual vibrationally excited levels.

In addition to the contribution from vibrational levels, four different methods exist through which to produce radicals from electronically excited molecular states as a result of electron impact [152]:

1. Excitation to a pre-dissociative state resulting in dissociation and the formation of two radi-

cals

$$O_2 + e \longrightarrow O_2(B^3 \Sigma_u^-) \longrightarrow O(^3 P) + O(^1 D) + e$$
 (R.9)

2. Excitation to an electronic state which produces radicals through chain reactions

$$O_2 + e \longrightarrow O_2(a^1 \Delta_g) + H \longrightarrow O(^3 P) + OH$$
 (R.10)

3. Excitation of the molecule with dissociation via quenching with another molecule

$$O_2 + e \longrightarrow O_2(A^3\Sigma_g^+) + CH_4 \longrightarrow O_2 + CH_3 + H(^1S)$$
 (R.11)

4. Excitation to an electronic state with radiative emission resulting in molecular dissociation

$$H_2 + e \longrightarrow H_2(a^3 \Sigma_g^+) \longrightarrow H_2(b^3 \Sigma_g) + h\nu$$
 (R.12)

$$O_2 + h\nu \longrightarrow O + O \tag{R.13}$$

While the second mechanism only requires a weak electric field due to low energy thresholds of excited states ( $\approx$  1eV for oxygen), the other mechanisms require a relatively large field strength in order to have high energy electrons reach threshold energies ( $\gtrsim$  5eV for oxygen). Depending on both the electron energy distribution function (EEDF) and electron density, these reactions can occur at a significantly faster rate than thermally driven radical generation. For example, with E/N of 100-300 Td, the electron impact dissociation occurs two orders of magnitude faster than classical radical sources at the equivalent temperature, as shown in fig. 3.3. With cross sections known for electron impact reactions, a Boltzmann equation solver can yield an EEDF for rate constants; however, the both the distribution and resulting rate depend on both the electric field strength as well as the ratio of gases involved. While comprehensive kinetic models exist for different gas mixtures (e.g N<sub>2</sub>-O<sub>2</sub> [91], H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> [150],O<sub>2</sub>-C<sub>x</sub>H<sub>y</sub> [3]), it is agreed that rates are not necessarily well known in all regimes and cross section data may not be available.

Finally, ions can also participate in dissociation and recombination reactions resulting in radical generation. While ionization requires a significant amount of discharge energy and ions typically have a quick recombination time (1-10  $\mu$ s with T<sub>g</sub> of 300-3000 K respectively), it bears responsibility for maintaining the electron population in the system along with introducing new pathways by which to produce radical species:

1. Electron-ion dissociative recombination

$$O_2^+ + e \longrightarrow O(^{3}P) + O(^{1}D)$$
 (R.14)

2. Recombination of cluster ions

$$O_4^+ + e \longrightarrow O_2 + O + O \tag{R.15}$$

#### 3. Ion-ion recombination

$$O_2^+ + O_2^- + M \longrightarrow O_2 + O + O + M$$
(R.16)

Compared to the four pathways discussed previously, ion reactions result in higher heat release and less radical generation [2]. Though not efficient pathways to alter radical production, these reactions are not so insignificant as to be excluded from considered chemistry mechanisms.

#### **3.3.2** Physical system for study of kinetics

The lack of spatial variation in a global modeling study makes it impossible to study the effects of flow perturbations and inhomogeneous radical flux, however, it bypasses the need for an extremely resource-heavy coupling of full reaction chemistry with a fluid or PIC code. As such, the experimental platform for numerical studies should demonstrate a weak dependence on geometry and flow variation. Studies of plasma discharge modifying ignition characteristics started back in the early 20<sup>th</sup> century with the work by Haselfoot and Kirkby [66], demonstrating ignition with electrical discharge in low pressure regimes which would otherwise not ignite. Gorchakov and Lavrov's study on the interaction between electrical discharge and autoignition times [56] demonstrated that this effect was mapped across the entire range of the classical explosion limits, fig. 3.4, and not just the first ignition limit. While applications of equilibrium plasmas have been extensively studied, thermal mechanisms from plasma interaction do not present an efficient method for combustion enhancement due to an inability to selectively choose excitation pathways. In searching for efficient methods of combustion augmentation, initial studies attempted to understand the interaction between the flame and electric field [102]. While showing increased electron temperature [21] and improvement of flame extinction limits [75], the strong electric field resulted in an ionic wind whose effect was not separable from electron and ion chemistry effects. Attempting to isolate the effects of electric field enhancement from the ionic wind, the use of microwave discharges showed both an increase in electron and burned gas temperatures [57]. Recent numerical modeling of the microwave interaction showed accelerated flame propagation with a flame temperature increase of  $\approx 200 \text{K}$  [157]. However, in limiting microwave power to avoid breakdown, the electron density was low, resulting in the burned gas absorbing a large portion of microwave energy and an overall



Figure 3.4 Experimental extension of explosion limits of  $H_2$ - $O_2$  combustion under electrical discharge from [149] with original reference to [56].

loss in discharge modification efficiency.

Further attempts to isolate flow effects from the plasma combustion chemistry with regards to ignition and extinction limits, while increasing the strength of the electric field and number of electrons relative to microwave discharge experiments, resulted in idealized experiments using gliding arcs in a counter flow diffusion flame [49]. Driven predominantly by thermal effects, the flame extinction limit increased by a factor of three, while kinetic effects were attributed to lowering the ignition temperature in hydrogen and methane air systems through reaction pathways involving  $NO_x$  species [122]. Followed by experiments using nanosecond discharges showing kinetic effects to both ignition (predominant) and extinction limits [158], questions arose as to what extent non-thermal effects can alter extinction limits and whether or not kinetic pathways could drive ignition speed so low as to bypass the classical flame extinction limit altogether.



Figure 3.5 Types of discharges with regards to electron density and electric field values, taken from [152].

#### 3.3.3 Nanosecond Discharge System

Nanosecond discharge (NSD) presents the best experimental platform for a focused study of plasma interaction with the combustion process by allowing for selective excitation gas. Relative to other discharge methods, fig. 3.5, NSD provides a large amount of input energy being consumed for the production of high energy level states, otherwise not attainable from lower E/N discharges, without resulting in large thermal effects. As a result of peak field intensities existing on the order of thousands of Townsend for 2-3 ns before decreasing to a few hundred, a uniform discharge develops in space allowing for modeling in a volume averaged context. The fast ionization wave created by the peak field intensities develops on a significantly shorter time scale than ignition, allowing for separation of the discharge and combustion kinetics.

Using a counter flow flame configuration, Sun et. al demonstrated the removal of the standard flammability limits as a function of input flow fuel mass fraction [159], further motivating the use of a NSD. The experimental system consisted of two stainless steel nozzles, with inner diameters of 25.4 mm and flow diffusers, facing each other at a separation of 16 mm. A counter flow system was chosen due to simplified 1-D flame geometry and a flow velocity gradient (strain rate) along



Figure 3.6 Experimental demonstration of the bypassing of extinction limits. Plotted against fuel mass fraction,  $X_F$ , with different cases of oxidizer mass fraction,  $X_O$ , left demonstrates the classical S-curve behavior, while the case with higher oxidizer levels, right, shows monotonic behavior; taken from [159].

the centerline as the two jets reach a stagnation plane [122]. The strain rate, dependent only on nozzle separation, gas densities, and flow velocities, is the inverse of the flow residence time and is used to scale ignition time measurements. Ignition occurring at the same temperature but with a higher strain rate corresponds to a lower ignition time. The nozzles attached to a high voltage pulse generator operating with a 12 ns (FWHM) pulse at a constant 7.6 kV and repetition frequency of 24 kHz. Time integration of voltage and current profiles estimated an energy input of 0.73 mJ/pulse corresponding to a total input power of 17.5 W. With the combustion chamber kept at a constant pressure of 72 Torr, CH<sub>4</sub> and O<sub>2</sub> flow through the anode and cathode nozzles respectively with He as a buffer gas. Oxidizer temperature was found to be  $650 \pm 20$  K and fuel temperature at  $600 \pm$ 20 K. Ignition times were observed while changing the fuel mass fraction and fixing a strain rate of 400 1/s (equivalently a residence time of 2.5 ms), the oxidizer mass fraction, and the driving frequency.

While cycling the fuel mass fraction both upwards and downwards between  $X_{\rm F} = [0.1, 0.35]$ , different configurations of fixed oxidizer mass fractions were used, with  $X_{\rm O}^{\rm a} = 0.34$  and  $X_{\rm O}^{\rm b} =$ 0.62, as shown in fig. 3.6. In the case of  $X_{\rm O}^{\rm a} = 0.34$ , fig. 3.6a, raising the fuel concentration (solid markers) did not have a measurable OH emission until  $X_{\rm F} = 0.265$ , at which point emission changed abruptly along with a visible flame, demonstrating ignition. Decreasing the fuel (hollow markers) showed the opposite behavior at  $X_F = 0.2$ , with visible emission disappearing and OH emission dropping quickly to noise levels. The second case, with  $X_O^b = 0.62$ , both directions of changing fuel concentration resulted in remarkably similar curves demonstrating an ignition and extinction limit of  $X_F = 0.09$ , shown in fig. 3.6b. A middle case of  $X_O = 0.55$  shows shifted limits with an ignition limit of  $X_F = 0.14$  and extinction limit of  $X_F = 0.1$ . With fixed fuel and oxidizer mass fractions, similar curves can be created as a function of repetition frequency with a cutoff of 1k Hz, or else radical species begin to quench between pulses.

# 3.4 KGMf overview with PAC

With NSD systems representing the most appropriate platform for global model studies, this section covers the specifics of the system of equations, considered mechanisms and experimental conditions replicated.

## 3.4.1 KGMf analytic additions

In order to adequately describe the kinetics of NSD experiments in the literature, terms for gas heating during discharge, heat flux lost to the combustor walls, and flow induced species flux need definitions for inclusion in the KGMf global model. Modeling results from Popov [130], corroborated by experimental data, demonstrated that gas heating during air plasma discharge predominantly occurs during the preliminary dissociation of electronically excited states of oxygen molecules. These states come from either electron impact reactions or via quenching of higher excited gas species. Further, they showed that over a wide range of reduced electric field values (E/N), the amount of discharge power involved in heating the gas corresponds to the energy lost during excitation of electronic degrees of freedom. This agrees with adiabatic theory whereby the gas heating rate follows from an energy balance. With inspiration from the work by Flitti et. al [47], the discharge power absorbed by electrons,  $P_{abs}$  from eq. 2.4, distributes between internal potential

energy of major species,  $P_{chem}$ , and translational degrees of freedom for the electrons,  $P_e$ , and major species,  $P_g$ ,

$$P_{abs} = P_e + P_g + P_{chem} \tag{3.1}$$

In a similar short notation, the two temperature equations from the previous chapter can be rewritten as

$$P_e = P_{abs} - S_{ei}$$
 and  $P_g = -P_{chem} + \dot{P}_{proc}$  (3.2)

where  $P_{chem}$  corresponds to enthalpy changes from chemical reactions,  $\dot{P}_{proc}$  is the heat flux from the adiabatic discharge process, and  $S_{ei}$  is the second term in eq. 2.4 for energy lost from electron impact reactions. Solving for  $\dot{P}_{proc}$ , the gas heating term from electrical discharge is equal to the energy lost by electrons in impact processes. The implementation of this term in the KGMf conservation equations takes advantage of the common-sub-expression algorithm and negligibly affects evaluation time.

Heat flux to the walls of the combustor is defined through classical conduction heat transfer theory,

$$\dot{Q} = \frac{\lambda(T_g)(T_g - T_w)}{\Lambda^2} \tag{3.3}$$

where  $T_w$  is the ambient wall temperature,  $\lambda(T_g)$  is the thermal conductivity of the wall material, and  $\Lambda$  is the characteristic length of the chamber cross section. In a similar approximation, species flux from gas flow is treated with linearized boundary conditions of inflow and outflow velocities,  $V_{in}$  and  $V_{out}$ , such that the flow flux for species k in eg. 2.2 becomes

$$(G-L)_{k} = n_{k}^{in} V_{in} A - n_{k}^{out} V_{out} A = n_{k}^{in} (V_{in} - V_{out}) A - 2n_{k} V_{out} A$$
(3.4)

where  $V_{in}$  and  $V_{out}$  are inflow and outflow velocities, A is the cross sectional area of the combustor chamber, and  $n_k^{in}$  is the density of species k within the inflow gas mixture. This assumes a laminar flow discharge region and relies on spatial uniformity of the flame, commonly demonstrated in NSD experiments.

#### 3.4.2 Mechanisms

In modeling with a volume-averaged framework, a major emphasis is placed on the evolution of chemical processes as opposed to other physical interactions. As such, the validity of the chemistry mechanism used is of the utmost importance. Mentioned previously, several attempts have been made to compile detailed kinetic models for different gas mixtures [91, 3, 150], however, their validity comes into question under different pressures, temperatures, and electric field strengths. In the case of gas phase reactions with excited species, many rate coefficients are approximated as no experimental measurements exist. Electron impact reactions are further plagued by the need to convolve reaction cross sections with an EEDF. Cross sections are notoriously difficult to measure experimentally and calculation methods typically do not extend to molecular targets. Reactions with unknown cross sections are typically provided as experimental fits of modified Arrhenius rates, however, the EEDF of the measured system is cooked into the result and not extractable. These rates may be the best option for a given reaction, as not including a pathway would be worse than misrepresenting it, but the context of their measurement needs consideration when applied to another system. System dependent sensitivity analysis can be used to determine which rates predominantly determine evolution; specifying which reactions must be represented accurately. Delving deeper, uncertainty quantification methods are used to estimate possible error in simulation results coming from reaction rate uncertainty bounds.

Further complicating matters, having cross section data for a given reaction does not guarantee validity, since the rate is also dependent on the EEDF. Outside of particle tracking software, the EEDF can be found in a variety of methods; such as solving the two-term Boltzmann equation approximation as a function of electron impact processes and the reduced electric field [60] or using an isotropic-collision Monte Carlo code to represent electrons [107]. Ignoring the fact that assumptions taken within most Boltzmann solvers (two-term approximation) do not allow for large exchanges of mass in a system, their accuracy is also limited by a lack of data. By definition, the Boltzmann solver should have access to every electron impact reaction cross section, which is not
always available. Secondly, due to the computational cost of evaluating the Boltzmann equation, it is common to evaluate the EEDF as a pre-processing step instead of a complete coupling with the energy and continuity equations. This reduces EEDF and/or  $T_e$  dependent rates to constant values, simplifying the mechanism evaluation at the expense of physical behavior. The majority of Boltzmann solvers available were not written with combustion in mind, resulting in few warnings about imposed assumptions. This is not a problem in systems evolving electrically without mass transfer (e.g pure argon discharge at low pressures such that  $Ar_2^+$  can be neglected), but in the context of non-equilibrium discharges in combustion, the mass fractions change considerably while electric field densities remain relatively constant. A complete coupling of the Boltzmann equation solver would provide the most physical results, with a severe increase in the overall evaluation time.

Of primary interest to this work is the role of plasma-induced excited species in the ignition process and their susceptibility to variations in the EEDF. Validation studies were performed with both  $H_2$  and  $CH_4$  in inert ( $O_2$ -Ar) and synthetic ( $N_2$ - $O_2$ -Ar) air, however, this analysis is composed of  $H_2$ - $O_2$ -Ar cases. This is done for three reasons: 1) the hydrogen mechanism contains a higher percentage of electron impact rates defined with cross section data, 2) a large amount of the plasma-induced combustion kinetics are attributed to electronic states of oxygen and nitrogen species (atomic hydrogen is still a major chain carrier), and 3) as discussed in appendix A.3, the inclusion of carbonic species greatly increases the computational intensity of global model evaluation.

### 3.4.2.1 Argon buffer gas

Argon is chosen to be the neutral buffer gas for two reasons: 1) as one of the cheapest noble gases, argon is commonly used in combustion experiments and 2) argon has a relatively low ionization energy ( $\sim 15.7 \text{ eV}$ ) compared to lighter inert gases and is used as an electron source. Remaining relatively inert even in excited states, the inclusion of argon brings five species (Ar, Ar<sup>+</sup>, Ar<sup>+</sup><sub>2</sub>, Ar<sup>\*</sup> Ar<sup>\*\*</sup>, the latter two are excited 4s states with Ar<sup>\*\*</sup> representing metastable states and Ar<sup>\*</sup> the other two states) and eleven reactions with explicit dependence on an argon species. Six of the eleven



Figure 3.7 Electron impact cross sections for Argon from the Morgan LXcat database [119]. reactions have cross sections from the LXcat Morgan database [119], shown in fig. 3.7. Though not included in this mechanism, systems with  $\geq 80\%$  Ar and high field strengths can experience dissociation of O<sub>2</sub> through quenching with excited argon,

$$\operatorname{Ar}({}^{3}\mathrm{P}_{0}, {}^{3}\mathrm{P}_{2}) + \operatorname{O}_{2} \longrightarrow \operatorname{O}({}^{3}\mathrm{P}) + \operatorname{O}({}^{1}\mathrm{D}, {}^{1}\mathrm{S})$$
(R.17)

Even without explicit dependence, argon behaves as a collision partner in any reaction with arbitrary impact species.

## **3.4.2.2** H<sub>2</sub> - O<sub>2</sub>

The  $H_2$ - $O_2$  combustion mechanism embodies the core data component of presented analyses and was created from a variety of sources depending on cross section data availability. A collection of rate data provided by Igor Adamovich [1], predominantly sourced from Kossyi et. al [91] and Itikawa et. al [72], which was combined with the GRI-Mech 3.0 [144], giving the former priority if both databases contained the reaction. This mechanism was then supplemented with cross section data from the Morgan database [119], replacing other reactions if not defined by cross section data.



Figure 3.8 Electron impact cross sections for Argon from the Morgan LXcat database [119]. This combination results in a mechanism with 55 distinct species and 231 reactions. Out of these, 106 reactions are defined with cross section data.

Experimental and modeling work has demonstrated that a primary avenue of PAC/PAI is through pathways involving excited molecular states of oxygen [142, 148]. Predominately produced through electron impact,

$$O_2 + e \longrightarrow O_2(a^1 \Delta_g) + e$$
 (R.18)

$$O_2 + e \longrightarrow O_2(b^1 \Sigma_g^+) + e$$
 (R.19)

singlet oxygen species,  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  are involved in a good number of dissociation and branching reactions. With extremely small threshold energies, these singlet states have a huge overlap with the convolved EEDF, resulting in fast reaction rates. Using a 0.7 m reactor at ~ 800 K and 10 Torr, with constant discharge power and gas flow of ~ 25 m/s, Smirnov et. al showed that a 5% increase of  $O_2(a^1\Delta_g)$  in the input flow resulted in an induction zone reduction by a factor of 5 (effectively related to the ignition time) [142]. This is attributed to the creation of ground and excited states (e.g.  $O(^1D)$ ) of atomic oxygen

$$O_2(a^1\Delta_g) + e \longrightarrow O + O(^1D) + e$$
 (R.20)



Figure 3.9 O generation from gas phase reactions. Reactions involving M collision species are scaled assuming 100 Torr for matching units.  $O_2(b^1\Sigma_g^+) + e \longrightarrow O + O + e$ (R.21)

which can drastically alter ignition time with high enough electron and singlet densities. Cross sections for reactions R.18, R.19, and R.20 are plotted in fig. 3.8 for comparison with argon.

### **3.4.2.3** Adding N<sub>2</sub>

In fuel-air mixtures, the dominant avenues of atomic particle production are dissociation of molecules from electron impact or quenching of electronically excited molecular nitrogen states [129]. This is partially due to these reactions having extremely short timescales,

$$N_2(C^3\Pi_u) + O_2 \longrightarrow N_2(v) + O(^3P, {}^1D) + O(^3P, {}^1D)$$
(R.22)

$$N_2(a^{-1}\Sigma_u^-) + O_2 \longrightarrow N_2(v) + O({}^{3}P) + O({}^{3}P)$$
(R.23)

of 3-4 ns and tens of ns respectively. Unlike argon however, nitrogen comes with the formation of  $NO_x$  products and significantly more reactions. In the used model, adding nitrogen results in 56 new species and 453 new reactions (68 of which are defined with cross section data).

In low initial temperatures, NO and  $NO_2$  have a catalytic effect on hydrogen and hydrocarbon fuels as demonstrated by Takita et. al [160]. In a plasma system, NO can be generated efficiently through the following pathway

$$N_2 + e \longrightarrow N(^2D) + N + e$$
 (R.24)

$$N(^{2}D) + O_{2} \longrightarrow NO + O(^{3}P, ^{1}D)$$
(R.25)

$$N_2(A^3\Sigma_u^+) + O \longrightarrow NO + N(^2D)$$
(R.26)

where  $N_2(A^3\Sigma_u^+)$  is likely also created from an electron impact reaction. The catalytic effect was found to decrease ignition time as the pressure increased, however, the pathway breaks down at higher temperatures relative to the effect from O radicals.

# 3.5 Modeling

The overarching goal of this work, relative to PAI, is to both analyze kinetic characteristics of deviations from classical combustion chemistry and to validate global models in a multi-physics scenario. The relative computational efficiency of volume-averaged modeling allows for computationally cheap parametric studies. This efficiency comes at the cost of a high-data dependency and needing a large amount of physics handled through approximations. Alluded to previously, for most gas mixtures, there does not exist a kinetic mechanism which the PAC/PAI community collectively agrees will function in all regimes. Even with regards to classical combustion, updates to mechanisms are regularly published, either for handling new regimes or concentration-dependent reaction pathways [173, 138]. This is due in part to the regime-dependent experimental nature of acquiring reaction rates of specific processes.

The validity of global models relies on a combination of: 1) a kinetic mechanism describing all relevant reactions, 2) a dominance of volumetric processes in conditions of reasonable homogeneity, and 3) models for spatial characteristics such as gas flow, excited species diffusion, and thermal conduction to better match experimental conditions. The selection of focusing on experimental NSD systems was made to meet the second criterion, as a system reliant on turbulence will not be well described by a global model. This work predominantly focuses on the first criterion, with the latter used as tuning parameters for matching experimental conditions. The intention



Figure 3.10 Plot of EEDF, eq. 2.9, with different values of X and values of Te.

being to match result variation that occurs under parameter changes, not necessarily to yield 1:1 result matches with experimental conditions.

The intention with this work is to study the plasma effects on ignition times. Two  $H_2$ -O<sub>2</sub>-Ar cases are considered with total system pressures of 10 and 100 Torr respectively. First, changes to reaction rates and integrated results, relative to EEDF selection, are quantified with regards to ignition times. Secondly, following the work of Smirnov et. al [142], an investigation of the effects of electronically excited oxygen species on the ignition process is performed. This experiment used a DC discharge for generation of oxygen singlet states, which although not the most power efficient manner of PAI, has been demonstrated to contribute to both flame-holding and ignition [101]. Finally, the dynamic characteristics of NSD are considered relative to constant power deposition in the ignition process.



Figure 3.11 Effect of EEDF selection on different electron impact rates: excitation of molecular oxygen on the left,  $O_2 \rightarrow O_2(a^1 \Delta_g)$ , and dissociation through quenching on the right,  $O_2(a^1 \Delta_g) \rightarrow O + O(^1D)$ .

### 3.5.1 Rate Variation From EEDF dependence

Beyond the relatively static nature of gas-phase reactions, the dependence of electron impact processes on EEDF selection can result in non-intuitive transitions of dominant pathway chains (e.g. the pair of reactions R.18 and R.20 producing atomic oxygen species). The evolution of an EEDF from a Maxwellian form results in a lower number of higher energy electrons, as shown in fig. 3.10, involved in collisional processes. This in turn modifies convolved reaction rates in a non-linear manner due to artifacts in individual reaction cross sections. The overall shifting of reaction rates is shown in fig. 3.11; however, changes relative to equilibrium distributions highlight the non-linear transitions occurring, fig. 3.12.

The collective effects of all electron driven reactions being altered is only realizable through integration of the system of equations as the strength of each reaction is also determined by the product of reactant species densities, which in turn are based on the evolution of the system. However, with the transitions that occur in the relative difference between rates, fig. 3.12, it is in principle possible to configure a system with a specified EEDF such that certain reaction rates have a larger effect. The severity of the transitions that occur imply that selection of the wrong EEDF can result in different pathways being treated preferentially.



Figure 3.12 Effect of EEDF selection on different electron impact rates, shown through relative error from rates calculated with a Maxwell-Boltzmann distribution (X=1).

# **3.5.2 O**<sub>2</sub>( $a^1\Delta_g$ ) Injection and Ignition Time

As a validation case, the KGMf is applied to the experimental and modeling work by Smirnov et. al [142] on the effect of excited singlet oxygen on the combustion process. Molecular oxygen has two low-lying electronically excited singlet states,  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$ , which are predicted to reduce the ignition time of H<sub>2</sub>-O<sub>2</sub> combustion [147]. The experiment is composed of a discharge cell with oxygen throughput piping into a heated flow reactor with hydrogen injection. The system is maintained at 10 Torr with reactor walls heated to 780 K and a gas mixture of H<sub>2</sub>:O<sub>2</sub>::5:2. A dc discharge, operated with I= 10 mA and V= 4.2kV, is used to excite a portion of injected oxygen into the  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$  states prior to mixing with hydrogen. At this temperature and pressure, the system is already in the auto-ignition region and will eventually ignite without introducing excited states, however reduction of the ignition time relative to  $O_2(a^1\Delta_g)$  concentration provide insight into the dominant reactions involved. Absorbed molar input power was measured to be  $W_s = 107$ Jmmol<sup>-1</sup> resulting in the singlet state reaching number densities of  $(1.13\pm0.3)10^{19}$  m<sup>-3</sup>. At a flow velocity of 25 ms<sup>-1</sup>, it was found that  $O_2(b^1\Sigma_g^+)$  depleted rapidly while traversing the drift tube due to quenching down to the  $O_2(a^1\Delta_g)$  state. Ignition times were found as a function of the singlet state mole fraction. Without excitation, the system achieved ignition in 12.9 ms at a

distance of 51 cm from the injection point of the hydrogen gas. As the concentration of  $O_2(a^1\Delta_g)$  was increased to 1.2%, 4%, and 6% of the total gas, the ignition time reduced to 6.8 ms, 4.7ms, and 4.2 ms respectively.

This system was replicated using the KGMf in the original pressure of 10 Torr with a few considerations; namely handling a characteristic of the reported flow and supplementing a small amount of power to maintain the excited oxygen species. Without adding any external power, the effective electron temperature equation remained extremely unstable and regularly trended to just above 0 eV. While the averaged electron energy is expected to be small in this regime, the zeroing is unphysical behavior brought out by unbalanced momentum transfer and attachment processes. Though momentum transfer reactions should be the dominant driving factor for lowering electron temperature, electron attachment to atomic oxygen, forming O<sup>-</sup>, was found to have an overestimated threshold energy. Using the experimental geometry of a cylinder with a diameter of D = 5.2mm and length of L = 0.3m, a background input power of 0.01W is required to maintain the electron temperature and density to reasonable values. As reported in the original modeling of the experiment, it is necessary to account for inhomogeneous flow from low pressure. At pressures of 10 Torr, the flow in the system has a parabolic velocity profile relative to the cross section of the flow regime [142]. Using the linear flow model in the KGMf, symmetric inflow and outflow from the system is tuned in order to match the baseline case of pure ground state oxygen being injected. Tuning resulted in an optimized flow of  $\sim 32m^{-1}$  to match the ignition time of the unsupplemented oxygen case.

For proof of concept of the previous section and calibration of the  $O_2(a^1\Delta_g)$  injection effect, base line temperature dependent ignition times were calculated for the system in the case of both a Maxwellian EEDF and a Druyvesteyn EEDF, fig. 3.13. In the relatively low pressure of 10 Torr, the combustion chemistry is dominated by other chain reactions and the effect of electrons is negligible. With an introduction of energy into the system, either through pumping in excited species or stronger discharge powers, electron impact processes become more dominant. Figure 3.14 presents the full reaction term (rate and product of reactant species) evaluated in time while integrating



Figure 3.13 Ignition time in 10 Torr of H<sub>2</sub>:O<sub>2</sub>::2:1 with equilibrium and non-equilibrium EEDFs.



Figure 3.14 Rates of radical producing reactions with (a) and without (b) singlet delta oxygen supplementation. Without external power, the rates appear quite similar but differ in scale. The total system number density is used for the M collision species.

the global model. Reactions which appear unimolecular are dependent on the electron density, which in the case of quasi-neutrality is the charge weighted sum of all ionic species in the system. Though no power is being explicitly passed to the global model, initializing  $O_2(a^1\Delta_g)$  at such a high concentration is effectively passed potential energy. The drop in reaction terms in fig. 3.14a is explained by a drop in electron density from an over production of O<sup>-</sup>. This is counteracted in fig. 3.14b by the higher initialized  $O_2(a^1\Delta_g)$  concentration and its reaction with O<sup>-</sup> releasing the captured electron.



Figure 3.15 Changes to ignition time due to injection of 6%  $O_2(a^1\Delta_g)$  at 10 Torr.

With the global model calibrated with background power and flow velocity, ignition times were found for  $O_2(a^1\Delta_g)$  initialized, and flowing in, at specific molar fractions of the total feed gas, fig 3.15. The ignition times found through integration with the KGMf were slightly slower than reported values. Though remaining within a factor of two of the experimental results under 6% singlet delta oxygen flow, the initial decrease in time is not as extreme. This may be explained by a lower simulated electron density than necessary to drive the O radical production chain. As the concentration of  $O_2(a^1\Delta_g)$  is increased, potential energy can trickle through to electrons after the excited species undergo quenching. Ignition times were also found for 1.0 W and 10.0 W power depositions for comparison purposes. The further reduced ignition time in the high power cases would physically be followed by breakdown resulting in a thermal ignition. The nearly unchanged ignition time in the 0 W case of fig. 3.15 is explained by the unbalanced drop in  $T_e$  from O<sup>-</sup> over production.

The effect of introducing  $O_2(a^1\Delta_g)$  in the initial flow is better seen when comparing the evaluated rate terms when using 0.1 W and 0.01 W of external power, fig. 3.16, to the un-powered cases, fig. 3.14. The rate at which the system consumes the fuel and oxidizer has also increased, resulting



(a)  $0\% O_2(a^1 \Delta_g)$  and 0.1W DC power

(b) 6%  $O_2(a^1\Delta_g)$  and 0.01W DC power

Figure 3.16 Effect of  $O_2(a^1\Delta_g)$  injection on the rates of reactions involved.

in a fast change of reaction rate dominance to matching the depletion of reactant species.

### 3.5.3 Nanosecond discharge

While the dc discharge provides insight into the underlying processes that are occurring during PAI, nanosecond discharge operates on a time scale that directs almost all of its energy into electronically excited species. These short kicks to the system are absorbed by the electrons and transmitted to the gas through collisions. For validation of the KGMf NSD dynamics, a global model is made to match experimental conditions by Yin et. [178]; hydrogen-air flows initially heated to 400-500 K, at pressures of 40-150 Torr and equivalence ratios of  $\phi = 0.5 - 1.2$  are ignited with 25 ns pulses at a repetition frequency of 40 kHz. Of interest to this work are the experimental measurements of power coupling, ignition delay time, and the effect of the stoichiometric ratio on the PAI process.

Analogous to the dc discharge study, baselines are made with a Maxwellian EEDF, X=1, and normal ignition time behavior is recognized, fig. 3.17. In the unpowered case, the ignition time vertically asymptotes along an isotherm of the used mechanism. In the over-powered case, 10W, ignition time plateaus until an unphysical overgrowth of charged species occurs. The electron number density remains within reasonable ranges, however they are only defined through the quasi-neutrality relationship with charged species. The cause is attributed to an imbalance of energy



Figure 3.17 Baseline results at 100 Torr with different EEDFs.



Figure 3.18 Pulsed power 60 kW 100 Torr. Electron impact reaction terms jump in magnitude due to temporary increases of  $T_e$  during pulses.

being deposited into the system and over production of electronic species which are not well represented in the gas phase mechanism. In the Druyvesteyn case, ignition times remain relatively unchanged, due to the higher pressure driving gas phase reaction dominance, however run stability limited lower temperature results.

Monitoring NSD effects is significantly more time and computationally intensive than modeling systems with constant or gradual external forces. In order to resolve smooth 25 ns impulses, time steps need to be on the order of 1 ns; resulting in  $10^7$  calls to the integrator evolving the global model system of ODEs. With a 'complete' set of air-fuel chemistry, aside from the function call time, the resulting set of ODEs is extremely stiff. Paired with the intensity on the NSD only operating on a subset of the ODE species, fig. 3.18, requires using stiff integrators which operate with iterative sub-stepping. An alternating time step scheme is used such that time steps just before and during a pulse are  $10^{-10}$  s, increasing in size as the system equilibrates before the next pulse. This can reduce the number of time steps by over an order of magnitude in lower temperature regimes.

Following from the work by Yi et. al, a 25 ns pulse operating at a repetition frequency of v = 40kHz and having a Gaussian envelope, is used to ignite hydrogen with synthetic air. In this regime, the contributions from nitrogen species are negligibly different from any other large collision partner, justifying the simplification. Experimentally measured pulse energy coupling to the plasma at 100 Torr is ~ 1.6 mJ, corresponding to a 60 kW discharge. Using this discharge, KGMf ignition times were found to agree with the asymptotic behavior of reported values from cooler temperatures and lower pressures. In lower temperatures, the ignition time is found to be five times faster than in the baseline case. However the upper temperature bound of 1600 K is well beyond the auto-ignition limit, and is ambivalent towards both NSD and introduction of  $O_2(a^1 \Delta_g)$  states, fig. 3.19. Overall agreement is achieved, however the fine tuning to initial conditions and integrator parameters required in lower temperature simulations hampers the ability to parameter scan as effectively.

## 3.6 Conclusion

In this chapter, motivation and fundamentals of PAC are discussed followed by validation examples with two experimental works. Relatively good agreement is found between KGMf and experimental results, however system calibration/tuning is typically required for simulation times longer than a few milliseconds. This is primarily associated with unbalanced system initialization and integration time step instabilities. In the first case, the effect of generating  $O_2(a^1\Delta_g)$  prior to combustion has a dramatic effect in reducing ignition times. In the second validation case, extrema of the experimental ranges are matched with KGMf results continuing on to higher temperature regimes.



Figure 3.19 Pulsed Ignition time at 100 Torr with a 60 kW 25 ns pulse. Contains modeling results for stoichiometric combustion,  $\phi = 1$ , with varied EEDF, and examples of lean and rich behavior.



Figure 3.20 Species densities in 1000K NSD ignition.



Figure 3.21 Pulsed 1000 K Temperatures.

The method proposed for handling integration difficulties is a double-mechanism configuration. A reduced chemistry model is integrated between NSD pulses, while a full chemistry mode is used during the pulse and cool down period thereafter. This is done as the electron temperature, shown in fig. 3.21, drops to thermal equilibrium between pulses. Complications arise at the interface between integrated models as some electronically excited species have significant lifetimes in these pressures. In order to significantly drop the evaluation time, the reduced model consists of only non-excited gas species. The long lifetime of  $O_2(a^1\Delta_g)$  otherwise requires that the full chemistry model is used until all excited species have dropped to negligible densities. Transitioning from the reduced model to the full model requires estimation of excited species density ratios relative to ground states. Since the cool down period can be longer than the pulse repetition rate, shown in fig. 3.20, excited species are re-initialized at non-negligible values resulting in significant differences as a function of chosen excited species ratios and switching time between models.

### **CHAPTER 4**

## **RARE GAS METASTABLE LASERS WITH KGMF**

## 4.1 Introduction

Since the conceptual advent of triggered stimulated emission in the middle of the 20<sup>th</sup> century, laser technology has expanded to cover a huge range of incorporated physics. Symmetries found in nature and similarities between systems have led to the development of multiple types of lasers operating on widely differing physical principles. While the principles of operation differ, the underlying fundamentals remain relatively unchanged. Requirements of different laser applications have fueled regular development of new technologies, opening the doors to new process optimization and physical manipulation of matter.

Optically-pumped rare gas lasers, first presented in 2012, represents a new hybrid of laser and plasma technology with novel avenues of laser characteristic optimization [64]. Relying on a combination of plasma discharge and optical pumping creates a system requiring a deep understanding of underlying electron kinetics. Despite experimental success, numerical study of these systems remains an immature field with several outstanding questions. This work aims to study the non-equilibrium interaction of plasma kinetics and laser operation. Starting from an overview of laser development and fundamentals, this work then derives an intracavity intensity model for coupling with previously discussed KGMf continuity equations. After validation of the chemistry and laser models, the effect of non-equilibrium plasma on laser properties is analyzed for optimum operating conditions.

## 4.2 General Laser History and Concepts

#### 4.2.1 Laser Background

Lasers have become common instruments with consumer, industrial, and research applications. The process of light amplification by stimulated emission of radiation, first given the acronym "laser" in a notebook by Gordon Gould on the 13<sup>th</sup> of November in 1957, relies on theory which took 40 years prove. Albert Einstein's ground breaking work, *On the Quantum Theory of Radiation* [44], laid the theoretical foundations for stimulated emission by combining the concept of probability coefficients for radiative reactions (now called Einstein coefficients) with Max Planck's law of radiation, earning him the Nobel Prize in Physics in 1921. Rudolf Ladenburg validated the concept experimentally in 1928 [90], but the idea of stimulated emission as an amplifier was not proposed until Valentin Fabrikant's 1939 doctoral thesis [108]. Bringing the laser theoretical piece required, Alfred Kastler proposed optical pumping as a stimulation method in 1950 [84] and demonstrated it experimentally in 1952 [22], earning him the Nobel Prize in Physics in 1966.

Overlapping with the final theoretical framework of lasers, Joseph Weber proposed the concept of a microwave amplifier by stimulated emission of radiation (maser) in 1952 at the Institute of Radio Engineers Vacuum Tube Research Conference in Ottowa, followed by the first device demonstration by Charles Townes and his graduate students in 1953. While novel, this original implementation could not demonstrate continuous-wave (CW) operation as a result of difficulties from the two-level excitation structure used. Concurrently in the Soviet Union, Nikolay Basov and Aleksandr Prokhorov built a CW maser by incorporating a three-level excitation through pumping to a higher energy level of ammonia gas [7]. These combined and independent works earned Townes, Basov, and Prokhorov the 1964 Nobel Prize in Physics.

The origins of the laser process, specific from masers, are shrouded in controversy as a result of patent claims and the Iron Curtain of the USSR. While accepted that the earliest reference of the laser acronym comes from a notebook of Gordon Gould, no single person can be credited for the overall concept. Gould's coining of the term came after discussions with Townes, who at the time worked at Bell Labs with Arthur Schawlow. Shortly thereafter in 1958, Bell Labs applied for a patent on an optical maser, or laser, and submitted theoretical calculations to Physical Review [136]. The patent office denied Gould's application in 1959, instead awarding it to Bell Labs in 1960, resulting in several decades of legal battles between the two entities. While Gould won the patent case in 1987, people familiar with the situation believe that instead of malicious idea theft, Townes simply had no interest in keeping the idea a secret [106]. Back in the UUSR, Prokhorov and Basov suggested in 1955 that a viable method for obtaining positive gain could come from optical pumping of a multi-level system. Further complicating matters, Fabrikant submitted a request for a patent in 1951, equivalently the laser process without the name, which was granted in 1959. Due to a lack of records on changes to the application, no one knows if Fabrikant took inspiration from works published in the mid 1950s [15]. Interestingly, Fabrikant developed this work without progressing through the maser process, but both maser and laser systems had been realized by the time the patent was published.

Regardless of initial conception, the first laser device was operated by Theodore Mainman in 1960 [113], using a solid-state ruby crystal as the gain medium. Ali Javan William Bennett and Donald Herriott demonstrated the first gas laser (helium and neon) in 1961 [77], followed by Robert Hall demonstrating the first semiconductor laser (gallium arsenide) in 1962. These three types of lasers, with the addition of liquid/dye lasers, make up the four major classes as defined by their gain medium. Before describing benefits and disadvantages of these different class, the next section will cover basic laser fundamentals and the metrics by which to judge different systems.

#### 4.2.2 Laser Fundamentals

The premise of both maser and laser operation relies on having two energy states, as shown in fig. 4.1a, between which radiative transfer is allowed, and a method to over-populate the higher energy state to produce a population inversion. Considering a system composed of two-particle states,  $|1\rangle$  and  $|2\rangle$ , with population densities  $N_1$  and  $N_2$  and energies  $E_1$  and  $E_2$ , a higher energy particle interacting with an field of frequency  $v_{21} = (E_2 - E_1)/h$  produces stimulated emission at



Figure 4.1 Two and three level laser schemes.

a rate of

$$\frac{dN_2}{dt} = -B_{21}\rho(v)N_2 \tag{4.1}$$

releasing a photon of the same frequency. Similarly, the absorption rate is expressed as

$$\frac{dN_2}{dt} = B_{12}\rho(v)N_1 \tag{4.2}$$

with radiation density  $\rho(v)$  and Einstein B coefficients. Einstein showed that the proportionality constants are equal,  $B_{21} = B_{12}$ , and therefore the difference between state populations directly correlates to net photon flux from stimulated emission,

$$\frac{dN_2}{dt} = B_{21}\rho(v)\left[N_2 - N_1\right] = B_{21}\rho(v)\Delta N \tag{4.3}$$

where  $N_2 - N_1 = \Delta N > 0$  defines a population inversion. If contained within a chamber having walls at temperature *T* and allowed to equilibrate without a source of external power, the relative number of particles in each energy level comes from Boltzmann statistics,

$$\frac{p_{21}}{p_{12}} = \frac{N_1}{N_2} = e^{(E_2 - E_1)/kT}$$
(4.4)

with Boltzmann constant k and transition probabilities,  $p_{21}$  and  $p_{12}$ , for  $2 \rightarrow 1$  and  $1 \rightarrow 2$  respectively. Since  $E_2 > E_1$ , the ratio is never less than unity and the higher probability of a downward transition,  $p_{21}$ , accounts for the difference in populations. With the addition of a radiation source that triggers the transitions between the two states with probability *S* and again allowing the system to reach a (non-thermal) equilibrium, fluxes between the two states must balance, resulting in

a new relation

$$\frac{N_1}{N_2} = \frac{S + p_{21}}{S + p_{12}} \tag{4.5}$$

which again is greater than unity as  $p_{21} > p_{12}$ . In the special case where  $S \gg p_{21}$ , a close enough equivalence of  $N_1$  and  $N_2$  results in a saturated state. Though attainable with microwave transitions, as hv is on the order of  $10^{-5}$  eV while kT at room temperature is ~ 0.026 eV, the high energy of photons in the visible spectrum,  $hv \sim 1-3$  eV, requires an excessively large input power in order to surpass thermal equilibration, destroying efficiency of the amplifier. Without a third pumping level with quenching to the laser level, the energy pumping mechanism contributes to the *S* term, populating both states and working against itself. In Towne's original maser experiment, the two energy states of ammonia were spatially separated with an electric field resulting in a beam formation of predominantly higher energy particles.

In order to demonstrate an efficient laser with optical photons, the lasing scheme requires at least one more energy level, as shown in fig. 4.1b. For a three level system undergoing pumping for the  $1 \leftrightarrow 3$  transition and allowed to equilibrate, the equivalent set of balanced flux equations are

$$N_1(p_{12} + p_{13} + P + S) = N_2(p_{21} + S) + N_3(p_{31} + P)$$
$$N_2(p_{21} + p_{23} + S) = N_1(p_{12} + S) + N_3p_{32}$$
$$N_3(p_{31} + p_{32} + P) = N_1(p_{13} + P) + N_2p_{23}$$

with pumping transition probability *P*. Defining the total particle density as  $N = N_1 + N_2 + N_3$  and assuming saturated conditions such that  $P \gg (p_{31}, p_{13})$ , the steady state solutions become

$$N_1 = N_3 = \frac{N}{2+\lambda}$$
 and  $N_2 = \frac{N\lambda}{2+\lambda}$  where  $\lambda = \frac{p_{12} + p_{32} + S}{p_{21} + p_{23} + S}$  (4.6)

and substituting the solutions into the population inversion condition produces

$$p_{12}\left[e^{\frac{E_2-E_1}{kT}}-1\right] > p_{23}\left[e^{\frac{E_3-E_2}{kT}}-1\right].$$
(4.7)

Finally, the laser amplification is directly proportional to the population inversion

$$N_2 - N_1 = N \left[ 1 - \frac{3}{2 + \lambda} \right] \tag{4.8}$$

which becomes larger as  $\lambda$  increases. Maximization of the population inversion and other laser characteristics greatly depends on the gain medium aside from effects not considered in this simplified case: transition probabilities  $p_*$  are temperature dependent, *S* may alter other transitions in the system (e.g. 2  $\leftrightarrow$  3), and all of these considerations assume CW behavior which is not required for pulsed operation. However, except in the special case of low transition energies, three or more levels are required for efficient operation [155].

Choice of the gain medium largely defines laser properties and the selection thereof is extremely situationally dependent. Though originally described as a "solution seeking a problem" by Maiman [114], the ability to generate a narrow, tight bandwidth, and intense beams of light has found applications in industrial, military, science, and medical fields. In being an amplifier system, a major metric of importance is the amount of power returned for a given pumping intensity, however, specific applications may have emphasis on different laser properties. For example, spectroscopy requires a tunable monochromatic light source whereas a medical application may only need a single wavelength and a military application demands only high-power scalability without a requirement as to output bandwidth.

At the most general level, four categories classify different gain media based on their phase: solid-state, dye, semiconductor, and gas lasers. Solid-state lasers rely on a crystal structure where a "dopant" maintains the population inversion and lasing is induced by optical pumping in the form of a arc lamp, or more recently, diode-pumping. As a result of the nature of the gain medium, solid-state lasers tend to have long energy storage times and high thresholds for damage making them appropriate for high power applications. Dye lasers use an optically-pumped liquid gain medium composed of a carbon-based, soluble, stain which yields a broad output spectrum with a high Stokes efficiency (difference between pump and output wavelengths) and high gain. The latter implies both a low pumping threshold and high incident noise. Semiconductor lasers, or

laser diodes, are electrically pumped and formed by a p-n junction in the gain material. Thanks to decreasing manufacturing costs, laser diodes are becoming commonplace in consumer products (eg. barcode reader) and as pumping mechanisms for other gain materials. Finally, gas lasers use an electrical or optical discharge in a gas mixture and resonant cavity in order to produce coherent light. Applications range from kilowatt-class industrial CO<sub>2</sub> lasers for cutting and welding applications to He-Ne frequency-tunable lasers.

A variety of methods exist for populating the excited states of gas lasers and all rely on a sealed cavity containing mirrors forming a Fabry-Pérot resonator. The CO<sub>2</sub> laser relies on a electrical discharge to populate vibrationally excited states of nitrogen which excites CO<sub>2</sub> through collisional processes. Chemical lasers rely on a chemical process (e.g.  $C_2H_4$ - $NF_3$  yielding fluorine radicals) to introduce energy to the system. Excimer lasers rely on electrical discharge and high pressure to create noble gas molecules, excimers, which undergo spontaneous and stimulated emission to a repulsive ground state followed by dissociation into unbound atoms. Ion lasers similarly use an electrical discharge to generate a population density; however, the energy cost is hampered by a large amount of produced waste heat. Metal-vapor lasers, such as the copper vapor laser, have extremely narrow linewidths making them excellent candidates for Raman spectroscopy. The generation of copper vapor requires temperatures on the order of 1200 K, limiting containment options and energizing pumping for both vapor generation and metal ionization.

## **4.3** Motivation of this Work

### 4.3.1 DPAL

Another gas laser of primary interest to this work is the concept of diode-pumped alkali vapor lasers (DPAL), coined by Krupke with a patent in the early 2000s [93]. Alkali metals present an attractive gain media due to having a single valence electron in the outer-most occupied shell however their reactivity can pose problems with regards to experimental configurations and longevity. The idea, as shown in fig. 4.2, comes from creating a three level laser system with the ground state,  $n^2S_{1/2}$ ,



Figure 4.2 Electronically excited levels of a 3-level DPAL system with ground state  $n^2S_{1/2}$  and further excited levels  $n^2P_{1/2}$  and  $n^2P_{3/2}$  [94]

and two low-lying electronically excited states of an alkali metal,  $n^2 P_{1/2}$  and  $n^2 P_{3/2}$ , with pumping transition line  $D_2$  and lasing transition  $D_1$ . This model has an extremely high quantum efficiency due to the similarity in energy of the two states. As one of the first tested gain media, CW operation of an optically pumped Cs vapor laser was demonstrated by Jacobs, Rabinowitz, and Gould in the early 1960s [73, 134], but did not see continued attention due to a lack of reliable pumping sources. In the following four decades, multiple experimental works demonstrated the effects of different buffer gases on the collisional relaxation from  $n^2 P_{3/2} \rightarrow n^2 P_{1/2}$  with different alkali metals. At the turn of the century, the concept of producing a continuous population inversion through pumping along the  $D_2$  transition was demonstrated, leaving questions as to which pumping source would spectrally match the centerline of the D<sub>2</sub> transition while efficiently coupling to the narrow atomic transition bandwidth.

The development of broad-area laser diodes (AlGaAs or InGaAs) coupled with techniques for reducing their spectral bandwidth from a few nm to a fraction of a nm answered the first question. The second question is handled by the buffer gas accompanying the excited levels [94]. Collisions with the buffer gas transform the  $D_2$  line into a Lorentzian lineshape. Assuming equal transition line-strengths, the Lorentzian transition will have a slightly smaller peak cross section and a wider cross section than with the Gaussian signal, allowing for off-center pumping. Though tight bandwidth overlap would be the most efficient pumping method, the off-center pumping allows for flexibility of the pumping hardware. The same effect presents itself on the  $D_1$  transition, however this mitigates spectral hole burning and facilitates single frequency DPAL operation.

Complications still remain with regards to energy scaled DPAL systems, independent on the reactivity of the alkali vapor. A considerable amount of pumped power is absorbed as heat by the gain medium resulting in thermal lensing. In a non-flowing system, the buffer gas is responsible for the thermal conduction to a cooling surface which is limited by the low thermal conductivity of He. While unique designs have mitigated thermal effects [182], typical DPAL systems employ a heavier buffer gas species or convective cooling. Secondly, while the He buffer gas is used to broaden the pumping absorption lines, it has a low cross section for alkali metal spin-orbit relaxation [65]. Increasing the gas pressure is not a viable means of accelerating the relaxation due to degradation of the beam quality from a lower system opacity. Instead, the addition of small chain hydrocarbons (e.g.  $CH_4$ ) results in an increase to the rate of spin-orbit relaxation without over quenching the  ${}^2P$  levels [69]. Hydrocarbon species also induce the potential for formation of metal hydrides, or "laser snow," which result in carbonaceous deposits damaging window transmittance and mirror reflectivity [82].

### 4.3.2 **OPRGL**

Motivated by the difficulties in handling the reactive alkali species, Han and Heaven demonstrated in 2012 that a similar three level system exists in electronic excitations of noble gases, resulting in the concept of an optically pumped rare gas laser [64]. Completely circumventing the problem of chemically reactive species, the proposed scheme mimics the electronic structure of the DPAL scheme by shifting up in energy. Under electric discharge, the  $np^5(n+1)s$  configuration of noble gases easily populates excited metastable levels  $(n+1)s[3/2]_2$  and  $(n+1)s'[1/2]_0$  [154]. Akin to alkali metals, strongly allowed optical transitions exist connecting these metastable states to the  $np^5(n+1)p$  excitation manifold [92]. Using the lower energy metastable state,  $(n+1)s[3/2]_2$ , as the bottom level, the laser scheme then pumps to populate the  $(n+1)p[5/2]_3$  state, which



Figure 4.3 Excited level diagram for an argon oRGL system.

undergoes spin-orbit relaxation to the  $(n+1)p[1/2]_1$  state followed by lasing emission back to the metastable state, fig. 4.3. Due to the similar electron excitation orbitals, the excited noble gas transitions between *s* and *p* manifolds are analogous to the DPAL transitions, exhibiting similar transition probabilities, upper state radiative lifetimes, lasing wavelengths, pressure broadening coefficients and ionization potentials. Along with the chemically stable nature of noble gases, heating is no longer required to populate the system (replaced by electrical discharge) and other heavy noble gases are available for the spin-orbit relaxation [82] without strong interactions to the rest of the system.

The use of electric discharge as opposed to thermal heating results in both a more efficient method of populating the bottom level of the laser system as well as longer hardware lifetime. Experimental DPAL systems require heating to roughly 120-145 °C and deposited thermal energy is absorbed by every species. By comparison, electric discharge deposits the majority of its energy into the electron population and the excited metastable level, which forms the bottom laser level, is the most readily excited of the argon states. Non-equilibrium discharges further offer the opportunity to focus electrical energy predominantly into species of interest. This can be done at room temperature without requiring the need for heat dissipation.

These first experimental studies demonstrated pulsed lasing with argon, krypton, and xenon metastable states, using helium as a buffer gas due to the high ionization threshold, operating at pressures of 0.2 - 2 bar [64]. With a repetition frequency of 10 Hz, a 10 ns discharge pulse is



Figure 4.4 Experimental time-resolved traces of  $5p[1/2]_1 \leftrightarrow 5s[3/2]_2$  gain in Kr, with colors denoting total pressures of 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.4, 1.6, 1.8, and 2 bar [64].

followed by a 10 ns optical pulse with a tuned gap time depending on the partial pressures. The discharge pulse operated at a minimum voltage of 18 kV with an electrode separation of 2.5 cm in the form of a commercial excimer laser cavity which was not optimized for RGL transitions. The tuned optical pulses had a linewidth of 30 GHz, beam diameter of 0.4cm, and approximately 0.25 mJ of energy. Initially tested with a Kr/He system, the population inversion heavily depended on fast collisional transfers between the two excited p manifold states. In order to explore this dependence, a fixed partial pressure of 27 mbar of Kr was combined with He to form total pressures ranging from 0.2 - 2 bar, with results shown in fig. 4.4. The optimized delay between discharge and optical pumping varied from 5-25  $\mu$ s.

Pressures above 0.6 bar showed nonzero gain; increasing until a saturation pressure of 1.4 bar as a result of competition between radiative and collisional relaxation of the top laser level. Other rare gas mixtures exhibited similar behavior with the additional case of argon lasing without a helium buffer above pressures of 1 bar. Efficiency characteristics are reported as being similar for each mixture, having a photon conversion efficiency of 13% and a metastable number density of at

least  $4 \times 10^{19} \text{ m}^{-3}$ .

Following this work, Demyanov et. al performed initial kinetic studies on CW operation of the RGL scheme with argon [39]. Assuming the metastable population is maintained by a glow discharge, laser efficiency, gain, and power output were found as functions of argon number fraction, total pressure, pump intensity, and system size by solving for the steady-state operation of a reduced reaction mechanism. Considering the four 1*s* excitations and first three 2*p* excitations, where the laser system cycles between  $1s5 \rightarrow 2p9 \rightarrow 2p10$ , electron impact reactions are only considered for excitation of the 1*s* states, spontaneous emission is only considered along the pump and lase transitions, collisional relaxation reactions are only included for the species involved in the laser process, and rates are considered independent of temperature. While the simplification of the mechanism allows for analytical solutions, the excluded state-to-state collisional excitations were neglected with an argument of no available rates in the literature and that experimental results at similar pressures show a larger 1*s*5 density relative to other states in *s* manifold, implying fast and complete energy transfer to the 1*s*5 state.

From steady-state analytic expressions, Demyanov et. al demonstrated that the discharge power, required for maintaining the 1s5 state population, and laser output power both increase with pumping intensity. Beyond saturation of the population inversion, the total efficiency of RGL operation also increases with pumping intensity. The simplified reaction mechanism causes estimates of the required discharge power to be considered as an upper bound of the physical system. The rates of both metastable and excimer production are proportional to total argon concentration in the system. Finally, the threshold pump intensity was found to be on the order of tens of watts with a saturation intensity an order of magnitude higher and quadratic in pressure. As such, lasing in this scenario should be achieved relatively easily.

Later in 2013, Han et. al demonstrated another RGL system using CW optical pumping and 1  $\mu$ s pulsed electrical discharges [63] in an argon helium system. Stable operation was achieved with a pulse repetition frequency of 1 kHz with pressures at or above 0.5 bar. Whereas the previous work relied on high instantaneous pump intensities (~ 0.2 MW cm<sup>-2</sup>) to achieve pulsed laser output,



Figure 4.5 Experimental time-resolved traces of  $5p[1/2]_1 \leftrightarrow 5s[3/2]_2$  intensity in Ar, with colors denoting total discharge voltages of covering [-1 kV,-2 kV] in steps of 100V [63].

Han et. al showed that the power range of a CW diode pumping source need only be on the order of 5-10 W. The DC discharge, operated between -1-2kV, used electrodes separated by 0.5 cm within 15 cm long glass cell of diameter of 5 cm. A mirror and output coupler were placed on either end of the glass cell forming a 35 cm long plane parallel resonance cavity. The cavity is end-pumped with a diode laser centered at 811.754 nm (wavelength of the  $4s[3/2]_2 \rightarrow 4p[5/2]_3$  transition) with a maximum power of 8 W and approximate beam diameter of 200  $\mu$ m. Laser power output was found to be dependent on cavity alignment, proving that lasing was occurring as opposed to emitting a laser-induced fluorescence. Unlike with the previous system, lasing with pure argon was limited to pressures of ~ 90 mbar due to arcing occurring at higher pressures.

Dependence of the lasing system on the discharge voltage was carried out using a mixture of 40 mbar and 420 mbar of Ar and He respectively. While glow discharges were created for lower discharge voltages, lasing was not observed until the voltage was below -1.2 kV. With lower voltages, both laser peak intensity and laser pulse duration increased; the latter to times of  $\sim 0.15\mu$ s. With-



Figure 4.6 Optical gain along microplasma vs pumping intensity; 2% Ar - 98% He at 769 Torr with flow of 3.7 mmoles/s and total microwave power of 9W, data adapted from [135].

out optical simulation, Ar metastables have a lifetime of several  $\mu$ s. Lasing threshold was found to be significantly lower than required intensity from the original RGL experiment at ~ 11 kW/cm<sup>2</sup>. A concluding remark implied a key requirement for further development is the identification of a discharge capable of continuous production of the  $(n+1)s[3/2]_2$  near atmospheric pressures.

In attempting to answer the question of continuous discharge without breakdown, Rawlins et. al demonstrated CW optical gain at atmospheric pressure using a linear micro-discharge array driven by a 900 MHz microwave [135]. Unlike traditional atmospheric discharge limited by short-term breakdown, the linear arrays, credited to Hopwood et. al [181, 176], provide a stable and spatially uniform CW discharge at driving frequencies of ~ 900 MHz. Though operated at low power (under 30 W), the array resonators have high field strengths and create electron and argon metastable densities on the order of  $10^{19}$  m<sup>-3</sup> in a 2% Ar-98%He mixture. Arrays composed of 15 micro-strip resonators, each producing a microplasma, resulted in a 19 mm long microplasma in a width of  $25\mu$ m from ~ 9W of discharge power. Optical excitation was end-pumped along the microplasma, without a resonance cavity, using a CW laser with up to 1 W of power.

Noting localized gas temperature increases up to 600 K, Rawlins et. al measured gains G<sub>0</sub> up to ~ 0.7 cm<sup>-1</sup> with pump saturation occurring ~ 2 kW/cm<sup>2</sup>. The temperature increase marks a larger effect of Doppler broadening, reducing the efficiency of single-frequency pumping but allowing for a wide pump bandwidth. Unfortunately this also implies that the pumping laser will also populate other 2*p* levels. Gain was found to vary significantly in space, with the maximum gain of ~ 1 cm<sup>-1</sup> located downstream from the discharge region. Following the discussion by both Han et. al and Rawlins et. al, kinetic modeling needs to include radiative loss from 2*p*10  $\rightarrow$  1*s*4 as this makes up over 20% of the radiative decay from the 2*p*10 state. Disagreeing with their own steady-state analysis (simplified mechanism) and counter to experimental observations in pulsed operation by Han et. al, Rawlins et. al report relatively small populations of the 1*s*4 state in CW discharge conditions. This was explained by a temperature dependence on the overall transition from 1*s*4  $\rightarrow$  1*s*5 with up to a 10x variation between Han's 300 K experiment and the 600 K measured by Rawlins' team. This suggests that scaling metastable lasers to higher gains in CW operation might require gas heating beyond room temperature. Limits of this analysis and results were attributed to unknowns in the rate coefficients at higher temperatures.

## 4.4 Derivation of Lasing Model

In order to describe these laser systems, the KGMf requires additional terms for both the lasing and pumping processes. Acknowledging the similarity between DPAL and RGL systems, an analytic model for CW DPAL operation is implemented alongside KGMf continuity and conservation equations. Building from initial modeling attempts of DPAL systems assuming longitudinally averaged number densities [8, 10], Hager and Perram developed an analytic two-way averaged plane-wave model assuming single frequency optical pumping of a three-level laser system [62, 61]. Since extremely narrow band pumping is not required for DPAL systems due to broadening of the  $D_2$  absorption line, Zameroski et. al extended this model to account for broadband pumping and spectral overlap of the pump and transition lines in 2011 [180]. While the analytic model presented



Figure 4.7 Assumed two-way passing schemes for induced lasing emission, adapted from [62].

only accounts for the three species involved in the laser process, the continuity equation for intracavity intensity and terms corresponding to pumping and stimulated combine with collisional dynamics to form a complete reaction mechanism for the system.

With spontaneous emission and collisional rates previously defined with regards to KGMf implementation, fine-structure mixing, pumping, and stimulated emission terms are discussed herein. Consider the continuity equations of an example model with the three laser states:  $n_1$  corresponds to the number density of the lower laser level,  $n_2$  the upper laser level,  $n_3$  the relaxing level above  $n_2$ :

$$\frac{dn_3}{dt} = \frac{\Omega(t)}{hv_{31}} - \tilde{K}_{32}^{\min} \pm \sum O_3$$

$$\frac{dn_2}{dt} = \tilde{K}_{32}^{\min} - \tilde{K}_{21}^{\min} \pm \sum O_2$$

$$\frac{dn_1}{dt} = \tilde{K}_{21}^{\min} - \frac{\Omega(t)}{hv_{31}} \pm \sum O_1$$
(4.9)

where  $O_i$  represents particle flux from collisional and spontaneous emission losses described in the first chapter,  $\Omega(t)$  is the pump power absorbed per unit volume, and  $\tilde{K}^{\text{mix}}$  and  $\tilde{K}^{\text{stim}}$  are respectively the spin-orbit mixing and stimulated emission flux terms. The fine-structure mixing term is written as

$$\tilde{K}_{ij}^{\text{mix}} = k_{\text{mix}}^{ij} \left( n_i - n_j e^{\frac{\Delta E_{ij}}{k_B T_g}} \right)$$
(4.10)

with i > j, Boltzmann constant,  $k_B$ , gas temperature,  $T_g$ , mixing rate between states *i* and *j*,  $k_{mix}^{ij}$ , and  $\Delta E_{ij} = hv_{ij}$  is the energy difference between states. The latter two have constant values specific to the gas composition and states involved.

### 4.4.1 Lasing Model

As opposed to tracking the radiation density within the gain region, an intracavity circulating intensity model is used to account for multiple passes within a resonance cavity in a volume averaged context. Extending from sec. 4.2.2, the population inversion in the case of different degeneracies,  $g_i$  for each level, is written as

$$\Delta n_{21} = n_2 - \frac{g_2}{g_1} n_1 \tag{4.11}$$

which is paired with the stimulated emission cross section for transition  $i \rightarrow j$ 

$$\sigma_{ij}(\mathbf{v}) = \frac{c^2 A_{ij}}{8v_{ij}^2 \pi} G_{ij}(\mathbf{v})$$
(4.12)

where *c* is the speed of light,  $v_{ij}$  is the frequency of the transition line,  $A_{ij}$  is the Einstein coefficient, and  $G_{ij}$  is the spectral lineshape function. Assuming a Lorentzian lineshape function and inhomogeneous broadening in a gas [34],

$$G_{ij}(\mathbf{v}) = \frac{1}{2\pi} \frac{\Delta \mathbf{v}_{ij}}{(\mathbf{v} - \mathbf{v}_{ij})^2 + (\Delta \mathbf{v}_{ij}/2)^2} \qquad \Rightarrow \qquad G_{ij} = \frac{1}{\Delta \mathbf{v}_{ij}} \tag{4.13}$$

the dependence on v is removed, relying only on the collisionally broadened line width  $\Delta v_{ij}$ . With species dependent Doppler broadening rates as  $\gamma_{n_b}$ , for each broadening species,  $n_b$ , the linewidth is written as

$$\Delta v_{ij} = \sqrt{\frac{T_g}{298[K]} \sum \gamma_b n_b} \tag{4.14}$$

Assuming small signal gain resulting in stimulated emission from  $n_2 \rightarrow n_1$ , the governing equation for stimulated emission and corresponding solution are:

$$\frac{dI}{dz} = \sigma_{21}(\mathbf{v})\Delta n_{21}I(z) \quad \Rightarrow \quad I(z) = I_{in}e^{\sigma_{21}(\mathbf{v})\Delta n_{21}z} \tag{4.15}$$

with gain defined as the product of  $\sigma_{21}$  and  $\Delta n_{21}$ . Originally developed by Raymond Beach [9] with extensions by Hager et. al, the averaged two-way intracavity intensity,  $\Psi$ , is defined as the integrated intensities of left and right traveling plane waves,  $I_L^-$  and  $I_L^+$ , in the gain medium, averaged over the gain length,  $l_g$ ,

$$\Psi = \frac{1}{l_g} \int_0^{l_g} \left( I_L^+ + I_L^- \right) \mathrm{d}z \tag{4.16}$$

Substituting the solution in eq. 4.15 for each directional intensity in eq. 4.16 and using single pass intensities from fig. 4.7 for  $I_{in}$ , the expression for  $\Psi$  comes to

$$\Psi = \frac{1}{l_g} \left[ I_2^+ \int_0^{l_g} e^{\sigma_{21}\Delta n_{21}z} dz + I_2^- \int_0^{l_g} e^{\sigma_{21}\Delta n_{21}(l_g-z)} dz \right]$$
  
=  $(I_2^+ + I_2^-) \left[ \frac{e^{\sigma_{21}\Delta n_{21}l_g} - 1}{\sigma_{21}\Delta n_{21}l_g} \right]$   
$$\Psi = (I_2^+ + I_2^-) \left[ \frac{e^{\alpha_{21}} - 1}{\alpha_{21}} \right]$$
(4.17)

where  $\alpha_{21} = \sigma_{21} \Delta n_{21} l_g$  is introduced for convenience. The gain medium is assumed to be in a container with two windows facing each other and having transmission factor *t*. A perfect mirror and an output coupler, of reflection factor *r*, form the resonance cavity by encasing the ends of the container. With a reference point of  $I_1^+$  inside the cavity behind the coupler, the intensity is tracked through a round trip of the cavity, picking up a factor of  $e^{\alpha_{21}}$  through the gain medium and *t* through the glass. With relationships between intensities at different points, fig. 4.7, and boundary conditions across the coupler, four identities are used to relate  $\Psi$  to the output lasing intensity  $I_{\text{lase}}$ :

$$I_2^+ = trI_4^- \qquad I_2^- = \frac{I_4^-}{te^{\alpha_{21}}} \qquad I_{\text{lase}} = (1-r)I_4^- \qquad I_1^+ = \frac{r}{1-r}I_{\text{lase}}$$
(4.18)

Combining these relationships with eq. 4.17 allows for the laser output intensity to be written in terms of the average intracavity intensity

$$I_{\text{lase}} = \frac{\alpha_{21}(1-r)te^{\alpha_{21}}}{\left[1+t^2re^{\alpha_{21}}\right]\left[e^{\alpha_{21}}-1\right]}\Psi$$
(4.19)

Depending on the mirrors and glass used, a considerable amount of power may be lost from scattering and transmission loss from imperfect windows. Summing up the difference between intensities at each window transition,

$$I_{\text{scat}} = (I_1^+ - I_2^+) + (I_3^+ - I_4^+) + (I_1^- - I_2^-) + (I_3^- - I_4^-)$$
$$= I_{\text{lase}} \frac{r(1-t)}{1-r} \left[ 1 + e^{\alpha_{21}} \left( t + t^2 + t^3 e^{\alpha_{21}} \right) \right]$$
(4.20)

arrives at an expression for the scattered laser intensity. The conservation equation for  $\Psi$  incorporates gains induced from a round trip in the cavity along with a spontaneous emission noise term to start the laser oscillation,

$$\frac{d\Psi}{dt} = (rt^4 e^{2\sigma_{21}\Delta n_{21}l_g} - 1)\frac{\Psi}{\tau_{\rm RT}} + \frac{n_2 c^2 \sigma_{21} h v_{21}}{l_g}$$
(4.21)

where  $\tau_{\text{RT}}$  is the residence time in the cavity [62]. Finally,  $d\Psi/dt$  couples with the system of equations 4.9 through the stimulated emission rate

$$\tilde{K}_{21}^{\text{stim}} = \sigma_{21} \Delta n_{21} \frac{\Psi(t)}{h v_{21}}$$
(4.22)

which remains dependent on species densities  $n_2$  and  $n_1$  as well as intracavity intensity.

### 4.4.2 Pumping Model

Hager et. al assumed single-frequency (narrowband) pumping which is not quite representative of optical pumping at atmospheric pressures due to collisional broadening of both  $D_1$  and  $D_2$  absorption lines. Zameroski et. al extended the model to account for broadband pumping and spectral overlap of the pump and  $D_2$  transition [180]. Analogously to eq. 4.17, the two-way averaged pump intensity inside the gain medium is written as

$$\vartheta_P = (I_{P0}^+ + I_{P0}^-) \left[ \frac{e^{\alpha_{31}} - 1}{\alpha_{31}} \right]$$
(4.23)

with the new shorthand term  $\alpha_{31}$  for the D<sub>2</sub> transition. Assuming the rear mirror is not perfect with regards to the pumping wavelength (therefore having reflectivity  $r_P$ ) and the pump has a spectral distribution of f(v) and an amplitude time envelope of P(t), the tracked round trip pumping intensities form the identities

$$I_{P0}^+ = t_P P(t) f(v)$$
 and  $I_{P0}^- = t_P^3 r_P P(t) f(v) e^{\alpha_{31}}$  (4.24)

analogous to eq. 4.18, with glass windows having a different transmission coefficient for the pumping wavelength,  $t_P$ . Plugging the relationships back into eq. 4.23 yields the pumping intensity

$$\vartheta_P(t, \mathbf{v}) = \frac{f(\mathbf{v})P(t)t_P}{\alpha_{31}} (e^{\alpha_{31}} - 1)(1 + t_P^2 r_P e^{\alpha_{31}})$$
(4.25)

however this needs to be integrated across the frequency range of the pump for the total energy absorbed by the upward stimulated emission,

$$\Omega(t) = -\int_{-\infty}^{\infty} \sigma_{31}(v) \left[ n_3(t) - \frac{g_3}{g_1} n_1(t) \right] \vartheta_P(t, v) \,\mathrm{d}v \tag{4.26}$$

It can reasonably be assumed that the pump has a normalized Gaussian spectral distribution centered around the transition frequency  $v_{31}$ , such that

$$f_P(\mathbf{v}) = \sqrt{\frac{4\ln(2)}{\pi\Delta v_P}} \exp\left\{\left[-4\ln(2)\left(\frac{\mathbf{v} - \mathbf{v}_{31}}{\Delta v_P}\right)^2\right]\right\}$$
(4.27)

where  $\Delta v_P$  is the spectral pump width (FWHM). Using the pump spectral distribution and the broadened stimulated emission cross section, eq. 4.26 can be integrated to yield

$$\Omega(t) = \frac{P(t)}{l_g} t_p \sqrt{\Delta v_P} (e^{\alpha_{31}} - 1) (1 + t_P^2 r_P e^{\alpha_{31}})$$
(4.28)

Finally, imposing a pump power envelope in time

$$P^{G}(t) = \frac{E_{P}}{A_{P}} \sqrt{\frac{4\ln(2)}{\pi\Delta t_{P}}} \exp\left\{\left[-4\ln(2)\left(\frac{t-t_{0}}{\Delta t_{P}}\right)^{2}\right]\right\}$$
(4.29)

closes the system of equations defined in eq. 4.9 with terms for pump energy,  $E_P$ , beam area,  $A_P$ , and temporal width,  $\Delta t_P$ .

# 4.5 Modeling Results

This work was motivated by two main goals: 1) validation of the KGMf implemented laser model and 2) determining if it is possible to pump the laser scheme electronically as opposed to using another laser. While diode laser technology has both increased in performance and decreased in cost, optically-pumped RGL systems still require two different powering schemes for operation.


Figure 4.8 Excited levels of argon considered in the model. Levels involved in the laser process are in red. Data comes from the LXcat Biagi database [16].

Of interest is whether a 'tuned' EEDF is capable of selectively pumping the gas to maintain a population inversion without over-pumping the reversed laser transition. The experimental works by both Han and Heaven [64] and Rawlins et. al [135] are used for validation of the intracavity laser model. Both systems operate at atmospheric pressure using transitions between excited states of argon gas, fig 4.8. Argon was chosen as it was the only reported rare gas to demonstrate lasing without having a collisional partner. Cases with helium as a buffer gas are also included. Lacking data for interactions between excited species of argon and helium, only ground and ion species of helium are considered. The systems differ in the specifics of the optically pumping source and the method of maintaining the metastable state population. The first case uses a nanosecond discharge pulse while the latter uses an RF discharge.

## 4.5.1 Pulsed Discharge

Matching the original RGL example by Han and Heaven [64], the first case assumes a gain length of 60 cm inside of a resonance cavity. The discharge pulse is operated at 18kV across a distance



(a) Species response to pumping (b) Laser output vs. delay time

Figure 4.9 Optimized delay time between discharge and optical pulses depends on species equilibration.

of 2.5 cm for 10 ns. Optical pumping follows a pressure dependent optimized delay time of 5-25  $\mu$ s. Centered along the D<sub>2</sub> transition of 811.75 nm, the pumping laser has a bandwidth of  $\Delta v = 30$  GHz and deposits 0.25 mJ of energy in a 10 ns timespan. With a beam width of 0.4 cm, peak input intensity is assumed to be 3.14 kW/cm<sup>2</sup>. A repetition frequency of 10 Hz was used experimentally to separate the effect between pulses, allowing for single pulse simulation. An optimized delay time of 2.3  $\mu$ s between discharge and optical pumping was found, however the relative increase in output intensity is nominal, fig. 4.9.

Introducing a buffer gas to the system provides a faster quenching between the pumped and lasing states of argon. A ratio of He:Ar::1:1 was found to provide the greatest increase in output intensity. Keeping the gas temperature fixed removes any pressure dependent (explicit) terms, therefore comparison simulations varied total pressure to maintain the same argon number density in each case. With laser gain proportional to the weighted difference of species concentrations, varying the pressure provides an equal opportunity for each system reach a peak intensity

Overall good agreement was found between reported species densities in the original work [64] and temporal profiles of pulses match well with measurements in the following publication by Han et. al [63]. Differences from reported total output intensity are attributed to efficiency factors in the conversion from intracavity intensity and output intensity



Figure 4.10 Effect of adding helium to the system over a range of ratios. The line type in the right plot transitions from solid to dotted with the same labels as the colors in the left plot.

## 4.5.2 Continuous Discharge

The second validation case was in modeling the micro-discharge array presented by Rawlins et. al [135]. The experimental system is composed of 15 micro-strip resonators generating plasmas in a linear array. Modeling assumptions used here however, considers a single resonator and lasing region. This was done primarily to avoid the spatial variation of gain reported in the experiment. A secondary consideration was to avoid the amplifying effect lasing points releasing photons into neighboring lasing regions. The geometry of the strip was approximated as a cylinder with radius of R = 0.6 mm to match discharge volume. The gas mixture is composed of 2% Ar in a He buffer. Pumping intensities were reported to be as high as ~ 10 kW/cm<sup>2</sup> with a spectral width of  $\Delta v = 2$ GHz.

Unlike the previous example, this system is not within a resonant cavity, bringing into question the validity of using the two-way averaged plane wave model. Instead, the averaged model was reduced to a single-pass configuration [45] with a gain length of 1 cm as reported in the measurements of laser extraction in the original work.

Gain is observed in modeling results in the saturated limit with matching microwave power and species densities. Pulse lengths of optical stimulation are chosen such that population inversion, and therefore output intensity, maintains steady state operation. While in the experimental work



Figure 4.11 Species densities and involved intensities as a result of repetitive optical pumping.



Figure 4.12 Equilibration of species and intensities with 50% helium buffer gas.

the argon is at steady-state densities prior to optical pumping, fig. 4.12, demonstrates pumping during the equilibration phase of the integrator. The relative strength of the pumping process is significantly stronger by comparison to the electron impact excitation rates.

## 4.5.3 EEDF driven

With the start of this work, there was a question as to whether or not non-equilibrium kinetics could be used to optimize the laser process. This idea hinges on the ability to aid pumping to the upper level or quenching to the laser level by using a non-Maxwellian EEDF. This was shown to not be



Figure 4.13 Electron impact cross sections involved in the laser process from LXcat Biagi [16].

energetically favorable as a result of the sharpness of EEDF required for a non-trivial change to laser kinetics. In the ideal scenario, an EEDF and electron temperature would be chosen such that excitation to the (n+1)p excited levels occurred more rapidly than to the lower metastable level. As can be seen in the electron impact cross sections of argon, fig. 4.13, there is no point of overlap between the cross sections for the bottom laser level (1s5) and the two 4p states of the laser system (2p9 and 2p10). This implies that an electronic discharge could not pump the rare gas laser to the point of achieving a population inversion. Instead, the modified EEDF and system electron temperature required would need a narrow bandwidth such as to maximize production of the 2p9 and 2p10 excited levels while minimizing excitation to higher 4p and 4s states. This condition would allow for a more efficient optical pumping scheme. However, the gains from including an electron beam as well as a optical-pumping source would be significantly less efficient than using a more powerful diode-laser.

# 4.6 Conclusion

The implementation of the laser model in the KGMf has been validated, using acceptable tuning parameters, with regards to rare gas metastable laser operation. Validation cases demonstrating



Figure 4.14 Same cross sections fig. 4.13, zoomed in to look at relevant lasing states.

the relatively new process use both constant and pulsed discharge power to generate a plasma and optical pumping to maintain a lasing population inversion. Though the model takes into account spectral overlap in pumping intensities due to broadening, this work motivates the use of spectral tracking within the global model by tracking all spontaneous and stimulated emission processes in order to have a picture of radiation density in the system.

Studies were performed on pulsed and continuous electric discharge effects on populating the lower laser level in argon. Pulsed operation of the electric discharge was experimentally performed in order to avoid localized breakdown effects from the power requirements of exciting a large volume. Continuous discharge operation was stably achieved at atmospheric pressure using a micro-array microwave discharge. When comparing the two discharge methods, peak intensities were found with optical pumping during the electric discharge as opposed to when optical and electric pulses were offset. A population inversion is readily achieved under the combination of both discharge and optical pumping. Overlapping the optical pulse with the electric discharge onset resulted in the largest gain, explained by faster equilibration of the 1s5 state and correspondingly higher pump efficiency, though near steady state population inversion was observed with optical

pumping and steady state species densities.

The optimal EEDF for the laser process in argon would require a bump-on-tail EEDF with an extremely narrow bandwidth in order to avoid overpopulation of higher energy 4p levels. The difficulty arises from the proximity of 4p state threshold energies and similar cross sections. While this EEDF could be achieved with electron beam sources, it is not possible to directly drive a population inversion with an electric discharge. The equivalent effects of an optimized EEDF can be achieved with higher powered optical pumping in a more energy efficient manner.

#### **CHAPTER 5**

## **CONCLUDING REMARKS AND FUTURE WORK**

This dissertation work revolved around the development of a general-purpose global modeling framework and applications to non-equilibrium plasma chemistry. A good deal of effort was spent on guaranteeing generality through reaction data flexibility and the ability to add new physics effect modules (e.g. intracavity intensity). Verified relative to published global model implementations of both plasma and combustion chemistry, studies were then performed on the non-equilibrium chemistry found within plasma assisted combustion and the dynamics of optically pumped lasing between plasma generated excited states of argon after validating each respective global model with experimental results.

Mechanisms were compiled for plasma assisted combustion of hydrogen and methane in a variety of oxygen, argon and nitrogen compositions; incorporating a mixture of fitted and EEDF dependent rates. These mechanisms were used to study the effect of the electron energy distribution on alternative pathways for combustion reaction chains. In order to agree with experimental measurements, a linear transport model was implemented within the KGMf to incorporate spatial effects from gas flow. Following analysis of supplemental excited oxygen,  $O_2(a^1\Delta_g)$ , on the H<sub>2</sub>-O<sub>2</sub> combustion process, the effect of continuous RF discharge on electron-impact chain-branching reactions was studied. Though decreasing the ignition time, a significant portion of discharge power is wasted as thermal energy within the gas. Nanosecond discharges were shown to reduce ignition time through radical species production without significantly contributing to the gas temperature.

Integrating different physics into the KGMf, a stimulated emission and pumping model was developed to study the reaction kinetics of rare gas metastable lasers. Validation of the model was carried out with both continuous and pulsed electric discharge for populating the bottom laser level. Driving the population inversion through electric discharge was found to be inefficient relative to diode laser pumping with regards to direct excitation pathways.

# 5.1 Future KGMf

With any code development or research effort, there is always more that can be implemented or studied. Plans are in place for future development of the KGMf to: incorporate more self-consistent behavior, become a platform for sensitivity analysis and uncertainty quantification of reaction data, and act as a chemistry engine within a spatial framework including transport equations. While some of this work is being performed by new students within our research group (effectively inhouse), we hope that the open-source nature of KGMf will inspire collaboration for improvements beyond present design, as has been the case with other PTSG open-source codes.

#### 5.1.1 Self-consistent EEDF

The major limitation of the KGMf is the lack of a self-consistent EEDF. In order to remedy this, a Boltzmann equation solver or Monte Carlo method could be coupled with KGMf time integration. This development is multi-faceted and non-trivial in the context of maintaining global model computational efficiency. As opposed to the present version, where EEDF dependent reaction rates are pre-calculated assuming distribution dependence on a system variable, such as  $T_e$ , solutions for the EEDF result in scalar values of rate coefficients for considered densities and system parameters at a fixed instance in time. With regards to efficiency, a brute force implementation of solving for the EEDF on each time step reduces the speed advantages of global models. Instead, this implementation requires recognition of the multi-physics time scales involved and a prescription for updating the EEDF selectively. In the same manner that reaction data can be cycled for comparison, interaction between the KGMf and Boltzmann solvers allows for testing of the downstream effects of EEDF assumptions. This allows for a comparison of solution methods; for example, checking the validity of two-term Boltzmann equation approximations in the context of large collisional mass fluxes.

It should however be noted that solutions to the Boltzmann equation are just as data dependent as the global models relative to electron impact reactions. Mentioned in the PAC chapter, EEDF solutions are typically found for an initial gas mixture when fields are known to be relatively fixed. This assumption is questionable when concentrations of gas species no longer match initial conditions, however electron impact cross section data is often not available for radical and excited molecular species. Analysis of EEDF variation from considered gas species would lend credence to the ability to pre-compute the EEDF for a given configuration.

## 5.1.2 Uncertainty Quantification

With functional assumptions based in theory, the reaction mechanism required for plasma systems relies on a mix of gas and plasma phase reaction data. These measured and calculated data describe extremely non-linear systems benefiting from uncertainty quantification (UQ), beyond standard sensitivity analysis, for uncertainty driven result fluctuation estimates and reaction mechanism optimization.

In order to limit the UQ parameter space, dominant reaction pathways and parameters are determined using the PumpKin [116] package along with preliminary sensitivity analyses. Analogously to classical combustion UQ in the literature, uncertainty in the rate parameters, including cross section data and parameterized EEDF shape, is quantified for forward propagation. Focusing on ignition delay times, result confidence intervals are calculated using polynomial chaos expansion and non-intrusive pseudospectral projection tools from the Chaospy [46] package with a wrapper over KGMf batch methods.

#### 5.1.3 Spatial - Fluid Code

While global models are inherently light with respect to computational intensity, the KGMf was developed with evaluation time as a dominant focus. Though partly related to developer impatience, the run time optimizations motivate the inclusion of KGMf models as exportable chemistry engines in spatial resolving codes. The intention here is to create hybrid methods with active chemistry fluids. One major application is related to studying the interaction of plasma-chemistry with

turbulence effects in plasma assisted combustion systems. It has already been demonstrated that both radical and electron species densities can play a large role in the combustion process; spatial variation of these species can therefore lead to kinetic hot spots analogous to thermal hot spots from spark ignition. Localized heating, for example at sheath edge regions, and consequent active radical generation and transport may be key to improving PAC performance.

# 5.2 Future PAC/RGL

Each of the numerical research studies can be readily expanded for more thorough analyses of the underlying chemistry and non-equilibrium behavior. In both cases, global models can be created to match different experimental regimes in the literature. Development of the self-consistent EEDF also provides the opportunity for numerical PAC and RGL studies which have yet to be demonstrated.

With validated models for both PAC and RGL chemistry, large scale parametric studies can be performed with regards to system parameters and resulting ignition time or laser gain respectively. In both cases, sensitivity analysis methods should be used to account for result variation due to poorly known input parameters. Once the operating regimes are understood well enough for stable integration, result-search methods can be used to isolate pathways which can be optimized.

## 5.2.1 PAC

Plasma assisted combustion and ignition represents a breakthrough in the understanding of combustion kinetics. If developed beyond its infancy and incorporated into consumer products, PAC technology has the potential to dramatically change global resource requirements and power structure. In order for this to come to fruition, a firm understanding of the underlying fundamentals are necessary for future application development.

The study presented on PAC can be significantly built upon with new regimes, data, and selfconsistent physics. Of primary interest are the non-equilibrium effects on ignition below the autoignition threshold and contributions of nitrogen species when considering air as the oxidizer source. While our studies focused on the additional contribution that plasma can provide to the combustion process, efficiently achieving ignition below the autoignition threshold fundamentally distorts classical combustion concepts. Vibrational levels of nitrogen have also been shown to dramatically alter reaction pathways through collisional quenching [1] motivating the inclusion of more species. It is still not understood whether excited nitrogen or oxygen molecules are the main drivers behind PAC behavior.

First and foremost, the combustion mechanism including nitrogen species should be validated for low temperature operation. Once dominant pathways have been found through sensitivity analysis, we propose implementing nonlinear control in order to determine domineering parameters of the ignition time. If the KGMf has been coupled to the Boltzmann equation solver, a supplementary study should be performed on variation of the EEDF as a function of radical species densities to check the validity of pre-computing EEDFs. If not yet finished, a more exhaustive set of testing assumed EEDFs should be performed.

#### 5.2.2 RGL

The metastable rare gas laser was originally demonstrated in a number of noble gases while our analyses were performed assuming only argon and helium (as a buffer species). With the intracavity laser module validated, recommended studies revolve around testing behavior of other rare gases and determining if other excitation pathways exist so as to remove the need for optical pumping. Paired with the use of other lasing species, the effects of the helium buffer and possible diatomic gas contamination should be explored. Parasitic electron energy absorption by rotational and vibrational states could alter the discharge driven laser excitation pathways.

Few quenching rates for the upper laser level are available with temperature dependence or measured at the high micro-array operating temperature. Sensitivity analysis to these rates should be performed in order to determine the relative importance of having an accurate model for quenching at higher temperatures. Expanding upon the implemented laser model, which only takes photons of interest into account, an extension would be to include approximate spectral radiation density within the system to determine overlaps between stimulated emission pathways. This would allow for laser schemes with more than three levels along with an accurate description of broadening effects.

APPENDICES

#### **APPENDIX A**

## APPENDIX TO KGMF

# A.1 Derivation of Gas Temperature

The amount of heat released during a chemical process is governed by the laws of thermodynamics and directly results in a change in gas temperature. From the 1<sup>st</sup> law of thermodynamics, the balance between different forms of energy in the system is written as

$$du + pdv = dh - vdp = \delta q + \delta w \tag{A.1}$$

where *u* is the internal energy, *v* is the specific volume or inverse mass density, *p* is the pressure,  $\delta q$  is the heat transfer from external sources, and  $\delta w$  is the frictional work. Introducing the species mass fraction,  $Y_i$ , the total specific enthalpy of a multi-species system is related to species' partial specific enthalpies by  $h = \sum Y_i h_i$ . Using the temperature dependence of the partial specific enthalpies

$$h_i = h_{i,\text{ref}} + \int_{T_{\text{ref}}}^{T} c_{pi} \,\mathrm{d}T \tag{A.2}$$

where  $c_{pi}$  is the specific heat capacity at constant pressure,  $h_{i,ref}$  is the reference enthalpy, and  $T_{ref}$  is the temperature of the reference, eq. A.1 is differentiated to yield

$$dh = c_p dT + \sum_{i=1}^{N} h_i dY_i \tag{A.3}$$

with *i* summing over all species and  $c_p = \sum Y_i c_{pi}$  as the total specific heat capacity. In order to arrive at an equation for the temperature evolution of the system, mass and energy conservation equations need to be defined. Assuming a system with both mass and heat flux, the species continuity equation is defined as

$$\rho \frac{DY_i}{Dt} = -\nabla \cdot j_i + W_i \sum_{l=1}^R v_{il} \omega_l = -\nabla \cdot j_i + W_i \sum_{l=1}^R v_{il} K_i \prod_j n_j$$
(A.4)

where  $j_i$  is the diffusion flux,  $W_i$  is the mass of species *i*, *l* sums over all *R* reactions involving species *i*,  $v_{il}$  is the net stoichiometric coefficient of species *i* in reaction *l*,  $K_i$  is the reaction rate,

and *j* creates a product of all reactant species number densities. The last term of eq. A.4 is the chemical mass source term for species *i*. Ignoring the effects of thermodiffusion, the diffusion flux is defined as  $j_i = -\rho D \nabla Y_i$  where *D* is the binary diffusion coefficient.

Defining energy from external sources as  $q_r$  and the total energy flux as  $j_e$ , the total energy equation

$$\frac{\partial(\rho e)}{\partial t} = -\nabla \cdot j_e + \dot{q}_r \tag{A.5}$$

where *e* is the total energy per unit mass, is turned into a total derivative of the internal energy

$$\rho \frac{Du}{Dt} = -\nabla \cdot j_q - p \nabla \cdot v + \dot{q}_r \tag{A.6}$$

after dropping dependence on the viscous stress tensor and substituting

$$j_e = \rho ev + pv + j_q \tag{A.7}$$

for the total energy flux, where v is the mass average velocity, p is the pressure, and  $j_q$  is the total heat flux. Using Fourier's law of thermal conductivity, the total heat flux is written as

$$j_q = -\lambda \nabla T + \sum_{i}^{N} h_i j_i \tag{A.8}$$

where  $\lambda$  is the thermal conductivity and the Dafour heat flux has been neglected. Using a substitution of  $\nabla \cdot v = \rho D(\rho^{-1})/Dt$ , eq. A.6 is re-written to be in the same form as eq. A.1 after having neglected the  $\delta w$  term

$$\frac{Du}{Dt} + p\frac{D}{Dt}\left(\frac{1}{\rho}\right) = \frac{1}{\rho}\left[-\nabla \cdot j_q + \dot{q}_r\right]$$
(A.9)

Noting the relationship between enthalpy, internal energy, and pressure,  $h = u + p/\rho$ , eq. A.9 can be re-expressed as the enthalpy balance equation

$$\rho \frac{Dh}{Dt} - \frac{Dp}{Dt} = -\nabla \cdot j_q + \dot{q}_r \tag{A.10}$$

In order to solve for the temperature equation, another expression for the total derivative of enthalpy is found by multiplying all terms in eq. A.3 by  $\rho/Dt$  and substituting eq. A.4 for the  $DY_i/Dt$  term, resulting in

$$\rho \frac{Dh}{Dt} = \rho c_p \frac{DT}{Dt} + \sum_{i=1}^{N} h_i (\dot{m}_i - \nabla \cdot j_i)$$
(A.11)

where  $\dot{m}_i$  is the last term in eq. A.4 representing the species mass change due to chemical reactions. Finally, setting enthalpy derivatives in eqs. A.10 and A.11 equal to each other and replacing the heat flux with eq. A.8 yields the temperature equation

$$\rho c_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot (\lambda \nabla T) - \sum_{i=1}^{N} (h_i \dot{m}_i + j_i \nabla \cdot h_i) + \dot{q}_r$$
(A.12)

Prior to solving for a volume-averaged form of the temperature equation, it is worth considering the chemical source term in terms of heat contribution as opposed to mass changes. Writing out the third term from eq. A.12 and including the definition of  $\dot{m}_i$ , the heat release of reaction l,  $Q_l$ , is found through an exchange of summations

$$\sum_{i}^{N} h_{i} \dot{m}_{i} = \sum_{l=1}^{R} \sum_{i=1}^{N} W_{i} h_{i} v_{il} \omega_{l} = \sum_{l=1}^{R} Q_{l} \omega_{l}$$
(A.13)

Removing terms corresponding to spatial variation and including eq. A.13, the temperature equation comes to the general form

$$\frac{DT}{Dt} = \frac{1}{\rho c_p} \left[ \frac{Dp}{Dt} - \sum_{l=1}^R Q_l \omega_l + \dot{q}_r \right]$$
(A.14)

It should be noted at this point that eq. A.14 is extremely coupled to the species continuity equations. While the total specific heat,  $c_p$ , is dependent on the mass fractions, or effectively densities, of all involved species, the summation over heats of reactions includes scaled forms of every species continuity equation. Though easier to derive the temperature equation in terms of mass fractions, KGMf has equations implemented in units of species number density. In order to convert eq. A.14 to eq. 2.3, a conversion from mass fraction to molar concentration must be performed, followed by simplification of enthalpy and specific heat terms taking the NASA polynomial format into account.

# A.2 Control Files for KGMf

Operation of the KGMf is largely defined by two control files. The simulation input file, fig. A.1 defines system parameters, such as external power, pressure, and EEDF, and contains the flags for

#General (default) simulation input file for BASIC_PLAS_Ar
#
#Model Species Name , Constant Flag (T/F) , Initial Value
$ \begin{tabular}{lllllllllllllllllllllllllllllllllll$
GEO       , cyl       , R 0.025 [m]       , L 0.6 [m]         #GEO       , cyl       , R 0.01 [m]       , L 0.0042 [m]         SHEATH       , None         RATS       , Ar_g 1.0         GP2PLAS       , BASIC       , maj:T       , chrg:T         INIT_VALS       , unit=m^-3 , init0=1.4e12 , init1=1.1e14 , init2=1.1e9, init3=1.e12       CUSTOM_VAR         CUSTOM_VAR       , testval=0.0       CUSTOM_SET       , crossana_resolution=[geo;1.4;3.0;200.0]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Figure A.1 Example simulation input file for an argon plasma.

determining if a species is allowed to evolve or held fixed in time. Database values for threshold energy and degeneracy can be overwritten through declaration in this file.

The reaction file, fig. A.2, contains the reaction network and linking information for data corresponding to each reaction. The structure of these files is reduced to hash numbers in order to determine if a model can be recovered from saved data as opposed to fully recompiled. Reactions under the 'REACTIONS' header are included directly from the local database while reactions under 'EXTRA\_REACTIONS' are added by the user. These additions can be dependent on numerical data or passed algebraic expressions. The 'SPEC\_MAPS' section creates species placeholders for grouped species.

```
SPECIES
Ar_g, Ar_exc_1, Ar_exc_2, Ar_exc_3, Ar_exc_4, Ar_exc_5, Ar_exc_6, Ar_exc_7, Ar_exc_8, Ar_exc_9, Ar_exc_10,
→ Ar_exc_11, Ar_exc_12, Ar_exc_13, Ar_exc_14, Ar_pion_0, Ar_pion_1, Ar_pion_2, Ar2_pion_0, Ar_exc_48
SPEC MAPS
Ar_{exc_4s} = Ar_{exc_1} + Ar_{exc_2} + Ar_{exc_3} + Ar_{exc_4}
REACTIONS
Ar_g + Electron -> Ar_g + Electron === DATA( EI_CSmomen_list,0 )DATA
Ar_g + Electron <-> Ar_exc_1 + Electron === DATA( EI_CS_list,1 )DATA
Ar_g + Electron <-> Ar_exc_2 + Electron === DATA( EI_CS_list,2 )DATA
Ar_g + Electron <-> Ar_exc_13 + Electron === DATA( EI_CS_list,13 )DATA
Ar_g + Electron <-> Ar_exc_14 + Electron === DATA( EI_CS_list,14 )DATA
Ar_g + Electron -> Ar_pion_0 + 2*Electron === DATA( EI_CS_list,15 )DATA
A_r_exc_4 \rightarrow A_r_g = DATA(R_A\_const, 16)DATA Ar_exc_2 \rightarrow Ar_g = DATA(R_A\_const, 17)DATA
                                                      DATA( R_A__const, 16 )DATA
Ar_exc_5 \sim Ar_exc_3 == DATA(R_A\_const,45)DATA Ar_exc_5 \sim Ar_exc_4 == DATA(R_A\_const,46)DATA
EXTRA REACTIONS
Ar_ex_u^{-4s} + Electron \rightarrow Ar_pion_0 + 2*Electron = DATA(customEI, (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV), (1.37e-13)*(Te_eV * 0.5)*exp(-4.11/Te_eV * 0.5)*exp(-4.11/Te
                 units = m^3/s, thresh = 4.11[eV])DATA
Ar_{pion_0} + 2*Electron \rightarrow Ar_g + Electron
                                                                                                === DATA(customEI, (8.75e-39)*(Te eV**(-4.5)), units=m^6/s,
             \rightarrow thresh=1.5 * Te_eV)DATA
\rightarrow thresh=1.5 * Te_eV)DATA
#
Ar exc 4s + Ar g \rightarrow 2*Ar g
                                                              === DATA(custom, (3.0e-21), units=m^3/s)DATA
#Analytic cross sections
Ar_pion_1 + Electron -> Ar_pion_2 + 2*Electron === DATA(customElcrossana,
             \rightarrow \text{testval} * \text{cr_sc} * (1.0/((ep-thresh)+emax)) * (((ep-thresh)/((ep-thresh)+emax)) * * 1.127), \text{ cr_sc} = 2.4e - 20[\text{m}^2],
              \rightarrow emax=90.0[eV], units=m^2, thresh=5.5[eV], bounds=[5.6;100.0])DATA
Ar_pion_0 + Electron -> Ar_pion_1 + 2*Electron
                                                                                                           === DATA(customElcrossana,
            \rightarrow cr_sc*(Te_eV/((ep-thresh)+emax))*(((ep-thresh)+emax))**1.127), cr_sc=2.8358e-20[m^2],
             \rightarrow emax=78.954[eV], units=m^2, thresh=4.0[eV], bounds=[5.6;100.0])DATA
#Passed numeric cross section
\pi r_{ascel} a Helectron \langle - \rangle Ar_{asc} r_{asc} + Electron === DATA(customElcross, datafromplots.txt, units=m^3/s, ID=0)DATA
Ar_exc_3 + Electron <-> Ar_exc_11 + Electron === DATA(customElcross, datafromplots.txt, units=m^3/s, ID=1)DATA
Ar_exc_1 + Electron \iff Ar_exc_7 + Electron
                                                                                                     ===
                                                                                                                   DATA(customElcross, datafromplots.txt, units=m^3/s, ID=7)DATA
Ar_exc_1 + Electron <-> Ar_exc_6 + Electron
                                                                                                     === DATA(customElcross, datafromplots.txt, units=m^3/s, ID=8)DATA
```

Figure A.2 Example reaction input file for an argon plasma.

# A.3 Common-Sub-Expression Evaluation and Benefits

As can be seen above, the set of species continuity and conservation equations is extremely coupled. However, not only are they coupled, but there are repeated expressions when considering all equations together. Representing large repetitions, species continuity equations, eq. 2.2, appear in the energy equations in full and the electron energy equation, eq. 2.4, can appear in the gas temperature equation, eq. 2.3. A common smaller repetition is the product of reaction rate and reactant species densities, which appear in the continuity equation of each involved reactant and product species. While the repeated operations are barely registered in time for smaller systems, the number of species and considered reactions grows exponentially with the gas mixtures and physics involved, table. A.1, which in turn burdens evaluation and compilation times of the system.

Model and Phase	ID	# Var. Spec.	# Rates	Energy Eqns.
Ar Plasma	0	17	61	Te
Ar-H <sub>2</sub> -O2 Gas	1	10	64	$T_g$
Ar-CH <sub>4</sub> -O2 Gas	2	31	348	$T_g$
Ar-H <sub>2</sub> -O2 Mix	3	56	169	$T_g \& T_e$
Ar-CH <sub>4</sub> -O2 Mix	4	142	552	$T_g \& T_e$
Ar-H <sub>2</sub> -O2-N <sub>2</sub> Mix	5	115	691	$T_g \& T_e$
Ar-CH <sub>4</sub> -O2-N <sub>2</sub> Mix	6	213	1305	$T_g \& T_e$

Table A.1 Species and reaction counts for a range of chemistry models demonstrating a huge increase in complexity with included species.

Discussed previously, the algebra of the global model (and Jacobian) is separated from the evaluation of the spline reaction rates and compiled. This is done to both speed up evaluation time relative to a pure Python implementation and to support recovery of a previously run global model instead of recomputing it. Reaction rates defined as analytic functions are included in these expressions, assuming all used functions exist within the cmath library. This process is achieved by taking advantage of the symbolic description of equations and transcribing them into C-code. There is always motivation to have a faster evaluation time, but as the problems get larger, compiler optimization begins to have trouble with the extremely large and coupled expressions. In particular, the recursive nature of gcc results in astronomical memory usage; it fails to compile the two example methane cases due to a lack of RAM on a system with 64GB available. Interestingly, the non-recursive clang compiler finishes compilation in the same cases, however, the objects created segmentation fault during linking with the python instance.

ID	CSE	Setup (s)	F Op. Cnt.	F Call (s)	J Op. Cnt.	J Call (s)
0	False	4.29	518	7.88e-6	1251	1.08e-5
0	True	4.92	354	7.76e-6	807	1.02e-5
1	False	23.86	6139	8.07e-5	81264	8.91e-4
1	True	10.40	725	1.35e-5	3731	2.05e-5
2	False	7059.95	77182	5.17e-4	4704460	2.87e-2
2	True	156.94	4708	6.50e-5s	32295	1.08e-4
3	False	308.07	17630	8.37e-5	776015	3.07e-3
3	True	123.48	4771	2.60e-5	304263	3.01e-4
4	False	X	165612	X	23116971	X
4	True	1554.13	19434	8.96e-5	2596179	3.74e-3
5	False	12238.46	117938	3.47e-4	8328475	2.50e-2
5	True	1209.77	19020	7.37e-5	2132907	3.46e-3
6	False	X	335801	X	45667621	X
6	True	6599.70	42369	1.52e-4	8112852	1.18e-2

Table A.2 GCC-5.4 Compile and evaluation timing. Runs marked with X failed to compile due to a lack of memory on a machine with 64GB of RAM available.

Instead of simply throwing the system of ODEs at a compiler, it is possible to take advantage of the known structure of ODE expressions to reduce both the total operation count (linked to evaluation time) and the necessary compilation time. Inspired by SymPy's common subexpression (CSE) detection and collection algorithm, the C-code is written with local variables pre-computing expressions which are repeated throughout the ODE system. First, any species continuity or conservation equations which exists in another ODE equation are given a symbolic placeholder and evaluated before the ODE system. Secondly, rate terms and similarly created shared expressions

are given placeholders and moved earlier in the evaluation time line. Finally, SymPy's CSE algorithm is employed to recursively scan over local variable expressions and ODE equations (with placeholders) such that no operation chain is repeated in a given evaluation of the system of ODEs or Jacobian. This optimization not only reduces evaluation calls by up to an order of magnitude, but also reduces compilation time and memory consumption significantly, as shown in tables A.2 and A.3.

ID	CSE	Setup (s)	F Op. Cnt.	F Call (s)	J Op. Cnt.	J Call (s)
0	False	4.64	518	9.35e-6	1251	1.21e-5
0	True	6.07	354	9.32e-6	807	1.20e-5
1	False	20.37	6139	6.65e-5	81264	8.32e-4
1	True	10.71	725	1.40e-5	3731	2.07e-5
2	False	1100.36	77182	5.18e-4	4704460	2.89e-2
2	True	154.65	4708	5.93e-5	32295	1.13e-4
3	False	169.155	17630	9.04e-5	776015	3.21e-3
3	True	113.36	4771	3.19e-5	304263	3.54e-4
4	False	X	165612	X	23116971	X
4	True	1133.84	19434	9.83e-5	2596179	4.04e-3
5	False	2502.094	117938	3.49e-4	8328475	3.00e-2
5	True	819.84	19020	7.19e-5	2132907	3.54e-3
6	False	X	335801	X	45667621	X
6	True	3150.56	42369	1.64e-4	8112852	1.26e-2

Table A.3 Clang-3.8 Compile and evaluation timing. Runs marked with X failed due to a segmentation fault during function loading.

# **APPENDIX B**

# **APPENDIX TO PAC**

# **B.1** Gas Phase Hydrogen-Oxygen Mechanism

The complete set of 16 reactions required to adequately describe  $H_2$ - $O_2$  combustion in a classical context. Double headed arrows imply the reaction is reversible

$$\begin{array}{c} H_2 \xrightarrow{k_0} 2H \\ O_2 \xrightarrow{k_0} 2O \\ O_2 + H \xleftarrow{k_1} OH + O \\ H_2 + O \xleftarrow{k_2} OH + H \\ H_2 + OH \xleftarrow{k_3} H_2O + H \\ H + wall \xrightarrow{k_4} 0.5H_2 \\ O_2 + H + M \xleftarrow{k_5} HO_2 + M \\ 2HO_2 \xleftarrow{k_6} H_2O_2 + O_2 \\ HO_2 + H_2 \xleftarrow{k_7} H_2O_2 + H \\ HO_2 + H \xleftarrow{k_8} 2OH \\ HO_2 + H \xleftarrow{k_9} H_2 + O_2 \\ HO_2 + H \xleftarrow{k_10} H_2O + O \\ H_2O_2 + M \xleftarrow{k_{11}} 2OH + M \\ H_2O_2 + H \xleftarrow{k_{12}} H_2O + OH \\ H_2O_2 + H \xleftarrow{k_{13}} H_2 + O_2 \\ H_2O_2 + OH \xleftarrow{k_{14}} H_2O + HO_2 \\ H_2O_2 + OH \xleftarrow{k_{14}} H_2O + HO_2 \\ H_2O_2 + OH \xleftarrow{k_{15}} H_2O + M \\ H_2O_2 + H \xrightarrow{k_{16}} H_2O + H \\ H_2O_2 + H \\ H_2O_2 + H \\ H_2O_2 +$$

BIBLIOGRAPHY

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