Modeling and Simulation of High-Density Spray Combustion

Chenwei Zheng
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ABSTRACT

High-efficiencies and low-emissions can be realized in combustion engines that operate at high-pressures and low-temperatures conditions (high densities). The design of such engines relies on accurate models of the physical processes involved. Three areas of concern are multi-phase phenomena, the equation of state for the gas phase and cost-effective chemical kinetic modeling. Fuel injected as liquid must break up into droplets, evaporate, and mix with air before combusting. Models for these processes have been developed and need to be tested against experiments. As for the gas phases, the ideal gas model fails to capture thermodynamic relations at high density combustion. A real gas model is needed, including a convenient method of implementing it in combustion simulations that involve multiple species. Detailed chemical kinetic models are too expensive for computational analysis. Reduced chemical kinetic models are therefore needed.

This thesis develops a framework for accounting for real gas effects in chemically reacting flow. It verifies the need for this complicated solution by comparing the simulations of standard flows with real gas and ideal gas models. The method draws from existing kinetic model resources and the relation of real gas behavior to intermolecular potentials.

An efficient chemical reduction methodology that considers the species production and consumption rate as a solution to reduce the reacting flow simulation is also developed. Four \( n \)-dodecane detailed kinetic models are analyzed and compared to experimental data, then the developed method is applied to obtain a preferred skeletal chemical model for simulation of spray ignition.

After choosing and calibrating a spray break-up and evaporation model, the combined models are applied to the simulation of a standard sprays from the international Engine Combustion Network. The simulations predict liquid and vapor lengths as well as ignition times and lift off lengths reasonably well. The thesis advances the computational analysis of high density combustion, such as found in the spray combustion typical of diesel and rocket engines.
Modeling and Simulation of High-Density Spray Combustion

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Dissertation

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To my wife and our parents for their love, encouragement, and support.
A scientist studies what is, whereas an engineer creates what never was.

- Theodore Von Kármán
Chapter 1

Introduction

1.1 Motivation

This thesis is concerned with the science based simulation of spray combustion that can occur in engines. It is motivated by the importance of energy conversion, the energy outlook, and the challenges that need to be overcome in improving the prediction power of spray combustion simulations.

World energy consumption is projected to doubled in 2040 compared to 1990. Macroeconomic growth of two heavily populated continents, Asia and Africa, is the driving force of the energy consumption growth. Figure 1.1 shows the energy consumption history and projections for the time period of 2000 to 2040. A few observations can be made: projected world energy consumption increases for bio and renewable energy is steady but is about 10% of the total consumption. Globally, the most dominated energy source remains fossil fuels, which include oil, coal, and natural gas. Nuclear energy will remain steady. These projections therefore point to the continued importance of oil, natural gas, and other fossil fuels.

Useful energy for transportation is obtained from fuels through combustion. Accompanied with the combustion process are unburned hydrocarbons (UHCs), particulate matters (PMs), carbon...
monoxide (CO), carbon dioxide (CO$_2$), and various oxides of nitrogen (NOx). These can cause smog, acid rain, ozone depletion, climate change, and health problems. Tightening restrictions on pollutant emissions for in-land, marine, air vehicles is adopted by many countries.

In order to reduce pollutant emissions and economize the limited fossil fuel resources, combustion systems with low-emissions and high-efficiencies need to be developed. As far as high efficiencies are concerned, compression-ignition (CI) engines are better than spark-ignition (SI) engines because of higher compression ratios. Historically, in-cylinder combustion strategies include increasing fuel injection pressure, elevating intake boost, lowering the intake temperature, adjusting injection and ignition timing, as well as exhaust-gas recirculating [2]. Such strategies can be broadly understood as moving toward combustion processes at high pressures and low or moderate temperatures conditions (high densities). For example, as demonstrated in Fig. [2], aviation gas turbines now approach pressure ratio of 50, which could be 50 atm at take off. Modern diesel engines with turbo chargers can reach pressures of about 100 bar. Table [1,1] shows that rocket engines operate around 200 - 300 atm. The indicated specific impulse is defined as the ratio of thrust generated to the propellant
mass flow rate. These conditions could easily exceed the critical point of some fuels and oxidizers as shown in Table 1.2. The fuel and oxidizer are therefore at conditions where the ideal gas law is not applicable.

![Figure 1.2: Pressure ratio trends of gas turbine engine](image)

**Table 1.1: Propellants and chamber pressure for selected liquid rocket engines**

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<th>RS-25 (SSME)</th>
<th>RD-180</th>
<th>Merlin 1D</th>
<th>Raptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propellants</td>
<td>LH2/LOX</td>
<td>RP-1/LOX</td>
<td>RP-1/LOX</td>
<td>CH4/LOX</td>
</tr>
<tr>
<td>Chamber Pressure [bar]</td>
<td>206.4</td>
<td>261.7</td>
<td>97</td>
<td>300</td>
</tr>
<tr>
<td>Thrust (SL) [MN]</td>
<td>1.86</td>
<td>3.8</td>
<td>0.845</td>
<td>1.7</td>
</tr>
<tr>
<td>Specific Impulse (SL) [s]</td>
<td>452.3</td>
<td>338.4</td>
<td>282</td>
<td>356</td>
</tr>
</tbody>
</table>

In recent times, the design and control of engineering systems are carried out with the help of computer simulations. In the case of combustion engines, this is limited by the complexity of the physical processes involved in combustion. In the specific case of CI engines where the fuel is often injected as a liquid, one has to properly account for the liquid fuel break-up, evaporation and
mixing processes. The resulting fuel and oxidizer gases react at high temperatures in accordance with chemical kinetic processes.

Although these challenges have been recognized and subjected to investigations, there are still many challenges that prevent the emergence of predictive and cost-effective simulation tools. More work is therefore needed to resolve these challenges.

Among these challenges, are the real gas behavior, spray model, and chemical kinetic mechanisms. While real gas equations of state (EOS) have been proposed and tested, the challenge for combustion simulation is associated with the determination of the parameter for each of the many species to be encountered in combustion. In the case for the two phase behavior of the spray, many models have been developed, with strengths and weaknesses at different conditions, which must be known before selecting a model for computation. With respect to the chemical kinetic models, while detailed models with reasonable prediction ability have been developed. They are too large for direct simulations (often over a thousand species).

Reduced chemical kinetic models can therefore needed for cost-effective spray combustion simulations. Although some model reduction methods have been developed, simpler and effective reduction techniques are needed.

If the various physical-chemical processes could be properly modeled and simulated, then engine design options can be effectively screened for those that can lead to clean combustion at conditions that yield higher system efficiencies.

This thesis therefore examines past work in spray combustion and contributes toward making spray combustion practical.
combustion simulations both accurate and affordable.
1.2 Literature review

This section reviews past work on spray combustion simulations. It begins with work on real gas equations. It then looks at progress in two phase flow modeling before reviewing work on combustion chemistry. A standardized database of experiments has been developed to constrain model optimization and simulations. This database is then described before the objectives of this thesis are stated.

1.2.1 Real gas equation of state in combustion

The following subsection describes the real gas descriptions in combustion-related analysis. The review ends with describing the theoretical link between intermolecular forces and real gas equation of state.

Non-ideal behavior in combustion modeling

Early non-ideal gas effects in combustion modeling sought to accurately predict properties of detonations [4, 5]. In a matter of 100 $\mu$s, the pressure of the detonation process can vary from 0.1 MPa to 20 GPa [6]. Reactions transform reactants from dilute gas to very dense gas products. Confronting the phenomenon described above, an accurate equation of state needs to cover a wide range of density and pressure, including pure compounds and mixture of various species. The Van der Waals equation of state is a well-known major improvement over the idea gas law. By neglecting the effects of intermolecular attractive forces at high temperature, Nobel-Abel equation simplified the Van der Waals equation and is widely used in simulation for its simplicity and efficiency [7–10]. The Virial equation of state provides close agreement with practical conditions and establishes relationship between the theory and engineering [11, 12]. However, it is often difficult to find the
coefficients for a given gas.

![Graph showing typical operating envelopes for advanced diesel, gas turbine, and gasoline direct-injection systems using n-dodecane, n-decane, and iso-octane as respective fuel surrogates. The diagram is constructed for liquid injection temperature from 300 K to 363 K. The reduced pressure and temperature represent normalized values by the corresponding critical properties of respective fuels [13].](image)

Figure 1.3: Typical operating envelopes associated with advanced diesel, gas turbine, and gasoline direct-injection systems using n-dodecane, n-decane, and iso-octane as respective fuel surrogates. The diagram is constructed for liquid injection temperature from 300 K to 363 K. The reduced pressure and temperature represents for normalized values by the corresponding critical properties of respective fuels [13].

Typical operating conditions of combustion systems are presented in Figure 1.3, where the reduced pressure and temperature are obtained by normalizing values using the critical properties, that is, $P_r = P_G / P_{C,L}$ and $T_r = T_G / T_{C,L}$. Therefore, spray and droplet combustion at elevated pressures as found in combustion engines need to be analyzed with consideration of the real gas effect as well [13–17]. Compressibility effects and enthalpy deviations are considered in some high-pressure spray studies by employing the Redlich-Kwong equation of state [18]. Delplanque and Sirignano [19] studied droplet vaporization in a high pressure quiescent environment with an improved Redlich-Kwong EOS [20]. The study investigated the behaviors of gas phase surrounding a spherically symmetric combustion of a single droplet in an unsteady manner. It was found that under supercritical conditions, compared with the thermal diffusion time in the liquid, the surface temperature increased very quickly. The Redlich-Kwong equation of state with Chueh-Prausnitz mixture rule is needed for phase equilibrium computation.
With respect to combustion analysis, these real gas effects need to be included in simulations. The need to account for real gas effects in Computational Fluid Dynamics (CFD) simulations has been recognized, with the result that increasingly more studies try to address this problem \[21-28\]. Recent comprehensive reviews of work on real gas behavior in reacting flows have been presented by Bellan \[29\], Sazhin \[30\] and Yang \[31\]. These works established that the fluid flow is different once either pressure or temperature exceeds the critical state values. In addition to all of the classical problems of multiphase chemically reacting flows, a unique set of problem arises from the introduction of thermodynamic non-idealities and transport anomalies. Models of real gas behavior are needed.

There are many models of real gas equations of state used in CFD. These include theoretically grounded equations, such as the Van der Waals equation. Complex empirical equations of state are also used, including the 32-term version of Benedict-Webb-Rubin (BWR) equation \[32, 33\]. Most practical real gas EOS are modifications of the semi-empirical Van der Waals equation of state. Currently, in order to simplify computational tasks associated with EOS evaluations, two-term cubic equations of state such as the Redlich-Kwong (RK) model \[34\], Soave-Redlich-Kwong (SRK) \[35\] and Peng-Robinson (PR) \[36\] are widely used for research projects.

These models should also bridge the vapor and liquid states. Vapor-liquid equilibrium (VLE) processes of \(n\)-alkanes from \(C_2\) to \(C_{20}\) were presented by Zhu and Reitz \[37\] to examine the effects of real gas EOS. It was found that the Peng-Robinson and Soave-Redlich-Kwong EOS were superior to the Redlich-Kwong EOS in predicting non-ideal gas properties. However, Peng-Robinson and Soave-Redlich-Kwong require three parameters as input. Therefore, the Redlich-Kwong EOS is generally regarded as the best two-parameter equation \[38\].

Non-ideal effects in non-reacting flow simulations may arise in the study of mixing problems. In this area, Yang’s group \[39, 40\] and Bellan’s research group \[23, 41, 42\] have carried out several simulation studies. Oefelein and Yang \[39\] used LES to study the 2D mixing of hydrogen and oxygen. Choices for real gas behavior were the 32-term Benedict-Webb-Rubin (BWR) EOS \[32\] of Jacobsen and Stewart \[43\] near critical points and the SRK real gas model elsewhere \[44\]. Bellan’s
team \([23, 41, 42]\) opted for the Peng-Robinson equation of state in Direct Numerical Simulation (DNS) and Large Eddy Simulation (LES) study of high-pressure mixing layers. However, they did not contrast these simulations with an ideal gas EOS to clearly show the need for real gas EOS.

Apart from non-reacting flows, real gas effects have been included in several reacting flow simulations with simplified chemistry models \([45-52]\). The consideration of real gas effects resulted in changes in the flow. Kim et al. \([49]\) simulated a liquid rocket reacting flow, where liquid oxygen (83 K) and gaseous hydrogen (275K) were introduced to a combustion chamber at 6.0 MPa. The simulation used a modified Soave-Redlich-Kwong equation of state and consistent thermodynamics along with a real fluid flamelet model. The real-fluid flamelet was found to be capable of realistically predicting the overall characteristics of a turbulent non-premixed \(GH_2/LO_x\) flame at supercritical pressures.

These limited but growing numbers of studies highlight the need for real gas equation of state. However, the resolution of the problem as attempted in previous work requires manually assigning properties and using a simple combustion chemistry model. For multi-species combustion chemical kinetic models, a more practical solution is needed to determine and assign the model parameters. This approach should be tested with standard combustion experiments. Testing with complex reacting flows such as multiphase flows can enhance the predictive nature of combustion simulations.

**Real gas and Lennard-Jones potentials**

For ideal gases it is usual to assume elastic collision to be such that no interacting forces are felt beyond a characteristic separation \(r > \sigma\), but the potential is infinite for \(r \leq \sigma\), necessitating bounce off. Ideal gases hold that most of the time, gaseous particles are sufficiently far apart such that no forces are felt except during collision. The situation changes in dense fluids.

In real fluids, particles interact with others according to an intermolecular potential which is a
superposition of nuclei-electrons attraction and electrons-electrons or nuclei-nuclei repulsion.

The real gas equation can be theoretically linked to intermolecular potentials such as the Lennard-Jones potentials. According to statistical mechanics, the second coefficient, $B_2$, in the virial equation of state can be expressed obtained from an integral that requires the intermolecular potential $[53]$,

$$B_2 = -2\pi \int r^2 \left( e^{-u(r)/(k_BT)} - 1 \right) dr. \quad (1.1)$$

where $r$ is the distance between particles, $u(r)$ is the intermolecular potential model. Various modeling approaches exist for describing the potential in interacting systems, from the simplest model rigid impenetrable spheres to complicated four-parameter Buckingham potential. The most widely used Lennard-Jones 6-12 potential is defined as $[54]$:

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1.2)$$

where $\varepsilon$ is the potential energy depth, and $\sigma$ is the distance at which the inter-particle potential is zero. These parameters are illustrated in Fig. [1.4]

![Figure 1.4: A graph of strength versus distance for the 12-6 Lennard-Jones Potential][1]

---

10
The widely used two-term cubic equations of state such as the Redlich-Kwong (RK) model, Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) require the critical properties of chemical species. The critical and phase change properties of a fluid reflects the nature of intermolecular interactions. A direct theoretical connection or correlation has been sought to link critical state parameters to intermolecular properties. Therefore, real gas properties have been investigated by many groups using Molecular Dynamics and Monte Carlo simulations, starting with Wood and Parker [56]. Verlet [57] later used the Lennard-Jones potential to study the equation of state of a fluid. Subsequently, an accurate equation of state database was compiled by Nicolas et al. [58]. After many more studies, the equation of state was refitted by Johnson et al. [59]. Frenkel and Smit [60] used the Monte Carlo simulation to predict the results from Johnson et al. [59], including the vapor-liquid coexistence region. Traditionally, the Lennard-Jones potential is used to model hard-core neutral atoms or spherical molecules. With the development of statistical associated fluid theory [61], the Lennard-Jones equation of state was analytically studied for hard-core homo-nuclear chain molecules [62, 63]. Chen et al. [64] extended the theory into pure and binary n-alkanes systems and presented an accurate estimation of phase equilibrium.

With accurate description of the molecular interactions, it is therefore possible to predict real gas behavior. The connection between Lennard-Jones potentials of spherical molecules and their critical properties can be explored using Monte Carlo simulations. But for more practical applications, semi-empirical relations are needed for rapid estimation of state properties from molecular potential parameters. These molecular potential parameters are also obtained from experiments indirectly. In combustion modeling, Lennard-Jones potentials are widely existed to describe transport properties in detailed chemistry kinetic models [65–68]. The available potential for each species provides the possibility to account the real gas effect in combustion flow simulation.

This review has therefore shows that although real gas behavior is taken seriously by a limited group of researchers, there is no efficient way to determine the EOS parameters.
1.2.2 Two phase flow modeling in spray combustion

The dispersion and disintegration of a liquid fluid by gas streams abound in nature and engineered systems [69][70]. An image with spray produced by a swirl pressure atomizer might be able to illustrate the rich physics in the process (as shown in Fig. 1.5). Spray combustion is a process in which bulk liquid is broken up into small droplets, followed by evaporation and reactions. This section describes the conceptualization of the instability and liquid break-up. It is followed by description of the adopted framework for two phase flow simulation.

Figure 1.5: Example of a simple spray illustrating many features that need to be characterized [70].
Hydrodynamic instability and droplet breakup

Liquid fuel injected into a combustion chamber becomes unstable and breaks up into smaller droplets based on many factors. Hydrodynamic instability of liquid jets was recognized and formulated in the nineteenth century [71]. The pioneering works were carried out by Helmholtz, Kelvin, Rayleigh and Reynolds. Linear theories associated with jet atomization have been investigated over the last century. Helmholtz (1868) remarked the stream of fluid would dissipate at a distance, after entering a chamber through an opening with sharp edges [72]. The instability problem was later posed and solved by Kelvin [73], leading to the Kelvin-Helmholtz instability. Reynolds investigated the instability of water jet breakup process in a channel flow. The limitation of the instability was shown to be related to the dimensionless number, \( \rho \frac{uL}{\nu} \), that is the Reynolds number [74]. The Kelvin-Helmholtz instability was later explained through vorticity dynamics by Batchelor [75]. Accumulation of the self-induced vorticity and rotation at the vortex together leads to exponential growth of the disturbance.

Rayleigh introduced the stability analysis for liquid jets [76]. His study showed that with an infinitely small disturbance at the beginning of the propagation, a cylindrical jet would be expected to disturb itself due to the capillary force. The Rayleigh-Taylor instability is defined by the following two observations: Rayleigh’s investigation about the equilibrium character of the fluid with variable density under gravity [77], and Taylor’s recognition that the instability of the liquid surface induced by the acceleration between two superposed fluids of different densities in a perpendicular direction [78].

Weber constructed the breakup criterion as the ratio of the drag, or aerodynamic pressure \( \rho (u_2 - u_1)^2 \) and the surface tension \( \sigma \), as \( Wb = \rho (u_2 - u_1)^2 D / \sigma \) [79]. The \( \rho \) is the surrounding density of the fluid, \( u_2 - u_1 \) is the contrast of velocity between the fluid and the droplet, \( \sigma \) is the liquid surface tension and \( D \) is the diameter. Ohnesorge related the viscous effects to droplet breakup, the Ohnesorge number (On) is defined as, \( On = \mu_d / (\rho_d D \sigma)^{0.5} \), where \( \mu_d \) is the dynamic viscosity of
the droplet and \( \rho_d \) is the density of the droplet [80]. Regimes of disintegration based on \( Oh \) versus

Figure 1.6: Classification of regimes of disintegration [81].

\[ Re_L = \left( \frac{\rho_L U_L d_j}{\mu_L} \right) \]

\( Re \) numbers are mapped in Fig. [1.6] According to Reitz [81], there are four regimes of breakup as the liquid injection velocity increased:

- Rayleigh jet breakup. Induced by surface tension, the oscillations on the jet surface grow leads to breakup. Breakup happened a few jet diameters away from the nozzle. Droplet diameter surpasses the jet diameter.

- First wind induced breakup. The surface tension effect is enlarged by the relative motion between the liquid jet and ambient gas. This then produces a static pressure distribution across the jet, accelerating the breakup process. Similar to regime 1, breakup occurs a few diameters away from the injection. Droplet diameter is in the same order as the jet diameter.

- Second wind induced breakup. The relative velocity between the jet and the gas causes the
unstable growth of jet surface waves, which produces droplets. Droplets size is much less than the nozzle diameter.

• Atomization. The liquid jet is completely split up at the beginning of the injection. Diameters of the droplets are much less than the nozzle diameter.

Another key parameter to observe the droplet breakup mechanism is the initial Weber number \( W_b \). The breakup criterion for the droplet disintegration was found to be \( W_b \approx 10 \), in a shock tube study conducted by Hanson et al. \([83]\) and can be smaller if the liquid fluid is turbulent \([84]\). At a small Weber number, oscillations develop at the natural frequency of the droplet, interactions between flow field and droplet increase the amplitude and decompose the droplet into large fragments \([82]\). At moderate Weber numbers, the breakup process is analogous to the bursting of soap bubbles. The droplet deforms into bag shape, eventually bursts, forming a large number of small fragments \([82]\). At higher Weber numbers, the droplet is put at a high risk of Rayleigh-Taylor instabilities. High speed air-stream studies in a shock tube showed that the droplet is ‘stripped’ at its surface, forming liquid ligaments which produce child droplets \([85]\).

Methods and experiments were developed for studying the oscillations and stability of the fluids. There have been several review articles in the theory and applications of the jet breakup and spray combustion process \([16, 86-90]\). However, the essential fluid motion equations are partial differential equations, which leads to technical difficulties in hydrodynamic stability analysis. Up to today, there are only a few classes of flows with very simple configurations that have been resolved \([91]\). Numerical implementation of the CFD simulation enables the possibility to simulate the solution of the complex fluid problem. Some of these numerical simulations require model descriptions of the break up processes so that less detailed simulations can be done on the resulting fragments.
There are two approaches to describe the two-phase spray flows in CFD. Firstly, the Eulerian-Eulerian (E-E) method, where the spray and the gas flow field are both considered as a continuum across the domain. Secondly, the Lagrangian-Eulerian (L-E) approach as a methodology that is based on a statistical description of dispersed phase (particles or spray droplets) that is then coupled with an Eulerian statistical representation of the carrier fluid phase [92]. The inter-phase between the Lagrangian and Eulerian fluid transfers mass, momentum, energy, and species represented by coupling terms in the governing equations.

An accurate simulation of E-E method in an two-phase spray flow problem is a prohibitive task due to the mesh resolution required to track all the interfaces between the droplets and the gas phase. In a typical engine fuel spray process, the droplets size covers a broad range from 10 $\mu$s to 150 $\mu$s [94]. The velocity of the droplet can range from a few centimeters per second to several hundred meters per second [89]. Variations of the droplet size and velocity require Direct Numerical Simulation (DNS) to capture the liquid-gas interfaces [95]. To capture the liquid jet primary breakup (as shown in Figure 1.7), a DNS study performed by Shinjo and Umemura costs 6 billion grid points with
5760 cores running for 410 hours [93]. The domain size was $14.6 \times 4.5 \times 4.5$ in $D$, where $D$ is the nozzle diameter as 0.1 mm.

Alternatively, by representing a population of droplets, the Lagrangian-Eulerian method is cost effective and has been predominantly used in Reynolds-Averaged Navier-Stokes (RANS) and Large Eddy Simulation (LES). The renowned droplet (particle) distribution function, also recognized as the Williams’ spray equation laid down the theoretical foundation for Lagrangian description of the spray. Williams [96, 97] introduced the equation in order to describe the complex disorder encountered in sprays. The equation encompasses the probability density of droplet size and velocity as a function of space and time. It was shown that with a uniform size of initial droplets, simulations could achieve more complete atomization and greater combustion efficiency. The equation assumes the droplets distribution function is related to the radius of the droplets, position and velocity at time $t$,

$$f(r, x, v, t) dr dx dv,$$  

(1.3)

The governing equation is,

$$\frac{\partial f}{\partial t} = -\frac{\partial (Rf)}{\partial r} - \nabla_x \cdot (vf) - \nabla_v \cdot (Ff) + Q + \Gamma,$$  

(1.4)

where $R \equiv dr/dt$ is the droplet growth rate, $F \equiv dv/dt$ is the droplet acceleration, $Q$ represents the source term, accounts for the formation of new droplets, and $\Gamma$ is the rate of increase of the function $f$ caused by collisions between droplets.

L-E sub-models emerged, based on the droplet distribution function and conditions of the flow. A pioneering L-E method in CFD was developed by Duckowicz [98]. The work considered the fully-interacting combination of Eulerian fluid and Lagrangian particle calculations. Another one of the earliest spray models to be employed in CFD was done by O’Rourke [99], who implemented the L-E method in the KIVA code that is used for internal combustion engine application [100].

O’Rourke [101] proposed the Taylor Analogy Breakup (TAB) model, which is based on an analogy
suggested by Taylor [102]. The analogy is between the oscillating and distorting droplet and a spring mass system. The restoring force of the spring is analogous to the surface tension forces, while the external force on the mass is similar to the gas aerodynamic force. In addition, TAB model considers the damping forces caused by the liquid viscosity.

Reitz and Bracco studied the atomization of a round liquid jet and proposed a general mechanism that combines liquid-gas aerodynamic interactions [103]. Reitz then extended the study to high pressure regime, where a multi-dimensional model was used to study atomization and vaporization of the liquid jet [104]. The jet injection was initially described by a ‘blob’, whose size was equal to the nozzle exit diameter. The breakup of the blobs and resulting child droplets were modeled based on jet stability analysis and were subjected to Kelvin-Helmholtz instabilities. This break up mechanism is now called the Wave break up model. Later, the group improved the Wave model by considering both the Kelvin-Helmholtz (KH) and Rayleigh-Taylor (RT) instabilities [105]. The primary breakup of the intact liquid core is described by the KH instabilities model and the secondary breakup of the individual droplets is modeled with the KH instability model in conjunction with the RT instability model. The hybrid spray atomization model is widely use in both diesel and gasoline spray computations.

Although the TAB, Wave and KHRT models have been coupled with RANS and LES simulation successfully, the initial uniform droplets size is not realistic and is solely determined by the injector diameter. A stochastic approach was initially applied to the simulation of secondary atomization for LES [106–110]. The idea is to apply Kolmogorov’s theory about the breakup of solid particles, which describes the cascade of uncorrelated breakage events [111]. The resulting Stochastic Secondary Droplet (SSD) model showed that in a large time limit, for the parent droplets, the child droplet number distribution function can be represented by a Fokker-Planck type equation, treating the secondary breakup as a discrete random event. The implementation of LES provides accurate predictions of turbulent transport and used for estimating the maximum droplet diameter before breakup. The parameters of the model are obtained dynamically by relating them to the local Weber
number with two-way coupling between the gas and liquid phases.

In an L-E spray combustion simulation, a choice has to be made among these models and their parameters need to be validated or improved. By studying sprays at different conditions, recommendations can be made.

1.2.3 Combustion chemistry for turbulent spray simulation

Detailed chemical kinetics model development is a main area of combustion research supported by experimental observation of rudimentary combustion properties [112–116]. The availability of large fundamental kinetic data, advancement of estimation techniques for specific reaction rates, improvement of numerical methods to solve the “stiff” equations and development of fast computers have contributed to modeling the chemical kinetics. Mathematical equations for a general chemical reacting flows including the conservation of mass, momentum, energy, chemical species, equation of state and other thermo-transport properties. Chemical kinetics models provide the relationship in-between chemical components along with the energy equation through the release of heat.

The computational cost of a combustion simulation might determine by the kinetics terms because it involves species temporal and spatial transport equation, a coupled set of ordinary differential equations (ODE’s) for the species concentration and energy evolving with time. Take an \(n\)-dodecane reaction mechanism containing approximately 3,000 species as an example, if one assumes each dimension includes 100 grids, it will be a 10,000 grids in two dimension and 1,000,000 grids in three dimensions. The use of this mechanism requires to solve 3,000, 300,000, 30,000,000 and 3,000,000,000 coupled differential equations for zero dimensional, one dimensional, two dimensional and three dimensional models. In addition, reacting flows are unsteady simulations eventually necessitated solving these equations at each time step. As one of the solution, unsophisticated global reactions are frequently invoked in the flow simulation to compromise the cost produced by detailed chemistry. Chemistry mechanism reduction is another effective way to extract essential chemistry of
fuel surrogates. A well-developed reduced mechanism retains key features of the fuel chemistry that global reactions cannot predict, and it has improved computational efficiency regarding memory usage and CPU calculation time compared to the detailed mechanism.

In realistic computational simulation of combustion, turbulent fluid flow interacts with chemical reactions. Detailed chemistry mechanisms for larger fuels coupled with the flow governing equations are too costly for current computing resources. Figure 1.8 shows more than 20 detailed and moderately reduced mechanisms for hydrocarbon fuels over the last two decades [117]. It can be observed that the number of species, $K$, and reactions, $I$, increase exponentially with the size of the molecule. The Methyl Decanoate model, for example, consists of 3036 species and 8555 reactions [118]. Even with a 0-D simulation, computation of the mechanism to determine ignition behavior is time consuming.

![Figure 1.8: Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled [117].](image)

From the above, continuous efforts on developing mechanism reduction methods are ongoing to
enable researchers in the combustion field to obtain reduced models efficiently without the need for extensive knowledge of chemical kinetic modeling. Most of the existing methods minimized the need for detailed chemical kinetic knowledge. However, a few research groups have the knowledge of the algorithmic skill set necessary for model reduction. Nonetheless, some reduction criteria and species choices are informed by chemical kinetic knowledge.

Reduction methods to obtain skeletal models seek to partially overcome this challenge. Various mechanism reduction techniques have been developed, such as the computational singular perturbation (CSP) \cite{119,120}, intrinsic low-dimensional manifold \cite{121} and chemical explosive mode \cite{122}.

Directed Relations Graph (DRG) \cite{123} is a widely used technique, as well as other derivatives of its kind \cite{124,125}. According to the DRG method, species are preserved based on their local reaction rate in relation to a target species, such as the fuel. Sun et al. \cite{126} developed a path flux analysis method. A recent study by Jia et al. \cite{127} used the DRG method to extract different level skeletal models of $n$-heptane from a large mechanism by Mehl et al. \cite{128}.

In another reduction approach \cite{129,130}, the elemental flux analysis method, depends on the fluxes of different atoms between species. The sum of flux for each species is then compared to a user-defined threshold for deciding whether the species should be removed. The method is utilized for on-the-fly reduction \cite{131}, where each time step of the simulation, this method generates a reduced mechanism.

New mechanism reduction methods continue to emerge. Based on Principal Component Analysis of local sensitivity, Esposito and Chelliah obtained an ethylene-air skeletal model \cite{132}. Karadeniz et al. provided necessity analysis method for species reduction \cite{133}. Zhao et al. \cite{134} introduced the new concept of shortest path and betweenness centrality. Nodal fluxes and nodal relative positions are ranked to quantify the importance of species, showing a sufficient predictive ability in mechanism reduction.
It was recognized that the above methods, especially the DRG variants, require expertise that only a small group of researchers have. Also, DRG methods rely on the simulation of many combustion events from which the important species are discovered. Reduction methods are still needed that are straight forward enough to be applied by non-kineticists and require the simulation of few combustion events to discover a skeletal model. The Alternate Species Elimination (ASE) method, as a species sensitivity method, proposed by Akih-Kumgeh and Bergthorson [135], has been demonstrated in previous studies [136–139]. It has demonstrated its ability to obtain reduced mechanisms from small carbon to large carbon fuels. The ASE method is designed to simplify the complexity of a mechanism by eliminating species that are not sensitive to the reacting process. The method is performed using the open-source package, Cantera [140]. Through the “setMultiplier” function, the package provides the ability to deactivate reactions involving the species to be examined.

Addressing the need for reduced mechanisms of n-dodecane in this work, we will first adopt the ASE method to extract reduced mechanisms from detailed models. We then propose a new reduction method based on the species propensity. This is to further reduce the computational cost associated with ASE method [141].

1.2.4 Engine combustion network spray experiments and simulations

In order to develop science-based combustion simulation tools, a synergy is needed between standard experiments and simulations to test various models. Spray combustion experiments are challenging and the results can be very sensitive to experimental facilities and conditions. Standardizing the experimental procedure and communicating with simulation experts are needed. It is for this reason that an Engine Combustion Network (ECN) was created.

The ECN is formed among engine combustion research community with the goal to reach a consensus on the testing conditions. Based on the consistent experiments, the ECN obtains and
shares valuable spray data, including liquid/vapor penetration depth, ignition delay times and lift-off lengths for various fuels. Experiments of high pressure sprays have been conducted at Sandia National Labs (USA), IFP Energies Nouvelles (IFPEN, France) and Universitat Politecnica de Valencia (CMT-Motors, Spain), Caterpillar, and Eindhoven University of Technology (TU/e). The international collaboration among experimental and computational researchers, started with a \( n \)-heptane spray experiment (“Spray H”), the researches extended to an \( n \)-dodecane spray experiment (e.g. “Spray A”, conditions are listed in Table 1.3 [142–145]). The following section describes the typical experimental facility and the measured data.

Experimental setups for spray combustion

Standard experiments are recommended to generate a database for validation and optimization of spray combustion models. This work is concerned with spray experiments from the engine combustion network.

The standardized fuel spray, Spray A, is representative of conditions in a relatively low-temperature Diesel engine. For experiment studies, \( n \)-dodecane is selected as the single-component fuel surrogate for diesel fuel. It enables us to characterize the thermo-physical and chemical properties of the real diesel fuels, without having to deal with the complexity of the many components in diesel fuels.

<table>
<thead>
<tr>
<th>Table 1.3: ECN Spray A Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>Injection Pressure</td>
</tr>
<tr>
<td>Fuel Temperature</td>
</tr>
<tr>
<td>Orifice Diameter</td>
</tr>
<tr>
<td>Ambient Temperature</td>
</tr>
<tr>
<td>Ambient Pressure</td>
</tr>
<tr>
<td>Ambient Density</td>
</tr>
<tr>
<td>Ambient O(_2)</td>
</tr>
</tbody>
</table>
Fundamental spray combustion characterization can be carried out in heated constant pressure flow rigs [144] and constant volume preburn facilities [146, 147]. The constant pressure flow facility, typically consists of a gas compressor, gas heaters, test chambers, and a control system. The compressed oxidizer is resistively heated before entering into the steady flow chamber where the fuel is injected. The constant volume preburn facility, on the contrary, consists of an instrumental vessel in which a lean mixture of a very reactive fuel such as acetylene is carried out to generate conditions of high temperature. This work draws from experimental data obtained in a constant volume preburn facility.

### Table 1.4: Mixture composition comparison for constant volume preburn vessels.

<table>
<thead>
<tr>
<th>Inst.</th>
<th>Preburn mixture composition (vol-%)</th>
<th>C2H2</th>
<th>C2H4</th>
<th>H2</th>
<th>O2</th>
<th>N2</th>
<th>Ar</th>
<th>Mol. Wt. (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia</td>
<td></td>
<td>3.06</td>
<td>—</td>
<td>0.50</td>
<td>22.63</td>
<td>73.82</td>
<td>—</td>
<td>28.7</td>
</tr>
<tr>
<td>IFPEN</td>
<td></td>
<td>—</td>
<td>0.82</td>
<td>9.39</td>
<td>21.43</td>
<td>68.36</td>
<td>—</td>
<td>26.4</td>
</tr>
<tr>
<td>TU/e</td>
<td></td>
<td>3.15</td>
<td>—</td>
<td>—</td>
<td>22.64</td>
<td>70.07</td>
<td>4.14</td>
<td>29.3</td>
</tr>
</tbody>
</table>

### Table 1.5: Comparison of different vessels, ambient compositions for 15% oxygen Spray A conditions.

<table>
<thead>
<tr>
<th>Inst.</th>
<th>Spray A environment (vol-%)</th>
<th>O2</th>
<th>N2</th>
<th>CO2</th>
<th>H2O</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia</td>
<td></td>
<td>15.0</td>
<td>75.1</td>
<td>6.2</td>
<td>3.6</td>
<td>—</td>
</tr>
<tr>
<td>IFPEN</td>
<td></td>
<td>15.0</td>
<td>71.7</td>
<td>1.7</td>
<td>11.6</td>
<td>—</td>
</tr>
<tr>
<td>TU/e</td>
<td></td>
<td>15.0</td>
<td>71.2</td>
<td>6.4</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>CMT/Caterpillar</td>
<td></td>
<td>15.0</td>
<td>85.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The spray conditions for a given test are established by spark-igniting a combustion mixture such as that described in Table [1.4]. Following the spark-ignited premixed combustion, the test section cools down in a relatively long time due to heat transfer to walls and the vessel pressure slowly decreases. Throughout the process, a mixing fan stirs the mixture in the test chamber to minimize temperature
inhomogeneity and achieve a uniform gas mixture. When the temperature and pressure reach the target conditions, the injection of \textit{n}-dodecane fuel is triggered and the high-speed measurements devices are started. The detail description and operation of the constant volume preburn chambers can be found in literature [142, 148–150]. While the time needed for refilling the premixed gas limits the repetition of the experiment, the constant volume vessel design can achieve temperature and pressure conditions exceeding the current capabilities of constant pressure flow rigs. Although fundamental experimental setups are different between the two instruments, both chambers are capable of ECN Spray A conditions (15% O$_2$, as shown in Table 1.5).

Figure 1.9: Constant volume preburn vessel setup in Sandia National Lab [151].

Figure 1.9 shows the setup of the constant volume preburn vessel at Sandia National Lab [152]. To observe the spray characterization, detection techniques are used, such as, Mie-scatter imaging, Schlieren, and laser extinction. Shadow-graph and schlieren imaging techniques are used to investigate the boundary of the vapor penetration jet [153]. Naber and Siebers [153] showed that the ambient gas density has a significant effect on spray penetration and a small effect on spray dispersion. Compared to non-vaporizing sprays, vaporization decreases the penetration and dispersion by as much as 20%. Higgins et al. [154] diagnosed temporal and spatial evolution of the ignition and premixed-burn phases of the spray with natural light emission and pressure measurements. The investigation observed the two-stage ignition of diesel sprays and found that the first stage chemistry
moves closer to the liquid-phase region with a shorter ignition periods. Transition to the second stage is fast, with premixed-burn occurs. Lillo et al. [151] demonstrated several detection methods for the spatial position and timing of diesel ignition through the optical access. High-speed schlieren and broadband chemiluminescence imaging techniques combined with pressure measurements offer improved understanding of the ignition phenomenon.

Definitions of spray characteristics such as liquid and vapor penetration, ignition delay time and lift-off length have been widely discussed due to their sensitivity to facility effects. The liquid penetration length traditionally can be measured both by Mie-scattering and diffused back-illumination (DBI) imaging. However, the liquid length obtained by Mie-scattering changes depending on the fuel type and operation condition [155]. Therefore, the ECN recommends using DBI or laser extinction with sufficient beam-steering accommodation [152]. The time averaged DBI method is suggested based on the light extinction through the liquid core [150]. The liquid length is measured based on the evolution of the extinction factor $\tau$, defined as:

$$\tau(x,y) = -\log\left(\frac{I(x,y)}{\langle I_{BG}\rangle(x,y)}\right)$$

(1.5)

where the $\langle I_{BG}\rangle$ is the mean intensity of the background created by averaging 10 individual frames taken right before the start of ignition.

The vapor penetration is obtained using a shadow-graph setup. Results obtained by Schlieren set-up are similar but noisier due to the background disturbances [150]. A standardized post processing code is published on the Sandia ECN website. Extra background noise correction is needed under these elevated ambient condition as well as the relatively low frequency measurement.

The flame lift-off length is defined as the distance from the injector to where the initialized reaction zone stabilized. The lift-off length allows fuel and air to premixed before the hot zone and affects the combustion and soot formation downstream [146]. Therefore, it is an often studied characteristic of spray combustion. High speed recordings of excited-state OH (OH*) are implemented to identify
the location of the flame [146][154].

Ignition delay time is an important parameter of spray combustion. To evaluate the delay time, both natural luminosity and pressure measurement are applied in ECN [146][151][154]. For the natural luminosity based method, the recording setup is similar to lift-off length measurement. The goal is to capture the first emission of light emitted at the pre-ignition cool flame. The pressure based technique is based on a dedicated pressure sensor (Kistler 7061: 20 MPa 790 pC/MPa) installed inside the preburn combustion vessel. With a selected amplifier (Kistler 5011B), the signal to noise ratio around the ignition event is tuned to the lowest.

Meijer et al. [144] documented the details of boundary conditions for the two types of experimental setups within ECN. Payri et al. [145] tested a wide range of "Spray A" conditions to measure the spray penetration and spreading angle. It was suggested that gas compressibility at these high pressure conditions is important, resulting in a lower effective momentum transfer between the fuel droplets and the ambient gas. It is important to note that the real gas equation of state was used to determine the bulk temperature, calculated based on the measured pressure and initial mass-average bulk density [142]. However, real gas implementation in CFD has not been emphasized until recently.

**Simulation of standardized spray experiments**

Taking advantage of the extensive experimental database, several groups have carried out CFD studies of the configurations. These include Argonne National Laboratory (ANL) [156][157], Politecnico di Milano (PM, Italy) [158][159], the University of New South Wales (UNSW, Australia) [160], Lund University (Lund, Sweden) [161], and several other researchers [162][163]. In order to match the experimental results, research groups target different parts of the problem. The ANL group [156][157] developed an improved primary break up model, KH-ACT, based on Kelvin-Helmholtz (KH) break up model. PM [158] used OpenFOAM, together with a set of in-house solvers
and libraries to study the effect of combustion chemistry models. They used direct integration of chemical kinetic model. It was shown that at high pressure conditions, the well-mixed model is capable of properly predicting ignition delay with good accuracy. However, the overall burning rate and flame lift-off were not well predicted. Skeen et al. [164] pointed out that in order to match the experimental vapor penetration depth using URANS simulations with the standard $k - \varepsilon$ model, the constant $C_{\varepsilon_1}$ had to be augmented from 1.44 to 1.52. Nonetheless, the selection of equation of state was not mentioned in these simulation studies.

The Oefelein group [165–168] started addressing the real gas effects at the ECN by focusing on the liquid-vapor phase change problem. In high pressure diesel engine, the real gas effects will replace the classical liquid-vapor interface with continuous inter-facial mixing. Dahms and Oefelein [165] first presented a study, revealing that the two-phase interface is thickened at high sub-critical temperatures with a reduction of the mean free molecular path. At a certain point, accounting for the reduced surface tension, the inter-molecular forces dominated, leading to a continuous phase transition. Later, the Oefelein group [166, 167] presented high-speed imaging from Sandia, corroborating that continuous gas-liquid inter-facial mixing occurs at high pressure diesel engine conditions. More recently, the Oefelein group [168] employed LES techniques coupled with real-fluid thermodynamics and transport properties to analyze the “Spray A”. The chemical kinetic scheme they used contained 2,115 species and 15,787 reactions. The SRK EOS was employed for reduced temperatures less than unity, while the PR was chosen for higher reduced temperatures, using the corresponding state principle. Auto-ignition time was defined as the time for the perfectly stirred reaction (PSR) to reach 90-percent of its equilibrium temperature. Due to the high spray velocity, their study revealed supersonic regions in the mixing layer. The subsequent compressibility effects lead to pressure waves that affect the transient mixing of the injected fuel.

With advanced optical diagnostics, Crua et al. [169] observed that the diffusive mixing transition of microscopic droplets take place at a higher pressure and temperature ($T_r \sqrt{P_r} \geq 3.7$), while Spray A is within the sub-critical regime. In addition, the measurements demonstrate that the
diffusion mixing does not occur at the beginning of the injection. Therefore, the classical two-phase Lagrangian-Eulerian description for Spray A simulations can still be used for this spray.

Although the boundary conditions in experiments are treated as real gas, majority of the simulation studies either using ideal gas or do not mention choice of equation of state. For those studies using real gas equation of state, the parameters for intermediate species are unknown. This work will therefore develop a convenient framework to account for the real gas behavior of the multi-species gas mixtures that occur in the diesel engine spray.

1.3 Scope of the work

From the above motivation and literature review, we observe a number of gaps and open questions. First, the optimal combination of equation of state behavior and turbulent models has not yet been established at high pressure conditions. The lack of systematic assignment of real gas model parameters in high density combustion flows is noted. A framework to provide critical properties needs to be developed for each chemical species for further investigation of reacting flows. Moreover, with the large chemical kinetic models developed today, turbulent flow simulations are extremely costly. Large carbon fuel surrogate such as n-dodecane needs skeletal chemical reaction mechanism to reduce the species number. With respect to capturing the ignition behavior of spray A, a combination of liquid break-up, chemical kinetic model and turbulent model needs to be carefully identified. This work seeks to capture physical and chemical processes of high density flow using numerical simulations at a reasonable computation cost. Specifically, this thesis seeks to:

- Evaluate real gas and ideal gas differences in some standard flows so as to justify the need for real gas equation models, which are often more complex and avoided.

- Develop an estimation framework and evaluate real gas equation of state parameters based on intermolecular potential parameters that are available in current chemistry models.
• Apply and develop of the framework in combustion problems with multi-species. These include a LOX/kerosene fueled rocket and diesel spray.

• Extend the ASE method and develop a cost-effective species propensity method for reducing n-dodecane chemistry, demonstrating that the model results in reasonably accurate predictions for ignition delay times.

• Calibrate a CFD model for the prediction of liquid and vapor penetration length of Spray H/A by KHRT model. Further, demonstrated the use of the developed chemistry model in WM-LES simulation of ignition delay time and flame lift-off length of Spray A.

In the first part of this work, the real gas behavior of representative jet sprays is examined using Large Eddy Simulation technique. Mesh quality is carefully designed to capture the turbulent flow features. Simulations results with real gas equation of state show closer agreement with experimental data, leading to the development of a framework to provide real gas parameters for high-density combustion flow, where thousands of intermediate species have unknown properties. A LOX/kerosene rocket combustion problem is then used to demonstrate the framework of deriving real gas parameters from chemical kinetic files.

The second part of the thesis focuses on the ignition investigation of n-dodecane spray combustion. Several most recent detail mechanisms are validated against experimental data at elevated pressure. Reduced chemical kinetic models are derived based on methodologies developed by the group.

Lastly, CFD of auto-ignition behavior is examined for Spray A. Spray simulation is carried out based on Lagrangian-Eulerian method. A non-reacting case is calibrated with experimental data (liquid and vapor penetration length) provided by the Engine Combustion Network. Reacting simulations are then carried out using the reduced chemical kinetic model developed in the second part of the work. Real gas effects are counted for intermediate species based on the framework from the first part of the work. If these objectives are all achieved, spray combustion simulation will be advanced in terms of physically relevant models and computational cost.
Chapter 2

Modeling procedure and analysis

In this chapter transport equations for multicomponent and chemically reacting flows are first presented. This is followed by a description of real gas equations of state, thermodynamic properties and transport properties. The transport properties depend on intermolecular properties that can also be used to determine real gas equation of state parameters. Plausible correlations between intermolecular potentials and real gas equation of state parameters are then discussed. Subsequently, models needed to account for turbulence, spray processes and chemical reactions are briefly presented. This section concludes with a description of the procedure used to address the project objectives outlined in the previous chapter.

2.1 Governing equations of flow dynamics

The theoretical framework of fluid mechanics is based on the continuum assumption. The governing equations of fluid dynamics consist of the conservation of mass, momentum, energy, and species concentration. The index notation form of the conservation equations for chemically reacting flows is:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0, \quad (i = 1, 2, 3)
\]
\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_j} = \frac{\partial \sigma_{ij}}{\partial x_j}, \quad (j = 1, 2, 3) \tag{2.2}
\]

\[
\frac{\partial (\rho E)}{\partial t} + \frac{\partial [(\rho E + p) u_i]}{\partial x_i} = -\frac{\partial q_i}{\partial x_i} + \frac{\partial (u_i \tau_{ij})}{\partial x_j}, \tag{2.3}
\]

\[
\frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial (\rho Y_k u_j)}{\partial x_j} = \dot{\omega}_k + \frac{\partial (\rho D_k \partial_j Y_k)}{\partial x_j}, \quad (k = 1, 2, 3, \ldots, N). \tag{2.4}
\]

where \(\rho\) is the density, \(t\) is the time, \(u_i\) is the components of the velocity vector, \(\sigma_{ij}\) is the viscous stress tensor, \(E\) is the specific total energy, \(p\) is the pressure, \(q_i\) is the heat flux vector, \(\tau_{ij}\) is the deviatoric stress tensor, \(Y_k, \dot{\omega}_k\) and \(D_k\) are the mass fraction, chemical source term and mass diffusion coefficient of species \(k\). The species conservation equation (Eq. 2.4) is solved for \(k = 1, \ldots, N - 1\), where \(N\) is the total number of species. To minimize the numerical error, the \(N_{ih}\) species is selected as the one with largest mass fraction. For an Newtonian fluid, the Stokes’ hypothesis can be used for the viscous stress tensor, \(\sigma_{ij}\), found in Eq. 2.2:

\[
\sigma_{ij} = -p\delta_{ij} + \tau_{ij} = -p\delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_k}{\partial x_k} \delta_{ij}, \tag{2.5}
\]

where the deviatoric stress tensor is expressed as,

\[
\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_k}{\partial x_k} \delta_{ij}. \tag{2.6}
\]

The mass specific total energy is defined by the sum of the specific internal energy and the kinetic energy,

\[
E = e + \frac{1}{2} u_i u_i, \tag{2.7}
\]

where \(e\) as the specific internal energy, related to the specific enthalpy as:

\[
e = h - \frac{p}{\rho}, \tag{2.8}
\]
where specific enthalpy \( h \) is the sum of the specific enthalpies of all species,

\[
h = \sum_{k=1}^{N} Y_k h_k.
\]  

(2.9)

The detailed formulation of the thermodynamic properties will be discussed in Section 2.2.

The heat flux vector in Eq. 2.3 is defined as,

\[
q_j = -\lambda \frac{\partial T}{\partial x_j} + \sum_{k=1}^{N} j_{k,j} h_k + R \sum_{k=1}^{N} \sum_{l=1}^{N} X_l D_{T,k} \frac{\partial}{\partial x_j} (u_k - u_l),
\]

(2.10)

where \( j \) and \( k, l \) are indexes of spatial coordinate and species. Here, \( \lambda \) is the heat conductivity, \( T \) is the temperature, \( j_{k,j} \) is the multi-component species diffusion flux, \( h_k \) is the partial enthalpy of species \( k \), \( R \) is the universal gas constant, \( X_l \) is the mole fraction of species \( l \), \( u_k \) and \( MW_k \) are the dimensionless diffusion velocity and molecular weight of the \( k \)th species, and \( D_{T,k} \) and \( \mathcal{D}_{kl} \) are the dimensionless thermal diffusion coefficient of species \( k \) and binary mass diffusion coefficient between species \( k \) and \( l \).

The last term in the equation referred as the Dufour effect, represents the heat flux induced by gradient of mass concentration. As noted in other works [45, 170, 171], Dufour effects appear to be insignificant at elevated pressures due to enhanced chemical reaction rates that override changes in diffusion and is therefore neglected in the current study.

The multi-component species diffusion flux term, \( j_{k,j} \), in Eq. 2.10 is given by,

\[
j_{k,j} = -\left( \rho D_{k,m} + \frac{\mu_t}{Sc_t} \right) \frac{\partial Y_k}{\partial x_j} D_{T,k} \frac{1}{T} \frac{\partial T}{\partial x_j}.
\]

(2.11)

where \( D_{k,m} \) is the mass diffusion coefficient for species \( k \), \( \mu_t \) is the turbulent viscosity, \( Sc_t = \mu_t/(\rho D_t) \) is the turbulent Schmidt number set to be 0.7 as noted in a DNS work by Brethouwer
$D_t$ is the turbulent diffusion coefficient, the Soret term contributes to the mass diffusion associated with temperature gradient, it is suggested to be negligible for supercritical pressure LOX/H$_2$ flames [45].

These transport equation can therefore be used to simulate the flow field when these terms are all defined.

### 2.2 Equation of state and thermo-transport properties

To close the Navier-Stokes equations, however, an equation of state is needed to accurately determine the density, pressure and temperature relation. The flow field is sensitive to the chosen equation of state. This section describes the equation of state models. This is followed by a discussion of how thermodynamics properties and transport properties are incorporated. Subsequently, a new simulation framework to provide real gas equation of state parameters based on transport data files is introduced.

#### Equation of state models and mixing rules

In the present study, both ideal gas and real gas are considered. They are compared to establish differences in the high-density flow simulation. The formula of ideal gas EOS is given by:

$$P = \frac{\rho RT}{MW},$$  \hspace{1cm} (2.12)

where $R = 8.314$ J·mol$^{-1}$·K$^{-1}$ is the universal gas constant, the density of the mixture $\rho$ is calculated based on weighting of partial densities with the mole fraction of each species:

$$\rho = \sum_{k=1}^{N} X_k \cdot \rho_k,$$  \hspace{1cm} (2.13)
The molecular weight \( MW \) of the mixture is computed by weighting the molecular weight with respective mole fraction of the species:

\[
MW = \sum_{k=1}^{N} X_k \cdot MW_k.
\] (2.14)

Semi-empirical cubic equations of state for real gases are widely used in combustion simulations due to their simplicity. For a pure compound, the cubic equation of state requires critical properties, \( T_c \) and \( P_c \) as input properties, while some of the equations need the acentric factor, \( \omega \). By applying certain mixing rules, one can obtain the equation of state parameters for a multi-species mixture, such as one found in combustion problems.

According to Zhu and Reitz [37], the general form of cubic equations of state can be written as:

\[
P = \frac{RT}{V - b} - \frac{a}{V^2 + qbV + wb^2}.
\] (2.15)

where \( V \) is the volume of a system and \( R \) is the universal gas constant; \( q \) and \( w \) are constants depending on the type of cubic EOS.

For pure species, the expressions for EOS parameters are presented in Table 2.1 where \( T_c \) and \( P_c \) are critical temperature and critical pressure, \( \omega \) is the acentric factor, \( \kappa \) is a constant that depends on the acentric factor and the reduced temperature, \( T_r = T / T_c \). As shown in Table 2.1 the Redlich-Kwong EOS is a two parameters model, since only the critical properties \( T_c \) and \( P_c \) are needed. As for the Soave-Redlich-Kwong and Peng-Robinson, the acentric factor \( \omega \) is also needed. As an example, parameters for some combustion-relevant species are listed in Table 2.2.

For multi-species systems, a binary mixing rule with regard to \( a \) and \( b \) is suggested by Peng and
Table 2.1: Variables for cubic EOS

<table>
<thead>
<tr>
<th>Equation Name</th>
<th>b</th>
<th>a</th>
<th>q</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redlich-Kwong</td>
<td>$\frac{0.0867RT_c}{P_c}$</td>
<td>$\sqrt[3]{\frac{0.4278R^2T_c^{2.5}}{P_c}}$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Soave-Redlich-Kwong</td>
<td>$\frac{0.08664RT_c}{P_c}$</td>
<td>$\frac{0.42747RT_c^{2.5}}{P_c}[1 + \kappa(1 - T_r^{0.5})^2]$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Peng-Robinson</td>
<td>$\frac{0.07780RT_c}{P_c}$</td>
<td>$\frac{0.45724R^2T_c^{2}}{P_c}[1 + \kappa(1 - T_r^{0.5})^2]$</td>
<td>2</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[\kappa = (0.480 + 1.574\omega - 0.176\omega^2)\]

\[\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2\]

Table 2.2: Thermodynamic properties of representative combustion-relevant species

<table>
<thead>
<tr>
<th>Species</th>
<th>MW [kg/kmol]</th>
<th>Tc [K]</th>
<th>Pc [bar]</th>
<th>(\omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>28.0</td>
<td>126.19</td>
<td>33.98</td>
<td>0.040</td>
</tr>
<tr>
<td>O(_2)</td>
<td>32.0</td>
<td>154.58</td>
<td>50.43</td>
<td>0.022</td>
</tr>
<tr>
<td>CO</td>
<td>28.0</td>
<td>134.45</td>
<td>34.99</td>
<td>0.049</td>
</tr>
<tr>
<td>H(_2)</td>
<td>2.0</td>
<td>33.18</td>
<td>13.00</td>
<td>-0.220</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>44.0</td>
<td>304.18</td>
<td>73.80</td>
<td>0.228</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>18.0</td>
<td>647.00</td>
<td>220.64</td>
<td>0.350</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>16.0</td>
<td>190.60</td>
<td>46.10</td>
<td>0.010</td>
</tr>
<tr>
<td>n-C(_3)H(_8)</td>
<td>44.1</td>
<td>369.90</td>
<td>42.50</td>
<td>0.152</td>
</tr>
<tr>
<td>n-C(_7)H(_16)</td>
<td>100.2</td>
<td>540.00</td>
<td>27.40</td>
<td>0.350</td>
</tr>
<tr>
<td>n-C(_12)H(_26)</td>
<td>170.3</td>
<td>658.20</td>
<td>18.00</td>
<td>0.562</td>
</tr>
</tbody>
</table>

Robinson \[36\] as:

\[a = \sum_i \sum_j x_i x_j a_{ij},\]
\[b = \sum_i x_i b_i,\]
\[a_{ij} = (1 - \delta_{ij})a_i^{1/2}a_j^{1/2}.\]

where \(\delta_{ij}\) is an empirically determined binary interaction coefficient, characterizing the binary interaction formed by component \(i\) and component \(j\). In this equation, \(\delta_{ij}\) is observed to lie between \(-0.2\) to \(0.2\) and in majority binary mixtures it is postulated to be \(0.0\) \[91\]. This method is
implemented in this thesis.

Another method to deal with the mixing rule is the pseudo-critical method based on the corresponding state principle (CSP). To obtain an equation of state, we first calculate the pseudo-critical properties for the mixture. According to Poling et al. [44] the pseudo-critical temperature $T_{cm}$ can be estimated by the simplest mole fraction averaged method [173]: $T_{cm} = \sum_{i=1}^{n} y_i T_{ci}$. As for the pseudo-critical pressure, $P_{cm}$, a mole-fraction averaged pure-component critical pressure is normally unsatisfactory. This is because the critical pressure for most systems goes through a maximum or minimum as the composition varies. The only exception to this defect is if all components of the mixture have similar critical pressures or critical volumes. The simplest rule which can give acceptable $P_{cm}$ values for two-parameter or three-parameter CSP is the modified rule of Prausnitz and Gunn [174]:

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} = \frac{\left( \sum_{i=1}^{n} y_i Z_{ci} \right) R \left( \sum_{i=1}^{n} y_i T_{ci} \right)}{\left( \sum_{i=1}^{n} y_i V_{ci} \right)},$$

(2.17)

where all of the mixture pseudo-critical properties, $Z_{cm}$, $T_{cm}$, and $V_{cm}$, are given by mole-fraction averaging and $R$ is the universal gas constant.

The mixture pseudo acentric factor is commonly given by a mole fraction average [175]:

$$\omega_{cm} = \sum_{i=1}^{n} y_i \omega_{ci}.$$

(2.18)

Thus, with knowledge of the critical temperature and critical pressure (in some cases, the acentric factor) of each species, the EOS for the mixture is determined.

From the above discussion, the binary mixing rule of Peng and Robinson [36] seems simple and reasonably accurate.

Modeling real gas behavior is non-trivial but necessary because the deviation of density predicted by ideal gas law at high-density conditions is large and cannot be ignored. As an example, Figure 2.1 shows predicted densities of $n$-$C_3H_8$ and $n$-$C_7H_{16}$ using the ideal gas and different cubic EOS is
compared to experimental data from the NIST database [176]. The deviation of the density evaluated from the ideal gas model increases when the carbon number becomes larger, while the real gas equations of state provide good agreements with the experimental data. This is only for selected conditions. The problem therefore needs to be considered when simulating high density flows. The effect of different EOS on the flow field will be investigated as part of this thesis to emphasize the problem.

Thermodynamic properties

The thermodynamic properties uses in combustion simulations are given as NASA polynomial fits. The reference state for these fits is temperature of 298.15 K and a pressure of 1 bar.

For species $k$, the heat capacities, enthalpy and entropy at constant pressure is given as,

$$\frac{C_{p,k}(T)}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4,$$  \hspace{1cm} (2.19)
\[ H_k(T) = \int_{298.15K}^{T} C_{p,k}(T) dT + H_k^0(298.15K) \]

\[ = RT \left( a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{6} \right), \]  

(2.20)

\[ S_{p,k}(T) = \int_{298.15K}^{T} \frac{C_{p,k}(T)}{T} dT + S_k^0(298.15K) \]

\[ = R \left( a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \right), \]  

(2.21)

where the superscript 0 indicates the standard state properties.

Other thermodynamic properties can be calculated based on \( C_{p,k}, H_k \) and \( S_k \). The specific heat capacity at constant volume \( C_{v,k} \) is written as,

\[ C_{v,k}(T) = C_{p,k}(T) - R, \]  

(2.22)

The internal energy \( U_k \) is defined as,

\[ U_k(T) = H_k(T) - RT, \]  

(2.23)

The entropy is referred to standard state pressure \( p^0 = 1 \) bar and defined as,

\[ S_{v,k}(T, p) = S_{p,k}(T) - R \ln \frac{p}{p^0}. \]  

(2.24)

For ideal gas mixture, the averaged thermodynamic properties are defined based on molar composition of each species:

\[ C_p = \sum_{k=1}^{N} C_{p,k} X_k, \]  

(2.25)

\[ C_v = \sum_{k=1}^{N} C_{v,k} X_k, \]  

(2.26)

\[ H = \sum_{k=1}^{N} H_k X_k, \]  

(2.27)

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\[ U = \sum_{k=1}^{N} U_k X_k, \]  
(2.28)

\[ S = \sum_{k=1}^{N} \left( S_{p,k} - R \ln X_k - R \ln \left( \frac{P}{P^0} \right) \right) X_k \]
\[ = \sum_{k=1}^{N} \left( S_{v,k} - R \ln X_k \right) X_k. \]  
(2.29)

The real thermodynamic properties are generally taken as the sum of values provided by ideal gas model and a departure function accounting for the real gas effects. Differences in flow structure can be induced by the departure function in internal energy or enthalpy. Internal energy, enthalpy and entropy can be expressed as:

\[ dU - C_v dT = \left[ T \cdot \left( \frac{\partial P}{\partial T} \right) \bigg|_v - P \right] dV, \]  
(2.30)

\[ dH - C_p dT = \left[ v - T \cdot \left( \frac{\partial v}{\partial T} \right) \bigg|_P \right] dP, \]  
(2.31)

For the real gas, the entropy is evaluated from:

\[ dS = C_p \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right) \bigg|_P dP \]
\[ = C_v \frac{dT}{T} + \left( \frac{\partial P}{\partial T} \right) \bigg|_v dV. \]  
(2.32)

where the second terms are the departure terms. While the ideal gas EOS will result in zero for the departure term, real gas EOS contributes to the overall function. Therefore, the energy function would be different for the two EOS, and eventually causing the variation in the flow field.

These thermodynamic relations allow for the evaluation of energy changes that accompany changes in the state of the gases, including chemical reactions.
Transport properties

Accurate estimation of transport properties, such as the viscosity, thermal conductivity, and mass diffusion coefficient, is crucial for the multicomponent flow simulations. These properties determine the flow dynamics as well as the heat and mass transfer rates. This section first presents kinetic theory expression of transport properties as functions of intermolecular potential parameters.

In combustion simulations involving chemical kinetic models, Lennard-Jones potential parameters are widely used to determine transport properties, which are grounded in the momentum exchange of particles [177].

**Viscosity**

The viscosity of a simple component as outlined in Hirschfelder et al. [53], is:

\[
\mu_k = \frac{5}{16} \frac{\sqrt{\pi m_i k_B T}}{\pi \sigma_i^2 \Omega_{2.2}^*}. \tag{2.33}
\]

where \(m_i\) is the molecular mass, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(\sigma_i\) is the intermolecular potential collision, the collision integral \(\Omega_{2.2}^*\) depends on the reduced temperature \(T_k^* = \frac{k_B T}{\varepsilon_k}\) and the reduced dipole moment \(\tilde{\sigma}_k^*\), defined as \(\tilde{\sigma}_k^* = \frac{1}{2} \frac{\mu_k \bar{\mu}_k}{\varepsilon_k \sigma_k^3}\) [178]. Monchick and Mason [179] have calculated and tabulated the collision integrals.

**Thermal conductivity**

The thermal conductivity of single atoms (e.g., O atoms), with no internal contribution to \(C_v\), hence [178],

\[
\lambda_k = \frac{5}{2} \mu_k \frac{C_{v,\text{trans}}}{MW_k}, \tag{2.34}
\]
In the case of a single species, thermal conductivity can be assumed to be a combination of translational, rotational, and vibrational modes as given by Warnatz [180].

\[ \lambda_k = \frac{\mu_k}{MW_k} (f_{\text{trans}} C_{v,\text{trans}} + f_{\text{rot}} C_{v,\text{rot}} + f_{\text{vib}} C_{v,\text{vib}}), \]  

(2.35)

where

\[ f_{\text{trans}} = \frac{5}{2} \left(1 - \frac{2}{\pi} \frac{C_{v,\text{rot}}}{C_{v,\text{trans}}} A \right), \]  

(2.36)

\[ f_{\text{rot}} = \frac{\rho D_{kk}}{\mu_k} \left(1 + \frac{2 A}{\pi B}\right), \]  

(2.37)

\[ f_{\text{vib}} = \frac{\rho D_{kk}}{\mu_k}, \]  

(2.38)

\[ A = \frac{5}{2} - \frac{\rho D_{kk}}{\mu_k}, \]  

(2.39)

\[ B = Z_{\text{rot}} + \frac{2}{\pi} \left(\frac{5 C_{v,\text{rot}}}{R} + \frac{\rho D_{kk}}{\mu_k}\right), \]  

(2.40)

From standard results of statistical thermodynamic [178], the translation, rotation, vibration heat capacity can be expressed as:

\[ C_{v,\text{trans}} = \frac{3}{2} N k_B, \]  

(2.41)

\[ C_{v,\text{rot}} = N k_B \quad \text{(linear molecule)}, \]  

(2.42)

\[ C_{v,\text{rot}} = \frac{3}{2} N k_B \quad \text{(nonlinear, polyatomic molecule)}, \]  

(2.43)

And for each vibrational model, \( i \):

\[ C_{v,\text{vib}} = \frac{N k_B x_i^2 e^{x_i}}{(e^{x_i} - 1)^2}, \quad x_i = \frac{h v_i}{k_B T}, \]  

(2.44)

where \( N \) is number of molecule, \( k_B \) is the Boltzmann constant, \( h = 6.626176 \times 10^{-34} \text{ J} \cdot \text{s} \) is the Planck’s constant, \( x_i \) is the vibrational temperature of the \( i \)th model, and \( v_i \) is the vibrational
frequency of the \( i \)th mode.

The “self-diffusion” coefficient \( D_{k,k} \), is given by the kinetic gas theory \([53]\):

\[
D_{k,k} = \frac{3}{16} \frac{\sqrt{2\pi k_B^3 T^3 / m_k}}{p \pi \sigma_k^2 \Omega_{kk}^{1.1^*}}. 
\] (2.45)

The rotational relaxation collision number, \( Z_{\text{rot}} \), in Eq. 2.40 represents the number of collisions that it takes to deactivate an excited rotational molecule. It is assumed to be available at 298 K and generally is on the order of unity. The rotational relaxation collision number is temperature dependent, and can be estimated using the expression from Parker \([181]\) and Brau and Jonkman \([182]\) as,

\[
Z_{\text{rot}}(T) = Z_{\text{rot}}(298) \frac{F(298)}{F(T)}, 
\] (2.46)

where

\[
F(T) = 1 + \frac{\pi^{3/2}}{2} \left( \frac{e / k_B T}{T} \right)^{1/2} + \left( \frac{\pi^2}{4} + 2 \right) \left( \frac{e / k_B}{T} \right) + \pi^{3/2} \left( \frac{e / k_B}{T} \right)^{3/2}. 
\] (2.47)

**Binary diffusion coefficient**

The binary mass diffusion coefficient for species \( i \) and \( j \) is parameter has both temperature and pressure dependence \([180]\):

\[
D_{i,j} = \frac{3}{16} \frac{\sqrt{2\pi k_B^3 T^3 / m_{i,j}}}{p \pi \sigma_{i,j}^2 \Omega_{1,1}^{1.1^*}}, 
\] (2.48)

where index \( i \) and \( j \) indicate the species pair. \( \Omega_{1,1}^{1.1^*} \) is dimensionless collision integrals as a function of \( T^*_k = \frac{k_B T}{\varepsilon_k} \) and the reduced dipole moment \( \tilde{\delta}_{ij}^* \), haven been provided by Monchick and Mason \([179]\). The reduced molecular mass \( m_{i,j} \),

\[
m_{i,j} = \frac{m_i m_j}{m_i + m_j}. 
\] (2.49)

where \( m_i \) and \( m_j \) are the mass of a single \( i \) and \( j \) molecule.
Thus, with knowledge of collision distance $\sigma$ and potential well depth $\varepsilon$ of each species, the transport properties are fully determined.

**Transport data fitting procedure**

To speed up the calculation of transport properties in combustion modeling, software packages fit the temperature dependent parts of the pure species property. A third-order polynomial fit of the logarithm of the property versus the logarithm of the temperature has been adopted, and the fitting errors are within one percent \[183\].

For the viscosity:

$$\ln \mu_k = \sum_{n=1}^{N} a_{n,k}(\ln T)^{n-1}, \quad (2.50)$$

For thermal conductivity:

$$\ln \lambda_k = \sum_{n=1}^{N} b_{n,k}(\ln T)^{n-1}, \quad (2.51)$$

For each pair of binary diffusion coefficients in the system, the fits are done:

$$\ln D_{kj} = \sum_{n=1}^{N} b_{n,kj}(\ln T)^{n-1} \quad (2.52)$$

The fitting procedure is carried out for the particular system of gas mixture at the beginning of each simulation procedure. Unlike the viscosity and conductivity, the mass diffusion coefficient is dependent on pressure. The diffusion coefficient fits are first calculated at a reference pressure, then the actual value is evaluated by adjusting according to the relative pressure dependence.

**Real gas equation of state parameters from intermolecular potentials**

As discussed above, transport properties are given in the form of parameters of intermolecular potentials. These intermolecular potential parameters are found in transport data files of chemical
kinetic models as shown in Figure 1.4. This section discusses the relationship between intermolecular potential parameters and an equation of state that can be leveraged in real gas flow simulations.

An accurate equation of state can be grounded in statistical mechanics [184]. For example, based on the Monte Carlo simulation of grand canonical ensemble, inter-molecular potentials can be used to determine critical properties as well as phase transition behavior of real gases [185]. In order to provide a real gas equation of state for combustion gas mixtures, modelers need simplified correlations between real gas equation of state parameters and intermolecular potentials, instead of statistical mechanical simulation.

One can reverse-engineer the transport data in chemical kinetic files to obtain the critical state parameters needed for the EOS. Many empirical relations between parameters of intermolecular potentials and the critical state properties have been proposed, as reviewed by Tee et al. [186]. Some of these require knowledge of the acentric factor while others do not. The most widely used of these equations are in the form:

\[
\sigma \left( \frac{P_c}{T_c} \right)^{1/3} = a_\sigma - b_\sigma \omega \\
\frac{\epsilon}{k_B T_c} = a_\epsilon - b_\epsilon \omega
\]

(2.53) \hspace{1cm} (2.54)

<table>
<thead>
<tr>
<th>Methods</th>
<th>Tee et al. [186]</th>
<th>Kee et al. [187]</th>
<th>Holley et al. [188]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_\sigma)</td>
<td>2.3551</td>
<td>2.393</td>
<td>2.3551</td>
</tr>
<tr>
<td>(b_\sigma)</td>
<td>0.0874</td>
<td>0</td>
<td>0.3955</td>
</tr>
<tr>
<td>(a_\epsilon)</td>
<td>0.7915</td>
<td>0.75</td>
<td>0.8063</td>
</tr>
<tr>
<td>(b_\epsilon)</td>
<td>0.1693</td>
<td>0</td>
<td>0.6802</td>
</tr>
</tbody>
</table>

where \(\epsilon\) is the depth of the potential well and \(\sigma\) is the distance at which the potential is zero. The actual coefficients are shown in Table 2.3.
The acentric factor, $\omega$, poses a challenge that can only be resolved through structure-activity correlations. For instance, for $n$-alkanes, it can be established that $\omega$ depends on the number of carbon atoms ($N_c$) \[^{[189]}\]: 

$$\omega = 0.004423 \ln(3.3063 + 3.4381N_c)^{3.651}$$

The necessary carbon number can be obtained from the thermodynamic data file of the model. Taken together, the above relations offer ways to generate critical state properties, hence EOS parameters from currently available resources. A mixing rule can be used to determine the mixture critical properties and thus complete prescription of real gas EOS parameters.

### 2.3 Spray break-up modeling

When a liquid is injected into an enclosure, it ultimately breaks up into finer droplets as discussed \[^{[70]}\]. A sketch of the flow for the liquid breakup regime is illustrated in Fig. 2.2. The liquid core and the dispersed flow are the two main multi-phase flow parts of the dense spray. Primary breakup occurs due to the formation of ligaments and other irregular liquid elements along the surface of the liquid core. This is followed by secondary breakup into yet smaller droplets.

![Figure 2.2: Sketch of the near-injector region of a pressure-atomized spray in the atomization breakup regime \[^{[190]}\].](image)

To describe the motion of the droplets, with the trajectory is predicted by integrating the force balance on the droplet, with the governing equation expressed in a Lagrangian form \[^{[191]}\],

$$\frac{\partial u_d}{\partial t} = F_D(u - u_d) + \frac{g_x(\rho_d - \rho)}{\rho_d} + F_x,$$

(2.55)
where \( u_d \) is the droplet velocity, \( u \) is the main stream (Eulerian phase) velocity, \( g_x \) is the acceleration due to gravity, \( \rho \) is the density of main stream phase, \( F_x \) is any additional acceleration such as that caused by magnetic force, and \( F_D \) is the drag force per unit droplet mass,

\[
F_D = \frac{18\mu C_D Re}{\rho_d^2 \rho}.
\]  

(2.56)

where \( C_D \) is the drag coefficient related to the relative Reynolds number, \( Re = \rho g (u - u_d) D / \mu \). A detailed description of this approximation can be found in Morsi and Alexander [191].

Several breakup models are used to represent the spray breakup process. One of these is the hybrid KH-RT model proposed by Beale and Reitz [105] is employed in this work. The primary breakup is predicted by the Kelvin-Helmholtz (KH) instability model. The Rayleigh-Taylor (RT) accelerative instability model is used in conjunction with the KH model to describe the secondary breakup process, through which droplets are further disintegrated.

The length of the liquid core that remains intact is obtained from [192],

\[
L = C_L d_0 \sqrt{\frac{\rho_l}{\rho_g}},
\]

(2.57)

where \( C_L \) is the Levich constant and \( d_0 \) is the reference nozzle diameter.

KH instabilities are used to predict the breakup of the jet. According to the KH model, a parent parcel with radius, \( r \), breaks up into droplets with a new radius, \( r_c \), determined as:

\[
r_c = B_0 \Lambda_{KH},
\]

(2.58)

where \( B_0 = 0.61 \) is a constant, and \( \Lambda_{KH} \) is the wavelength with the maximum growth rate, \( \Omega_{KH} \).

The last two terms are approximated by:

\[
\Lambda_{KH} = \frac{9.02r(1 + 0.45\sqrt{Z})(1 + 0.47^{0.7})}{(1 + 0.865We^{1.67})^{0.6}},
\]

(2.59)
\[ \Omega_{KH} = \frac{0.34 + 0.38 \text{We}_g^{1.5}}{(1+Z)(1+1.4T^{0.6})} \sqrt{\frac{\sigma}{\rho_f r^3}}, \]  \hspace{1cm} (2.60)

where \( \text{We}_g = \rho_g U_r^2 r / \sigma \) is the gas Weber number and \( Z = \text{We}_l / \text{Re}_l \) is the Ohnesorge number based on the liquid Weber number and the Reynolds number. \( U_r \) is the relative velocity between the liquid and the gas, \( \sigma \) is the surface tension, while \( \rho_g \) and \( \rho_f \) are the gas and fuel densities. Finally the Taylor number is \( T = Z \sqrt{\text{We}_g} \).

During the break-up process, the parent parcel diameter rate of change is defined as:

\[ \frac{d r}{d t} = \frac{r - r_c}{\tau_{KH}}, \]  \hspace{1cm} (2.61)

where \( \tau_{KH} \) is the break-up time defined by,

\[ \tau_{KH} = \frac{3.726 B_1 r}{\Omega_{KH} \Lambda_{KH}}, \]  \hspace{1cm} (2.62)

with \( B_1 \) being a constant between 10 and 60, recommended as 40 by Xin et al. [193].

To predict the secondary break-up of the droplets, the RT model combines with the KH model. The fastest growing wave frequency of RT model is approximated by:

\[ \Omega_{RT} = \frac{2}{3\sqrt{3\sigma}} \left[ -g_t(\rho_f - \rho_a) \right]^{3/2} \rho_f + \rho_a, \]  \hspace{1cm} (2.63)

where \( g_t = \vec{g} \cdot \vec{j} + \vec{a} \cdot \vec{j} \) is the acceleration that depends on droplet acceleration \( \vec{a} \), and the unit vector tangent to the droplet trajectory \( \vec{j} \). The corresponding wave number is,

\[ K_{RT} = \sqrt{\frac{-g_t(\rho_f - \rho_a)}{3\sigma}}, \]  \hspace{1cm} (2.64)
Breakup will occur after a certain time, $\tau_{RT}$, given as:

$$\tau_{RT} = \frac{C_{\tau}}{\Omega_{RT}}.$$  \hfill (2.65)

where $C_{\tau}$ is a constant usually equal to unity $[193]$. After the breakup time, $C_{\tau}$, new and smaller child droplets are considered to be formed. The radius is then calculated as,

$$r_c = \frac{\pi C_{RT}}{K_{RT}}.$$  \hfill (2.66)

where $C_{RT} = 0.1$ as recommended by Beale and Reitz $[105]$ based on good performance.

The KH-RT hybrid atomization model is chosen for this work because it was found to satisfactorily predict the trends and properties of high density diesel jet experimental measurements $[105]$.

### 2.4 Turbulence modeling

**Large-Eddy Simulation**

Numerical simulations of turbulent flows fall into three major numerical categories: Direct Numerical Simulation (DNS), Reynolds-Averaged Navier-Stokes Equation (RANS), and Large-Eddy Simulation (LES) $[194]$. The computationally intensive DNS accurately resolves the turbulent flow field while the practical RANS approach determines the averaged flow field at a lower computational cost. LES is a trade-off technique between the accuracy and computational cost of RANS and DNS. It is essentially a numerical scheme that divides the turbulent flow into large-scale and small-scale structures. The energy containing large-scale motions are fully resolved using the grid and a filter, while the effect of the small-scale motions of turbulence is modeled $[195]$.

A low-pass filtering operation can be performed explicitly or implicitly to separate the large-scale
motions from the small-scale ones. The filter is defined as:

\[
\tilde{f}(x) = \int_{\infty} f(x) G_f(x - x')dx'
\]  

(2.67)

where \( G_f \) is the filter function that satisfies the normalization condition: \( \int G_f(x')dx' = 1 \). The size and structures of the small scale motions are thus determined by the filter function. According to the Favre filter of the transport equations \[196\], any instantaneous variable \( f \) can be expressed as the sum of a Favre-averaged filtered quantity \( \tilde{f} \) and a sub-filter quantity \( f'' \):

\[
f = \tilde{f} + f''
\]  

(2.68)

where

\[
\tilde{f} = \frac{\rho \tilde{f}}{\rho}
\]  

(2.69)

The filtered Favre-averaged mass and momentum equations can be expressed in index notation forms as:

\[
\frac{\partial \tilde{\rho}}{\partial t} + \frac{\partial \tilde{\rho} \tilde{u}_i}{\partial x_i} = 0
\]  

(2.70)

\[
\frac{\partial \tilde{\rho} \tilde{u}_i}{\partial t} + \frac{\partial \tilde{\rho} \tilde{u}_i \tilde{u}_j}{\partial x_j} = -\frac{\partial \tilde{p}}{\partial x_i} + \frac{\partial (\tilde{\tau}_{ij} - \tau_{ij}^{SGS})}{\partial x_j}
\]  

(2.71)

where effects of small scales appear through the sub-grid-scale (SGS) terms:

\[
\tau_{ij}^{SGS} = \tilde{\rho} u_i u_j - \tilde{\rho} \tilde{u}_i \tilde{u}_j
\]  

(2.72)

Most sub-grid scale models are based on the concept of eddy viscosity, \( \nu_t \), such that:

\[
\tau_{ij}^{SGS} - \frac{\delta_{ij}}{3} \tau_{kk}^{SGS} = -2 \nu_t \tilde{S}_{ij}
\]  

(2.73)
where $\tilde{S}_{ij}$ is the symmetric part of velocity gradient tensor, $\tilde{S}_{ij} = \frac{1}{2} ( \frac{\partial \tilde{u}_i}{\partial x_j} + \frac{\partial \tilde{u}_j}{\partial x_i} )$.

The Wall-Adaption Local-Eddy Viscosity (WALE) sub-grid scale model has been widely used because it improves the prediction of the wall stress rate as well as turbulent intensities \[197\]. For reasons connected with the wall behavior of the sub-grid scale model, Ducros et al. \[198\] defined a new operator based on the traceless symmetric part of the square of velocity gradient tensor $\tilde{g}_{ij} = \frac{\partial u_i}{\partial x_j}$:

$$S_{ij}^d = \frac{1}{2}(\tilde{g}_{ij}^2 + \tilde{g}_{ji}^2) - \frac{1}{3} \delta_{ij} \tilde{g}_{kk}$$  \hspace{1cm} (2.74)

Followed by the velocity gradient assumption, the WALE model is written as,

$$\nu_t = (C_w \Delta)^2 \frac{(S_{ij}^d S_{ij}^d)^{3/2}}{(S_{ij} S_{ij})^{5/2} (S_{ij}^d S_{ij}^d)^{5/4}}$$  \hspace{1cm} (2.75)

$$\Delta = (\Delta_1 \Delta_2 \Delta_3)^{1/3}$$  \hspace{1cm} (2.76)

where $C_w$ is a constant in the range $0.55 \leq C_w \leq 0.60$ \[197\]. The filter width $\Delta$ is usually proportional to the grid size.

### 2.5 Combustion chemistry models

In order to predict spray ignition and combustion, chemical kinetic models are needed. Chemical reactions enter into the flow simulation through chemical source term in species equation (Eq. 2.4) and through the heat released into the energy equation (Eq. 2.3). The section presents the physical models used in this research for chemical reacting flow simulation. Firstly, direct integration of species evolution is described, which can be used to predict the auto-ignition behavior. This is followed by the Eddy Break Up model and Steady Laminar Flamelet model employed that can describe steady combustion events.
Direct integration of finite-rate chemical kinetics

For a chemical kinetic mechanism with $M$ reactions and $N$ species, the evolution of a reaction can be described using the equation:

$$\sum_{k=1}^{N} v'_{k,m} S_k \xrightarrow{k_{fm}/k_{bm}} \sum_{k=1}^{N} v''_{k,m} S_k, \quad m = 1, 2, \ldots, M$$ \hspace{1cm} (2.77)

for $k = 1, \ldots, N$, where $S_k$ is the chemical symbol of species $k$, and $v'_{k,m}$ and $v''_{k,m}$ are the stoichiometric coefficients in the forward and reverse directions. For the $m^{th}$ reaction, the forward and reverse rate constants are denoted as $k_{f,m}$ and $k_{r,m}$, that often take the form of Arrhenius’s equation:

$$k_m(T) = A_m T^{\beta_m} \exp\left(-\frac{E_{a,m}}{RT}\right),$$ \hspace{1cm} (2.78)

where $A_m$, $\beta_m$ and $E_{a,m}$ are the pre-exponential factor, the dimensionless temperature exponent coefficient, and the activation energy.

While most rate constants depend only on temperature, others also exhibit pressure dependence [199–201].

The net rate of a chemical species, $k$, can be expressed as the sum over reactions that include the $k$ species,

$$\dot{\omega}_k = MW_k \sum_{m=1}^{M} \dot{\omega}_{k,m}$$ \hspace{1cm} (2.79)

where $MW_k$ is the molecular weight of species $k$, $\dot{\omega}_{k,m}$ is the net molar rate of species $k$ in reaction $m$, which is determined by the creation and destruction rate:

$$\dot{\omega}_{k,m} = k_{f,m} \prod_{m=1}^{M} [X_k] v'_{k,m} - k_{r,m} \prod_{m=1}^{M} [X_k] v''_{k,m},$$ \hspace{1cm} (2.80)
where \([X_k]\) represents the molar concentration of species \(k\) and can be calculated as,

\[
[X_k] = \frac{\rho Y_k}{WM_k}.
\]  

(2.81)

The energy contribution from the chemical energy release of species is obtained from:

\[
\dot{h} = \sum_{m=1}^{M} \dot{\omega}_{k,m} h_k^\alpha.
\]  

(2.82)

where \(h_k^\alpha\) is the formation enthalpy of the \(k^{th}\) species.

These evaluations need a chemical kinetic scheme with reaction rates, a thermodynamic file with thermo-chemical properties and a transport data file. In each computational cell, the equations for the evolution of each chemical species can be carried out. Their diffusion, conduction and viscous exchange occur in accordance with the transport properties. The chemical kinetic scheme can be a detailed chemical kinetic model or a reduced version. The reduced version only contains species and reactions that are indispensable.

**Eddy Break-Up Model**

Direct integration of chemical kinetics as described above can be very costly. For instance, simulating a 2755 species kinetic model in a single reactor using a 7th generation Intel i7-3770 is about 30 minutes. Therefore, combustion model techniques emerged to reduce the computational cost when simple switching from an unburned to burned state is needed. The Eddy Break-Up model is developed for fast combustion event where the reaction rate is determined by the turbulent mixing time scale \([202, 203]\). The model assumes that the reactions are completed at the moment of mixing, therefore, it is not possible to predict the ignition delay time. Combustion is presented as a one global chemical reaction,

\[
\text{Fuel} + \text{Oxidizer} \rightarrow \text{Products},
\]  

(2.83)
the mean reaction rate is given by,

\[
\tilde{\omega}_F = A_{EB} \varepsilon k \min \left[ \bar{c}_F, \frac{\bar{c}_O}{\nu}, B_{EB} \frac{\bar{c}_P}{1 + \nu} \right]
\]  

(2.84)

where \( \bar{c} \) is the mean concentration of fuel, oxidizer and products respectively, \( \nu \) denotes the stoichiometric coefficient. \( A_{EB} = 0.5 \) and \( B_{EB} = 4.0 \) are model constants. By using this simplified model, steady combustion can be studied as controlled switching processes. This model is used here to contrast ideal gas and real gas model in steady jet combustion.

**Steady Laminar Flamelet Model**

Another cost-effective method to include chemistry effects is the Steady Laminar Flamelet (SLF) model. It embeds steady diffusion flamelets in the turbulent flow [204, 205]. The chemical and thermal state of the system can be parameterized by mixture fraction \( Z \) and a scalar dissipation rate \( \chi \).

\[
Z = \frac{m_f}{m_f + m_o},
\]  

(2.85)

\[
\chi = \frac{C_\phi Z}{\tau_{turb}}.
\]  

(2.86)

where \( m_f \) is the total mass of all elements that from the fuel stream and \( m_o \) is the total mass of the oxidizer stream. The turbulent timescale, \( \tau_{turb} = \frac{k}{\varepsilon} \), and \( C_\phi \) is a constant with value of two.

The mixture fraction can replace the space coordination, yielding the following equations:

\[
\frac{\partial Y_i}{\partial t} = R_i + \frac{1}{2} \chi \frac{\partial^2 Y_i}{\partial Z^2},
\]  

(2.87)

\[
\frac{\partial T}{\partial t} = - \sum_{i=1}^{N} \frac{h_i R_i}{C_p} + \frac{1}{2} \chi \left( \frac{\partial^2 T}{\partial Z^2} \right) + \frac{1}{2} \frac{\chi}{C_p} \left( \frac{\partial C_p}{\partial Z} + \sum_{i=1}^{N} \left( C_{p,i} \frac{\partial Y_i}{\partial Z} \right) \right) \frac{\partial T}{\partial Z}.
\]  

(2.88)

where \( Y_i \) is the mass fraction of species \( i \), \( R_i \) is the chemical source term, \( C_p \) is the specific heat, \( h_i \)
is the enthalpy and $\chi$ is the scalar dissipation rate.

A flamelet table is generated based on Eq. 2.87 and Eq. 2.88 with different values of $\chi$. Results are tabulated as function of mixture fraction and scalar dissipation. In simulating combustion flows, the thermo-chemical state is read off the table based on the prevailing parameters of the flow field.

The SLF model is capable of capturing diffusion effects, since it couples chemical reactions and molecular transport process [206]. This combustion model is used in this work to evaluate differences of ideal gas and real gas models in high density combustion flows.
Chapter 3

Modeling real gas effects in high density flows

This chapter focused on the effects of real gas on CFD high density flow simulations as revealed by comparing with the ideal gas model. It first looks at a trans-critical N$_2$ injection problem that requires a real gas EOS. It then examines effects of the real gas in non-reacting and reacting n-C$_7$H$_{16}$. This is followed by a suggested approach to estimating real gas EOS parameters based on transport data of a chemical kinetic model. It ends with a demonstration of this estimation on a single element rocket combustion chamber simulation.

3.1 High density N$_2$ jet validation against experiment

The turbulent round jet is a subject that is widely studied using RANS and LES [207–209]. However, there are limited studies on the combination of real gas effects and turbulence models. We therefore investigate the effect of real gas models with two different turbulence models. The simulations seek to validate experimental data of a trans-critical nitrogen jet at room temperature.
Experimental and numerical setups

Equipment setups

Figure 3.1a shows the experimental setup they used. The target experimental data were obtained by Mayer et al. [210]. The chamber is designed to be pressurized up to 6 MPa and equipped with an electric heater to control the wall temperature. Four windows in the test section provide optical access to the spray. The chamber is first filled with warm nitrogen while the cryogenic nitrogen jet is then injected through a 2.2 mm diameter injector. Case 3 and Case 4 from the experiments are considered in this work, where the Case 3 has a turbulent Prandtl number, $Pr_T = \nu_T/ (k_T/\rho C_p) = 1.0$. The chamber and injection conditions details are shown in Table 3.1.

![Figure 3.1a: Test setup overview](image)

![Figure 3.1b: Raman equipment setup](image)

*Figure 3.1: The test chamber and the Raman setup for density measurement [210].*

Table 3.1: Injection Conditions by Mayer et al. [210]

<table>
<thead>
<tr>
<th>Investigated cases</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Velocity</td>
<td>4.9</td>
<td>5.4</td>
<td>m/s</td>
</tr>
<tr>
<td>Injection Temperature</td>
<td>126.9</td>
<td>137</td>
<td>K</td>
</tr>
<tr>
<td>Injection Density</td>
<td>455.1</td>
<td>163.5</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Chamber Pressure</td>
<td>3.97</td>
<td>3.98</td>
<td>MPa</td>
</tr>
<tr>
<td>Chamber Temperature</td>
<td>298</td>
<td>298</td>
<td>K</td>
</tr>
</tbody>
</table>
The detailed description of the setup can be found in [211]. Figure 3.1 presents the optical equipment and the test chamber setup. The key measurement from the experiment is the density, obtained using the Raman setup in Figure 3.1b. To obtain the density, a calibration image is needed. The ambient density is calculated based on a real gas equation of state using the ambient temperature and pressure that are measured. The density is assumed to be a linear function of the light intensity, such that at a given intensity, it can be evaluated using:

\[ \rho = \frac{I}{I_\infty} \rho_\infty. \]  

(3.1)

Further, to avoid large density uncertainties, images of the density profiles are averaged by 5 pixels in upstream and 5 pixels in downstream. The acquired density data is later analyzed with simulation data. Various subsets of the reported data have been used in previous numerical studies [25, 209]. However, the simulation performed by Park [209] was on 2D mesh, which cannot provide the complete flow dynamics. The interactions from the third dimension with main stream and the second direction are therefore omitted. Schmitt et al. [25] obtained close results for the Case 3 but failed to predict the Case 4 jet trajectory. This work therefore seeks to provide 3D simulations with accurate predictions for both Case 3 and Case 4, while also evaluating turbulence model effects.

**Equation of state**

Previously, Section 2.2 introduced the modeling methods for equation of state. The relative merit of each EOS can be judged by comparing their prediction of \( P, \rho \) and \( T \) relations. These models are now used to examine a high density \( \text{N}_2 \) jet. Figure 3.2 shows the validation of nitrogen density over a range of temperature. It is observed that ideal gas law departs from experimental data particularly when the temperature is below 200 K. The three real gas equations of state are in close agreement with NIST data [212], where Peng-Robinson slightly over-predicts the density at the low temperature regime. For cryogenic flows of nitrogen, the ideal gas model is therefore inappropriate.
Figure 3.2: Real gas model density validation at 40 bar for $N_2$, demonstrates the necessity to choose real gas equation of state at high pressure and low temperature regime.

Some differences might arise in the flow field simulated using each of the three real gas EOS. To see these, CFD simulations of relevant flows are needed.

Turbulence models

The following sections introduce the mathematical expressions for standard $k - \varepsilon$ model. The Wall-Adaption Local-Eddy Viscosity (WALE) sub-grid scale model is also used and is described in Section 2.4.

Standard $k - \varepsilon$ model is considered here determines the Reynolds stresses using the isotropic viscosity hypothesis,

$$\bar{u}_i\bar{u}_j = \frac{2}{3}k\delta_{ij} - \mu_{eff}\left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i}\right)$$

(3.2)

with the effective viscosity determined as:

$$\mu_{eff} \equiv C_\mu k^2/\varepsilon$$

(3.3)

in which the turbulent kinetic energy, $k = \frac{1}{2}\bar{u}_i\bar{u}_i$, and the rate of dissipation, $\varepsilon$, is determined by
the transport equations:
\[
\begin{align*}
\frac{Dk}{Dt} &= \frac{\partial}{\partial x_i} \mu_{eff} \frac{\partial k}{\partial x_i} + P - \epsilon \\
\frac{De}{Dt} &= \frac{\partial}{\partial x_i} \mu_{eff} \frac{\partial \epsilon}{\partial x_i} + \frac{\epsilon}{k} (C_{\epsilon 1} P - C_{\epsilon 2} \epsilon)
\end{align*}
\] (3.4) (3.5)

\(P\) is the rate of production of kinetic energy given by
\[
P = -u_i u_j \frac{\partial U_i}{\partial x_j}.
\] (3.6)

Commonly used values for the constants \(C_{\epsilon 1}, C_{\epsilon 2}, C_{\mu}, \sigma_k, \) and \(\sigma_{\epsilon}\) are 1.44, 1.92, 0.09, 1.0 and 1.3 [213]. These constants are sometimes varied to improve performance. In this work, they are adopted without modification.

**Mesh Studies and physical setups**

Before carrying out the numerical simulations to test models of turbulence and EOS, a grid independence study is first carried out in RANS simulations. The selected grid is then evaluated based on its capability to capture the turbulent kinetic energy by LES simulation.

Figure 3.3: The computational domain is a cylinder with a diameter of 120 mm and a height of 250 mm. Injector diameter is 2.2 mm. The medium mesh consists of about 2.4 million cells with a minimum cell size \(\Delta x = 0.1\) mm, near the injection up to about 10 times of the injector diameter.

Figure 3.3a shows the overview of the computational domain, and a longitudinal cut of the mesh is presented in Fig. 3.3b. The injector diameter is \(D = 2.2\) mm and the cylindrical chamber diameter
and length are 120 mm and 250 mm, respectively. These fully unstructured meshes contain the finest cells within the first $10D$. This region is followed by a smoothly stretching region with a ratio of 1.05. The finer resolution of the mesh is informed by anticipated flow pattern of the jet.

To ensure the accuracy of the mesh resolution, a grid independent study is carried out first with RANS simulations. Three meshes are investigated, varying from the coarsest to the finest. These meshes have the same structure as shown in Fig. 3.3b. The first $10D$ region is occupied with uniform cells, followed by a region with a stretching ratio of 1.05. The minimum grid sizes for the three meshes are 0.05 mm, 0.1 mm, and 0.15 mm, resulting in total cell numbers of 1.08 millions, 2.39 millions and 4.29 millions, respectively.

Results of simulations are carried out with the Peng-Robinson EOS and the RANS $k - \varepsilon$ turbulence
model are shown in Figure 3.4. It is observed that the coarse mesh underestimates the jet penetration length in the center-line. Further, the radial density profiles indicate that the coarse mesh predicts a lower peak, which might be due to the dissipation of the less refined grid. The medium and fine meshes generate similar flow field profiles. The medium size mesh with about 2.4 millions cells is selected for further studies, as being sufficiently resolved.

The selected mesh is then examined in LES. Its ability to sufficiently capture the turbulent kinetic energy is evaluated. According to Pope [214], the turbulence resolution can be measured by a value $M(x,t)$, a property of space and time locations. $M(x,t)$ is defined as:

$$
M(x,t) \equiv \frac{k_r(x,t)}{K(x,t) + k_r(x,t)}
$$

(3.7)

where the turbulent kinetic energy of the resolved motions is $K(x,t) \equiv \frac{1}{2} \langle (W - \langle W \rangle) \cdot (W - \langle W \rangle) \rangle$, and the $k_r(x,t)$ is the residual motions. A smaller value of $M$ indicates a better resolution of the turbulent motions. An $M$ value of 0 corresponds to DNS resolution, while a value of 1 is for RANS. The brackets in $K(x,t)$ expression, $\langle \rangle$, represent the approximate mean. It is suggested that for good LES, $M$ should be smaller than 0.2, corresponding to a resolution of 80% of the kinetic energy [214].

A non-trivial methodology to evaluate $k_r$ is required. In this study, the kinetic energy of residual motions is estimated based on the recommendation by Vreman et al. [215],

$$
k_r = \frac{\sqrt{3}}{2} \nu_t S^{1/2} \quad \text{with} \quad S \equiv \frac{1}{2} \sum_{i,j} S_{ij}^2
$$

(3.8)

where $\nu_t$ is the eddy viscosity and $S_{ij}$ is the strain rate. Both properties can be obtained from the resolved flow field. This paper evaluates the $M$ value at centerline location and average data from 4 ms to 8 ms, we obtained a $M(x = (25D, 0, 0), t \in [4 \text{ ms, 8 ms}]) = 0.0055$, showing that the mesh is able to resolve 99.45% of the kinetic energy, according to the criterion of Pope [214]. Consequently,
the medium size mesh is accurate enough for RANS and LES simulations in current study. The mathematical formulations for the two different turbulence models lead to different flow field resolutions, even if the same mesh is used.

Injection and chamber conditions are taken from the experiments, as shown in Table 3.1. Cold nitrogen ($P_c = 3.34$ MPa and $T_c = 126.2$ K) jets are injected into a constant temperature nitrogen chamber. Whereas the chamber wall is treated as an iso-thermal wall with a constant temperature of 300 K, the wall near the injector is considered as adiabatic. The time step is chosen as $10^{-4}$ s to keep the maximum CFL number about 5.0.

To investigate the effect of a given equation of state and a chosen turbulence model, several of numerical simulations are setup. For Case 3 simulations, combinations of RANS and LES with ideal gas, RK, SRK and PR EOS are carried out. In all, there are eight simulations. It is found that ideal gas failed to accord with the measured data of Case 3. For Case 4 simulations, the ideal gas is not considered. We consider the combination of two turbulence model with the three real gas equations of state. This results in other six simulation setups. The simulations are performed using the STAR-CCM+, CFD package.

**Instantaneous and averaged flow field results**

**Instantaneous Flow Field**

The comparison between URANS and LES simulations is shown in Figure 3.5. The instantaneous flow field is obtained at 30 ms with the Peng-Robinson EOS. The compressibility of the jet and ambient gas is plotted together with the velocity vector field, using line integral convolution. It is observed that at this high pressure condition, compressibility of the ambient gas is less than unity. The penetration depth for both turbulence models is about the same as 80 mm. However, the spreading angle in LES result is wider than the URANS simulation, particularly in the region where
y = -15 mm. This can be explained by observing the velocity vector. In URANS, the entrainment from the ambient gas happened at the tip of the jet, at where x = 70 mm. But for the LES, the shear layer is disturbed near the beginning of the jet at various location, x = 10, 20 and 30 mm. Hydrodynamic instabilities in jet lead to the discontinuity at x = 32 mm, eventual breakup and dissipation after x = 50 mm.

Figure 3.5: Compressibility factor with velocity vector line integral convolution at 30 ms. LES shows a greater resolution of jet unsteadiness.

The compressibility of the cryogenic jet is 0.24 based on a real gas model; it departs from the ideal gas whose compressibility is unity. Thus, simulating the jet with ideal gas in this case would introduce a 76% deviation near the injector, and possibly larger deviations later.
Figure 3.6: Vorticity iso-surfaces of case 3 at $t = 30$ ms, $\lambda_2 = -1 \times 10^5$ colored by temperature, showing turbulent resolved structures, indicating the importance of EOS in flow development.

Figure 3.6 shows an instantaneous realization of vortical structures, as indicated by an iso-surface of $\lambda_2 = -1 \times 10^5$. The vorticity iso-surface is colored with the temperature magnitude. Coherent vortices evolve close to the injector, $x = 10$ mm, and grow quickly downstream, leading to a fully turbulent jet. Two observations can be made from comparisons between ideal gas and real gas. Firstly, with the same injection speed, the ideal gas result shows a shorter penetration depth. This is due to the lower density, hence lower flow momentum. Secondly, the temperature on the vortical structures is higher for the ideal gas. The reason is that the real gas predicts a higher density, that is, a greater amount of material that requires more heat for the same temperature increase. For the real gas equations of state, the break up process is similar, with comparable vortical structures before $x = 50$ mm. However, the vortex ring dynamics are different after 50 mm. For instance, at the region of $y = -12.5$ mm and $x \in [60, 70]$ mm, the vortex rings are detached from the main vortical structure in the case of RK and SRK. It can be observed that the ring in RK is broken, at the same time, the PR result show that vortex ring is intact and attached to the main structure. The main conclusion
from the instantaneous field comparison is that the ideal gas model is not applicable, while the real gas EOS give comparable results.

**Averaged Flow Field**

To compare simulations with experiments, the instantaneous fields are averaged from 20 ms to 30 ms in intervals. Averaged center line density profiles are plotted against the normalized distance from nozzle, as shown in Figures 3.7 and 3.8.

Figure 3.7a presents Case 3 RANS simulation results, with different equations of state, comparing them with experimental data. The ideal gas case under predicts the measured density profile, which was also observed at low temperature regime in Figure 3.2. The real gas models, on the other hand, provide closer agreement with experiment, but they over predict the jet penetration especially in the region of \( x/D \in [10, 30] \). It is observed that the PR predicts a higher density compared to RK and SRK, capturing the density value at the inlet. However, in experiment, after \( x/D = 2 \), the jet density drops, which is closer to RK and SRK results. The over-predicted jet penetration in RANS real gas simulations is due to the turbulent eddy resolution of the shear layer as shown in Figure 3.5, which can be greatly improved by LES.

As shown in Figure 3.7b, the penetration length of Case 3 predicted using LES is closer to experimental observation. Compared to real gas RANS simulations, where the jet density starts decreasing at \( x/D = 12.5 \) in LES, the density profile drops near \( x/D = 10.0 \), in closer agreement with the experiment. This could be explained by the capability of LES to resolve small scale turbulent eddies in the jet shear layer. The resolved small scale eddies transform the disturbance into the jet core and help the jet to dissipate quickly. The resolution of the flow field of Case 3 by LES is superior to RANS simulations.

The predictions of the centerline density profile of Case 4 are compared in Figure 3.8. Similar to Case 3, LES results are closer to experimental observation than RANS. In the RANS simulations
Figure 3.7: Case 3, centerline density profiles, density plotted with normalize distance from the nozzle. Comparison of RANS, results and averaged LES results with experimental data.

Figure 3.8: Case 4, centerline density profiles, density plotted with normalize distance from the nozzle.

(shown in Figure 3.8a) it is observed that the PR EOS leads to a higher density near the jet inlet, but after $x/D = 12.5$, when the jet entrains the ambient gas, the case of PR EOS is similar to the scales of RK and SRK EOS results. The same is seen in the LES results in Figure 3.8b. The resolved eddy motion in LES improve the prediction of mixing. While in LES, the density drops at $x/D = 7$, it is at $x/D = 11$ in RANS. In previous simulations of these data [47], the density profile has a steeper slop, indicating an intense vortical structure dissipation and resulting in a much lower density. This behavior is improved in this work, where the LES results show a milder density profile decline. It can be seen that in the experiment, between $x/D = 15$ and $x/D = 20$, there is a step-like density decline process, which has also been captured in this work.
The jet spread angle is an important parameter of the jet. The criterion used in this study to determine it is based on the half-width, half-maximum principle \cite{210,216}. The half-width $L_\rho$, is defined by the axial location where median density value is,

$$L_\rho = y \text{ at } \rho_{\text{median}} = \frac{1}{2}(\rho_\infty + \rho_{\text{core}}).$$  

(3.9)

where $\rho_\infty$ is the density of ambient gas and $\rho_{\text{core}}$ is the density at the core representing for the maximum value. This half-width can be normalized by the injector diameter, and serve as a validation target.

The experimental and simulated half-widths are compared in Figure 3.9 where the Case 4 plot includes only numerical results due to the limited experimental measurements. The range of axial distance is decided by the 2D Raman images, where the spreading rate is very small at $x/D \in [0, 10]$ and the jet warm up and dissipate after $x/D = 25$. In Case 3, it is observed that results from LES are closer to experimental measurement. As for RANS, the spreading rate is reduced due to the inability of capturing the shear layers. However, in Case 4, where the jet is warmer and surpasses the critical temperature, the two turbulence methods are in close agreement. This could be explained by the increased mass diffusion in the process. When the temperature is higher, the viscosity is no longer the only factor that dominates the jet spread rate.

From the foregoing, it can be said LES combined with real gas EOS can predict the tran-critical N\textsubscript{2} jet successfully. Among real gas EOS, RK and SRK produce similar results, while PR is less accurate in the condition studied in current work. This N\textsubscript{2} jet studies shows how the joint consideration of turbulence and EOS models can impact prediction of high density non-reacting flows.
Figure 3.9: Spread rates of jets at various combination of turbulent and real gas model. (a) Case 3, spread rates; (b) Case 4, spread rates.

3.2 Real gas effects in $n$-heptane jet by LES

Unlike the previous case study, combustion flows involve high temperatures and higher pressures. The effect of EOS on the simulation of these flows need to be demonstrated. The problem we consider here consists of a $n$-heptane jet introduced into a hot chamber of air. Three different types of inlet conditions are kept constant for the simulations being compared. In the first case, we keep the inlet velocity of 86 m/s using both ideal gas EOS and real gas EOS. In the second case, the inlet mass flow rate is 0.1 kg/s. The third case, the momentum is the same, thus, when the ideal gas EOS velocity is 86 m/s, the real gas the velocity is reduced to 53.73 m/s in order to obtain the same momentum, given the density difference.

The conditions are such that the chamber filled with air at 50 atm has a temperature of 1050 K. The subsonic $n$-heptane jet is injected with a temperature of $T = 575$ K. The boundary walls are assumed to be adiabatic. The inlet and outlet conditions are chosen to be velocity inlet and split ratio outlet. Simulations are carried out using both ideal gas EOS and real gas (PR) EOS for the chemical species. The real gas EOS requires critical state parameters and acentric factor, which for $n$-heptane are $T_c = 540.15$ K, $P_c = 27.36$ bar, $\omega = 0.349$; for oxygen are $T_c = 154.58$ K, $P_c = 50.43$ bar.
ω = 0.025; and for nitrogen are \( T_c = 126.20 \) K, \( P_c = 34.00 \) bar, \( \omega = 0.039 \).

In order to properly resolve the flow field, the turbulence model chosen here is LES with the Wall-Adapting Local Eddy (WALE) formulation as the sub-grid-scale (SGS) model. To simulate the combustion flow field, the Eddy-Break Up (EBU) model is employed. The mesh consists of 2,393,042 cells in total with a minimum cell size \( \Delta x_{min} = 0.1 \) mm. Simulations are carried out using the segregated solver in the Star-CCM+ software packages. The time discretization is implicit, and to obtain good convergence of the solver at each time step the following under-relaxation factors were used: 0.8 for velocity, 0.2 for pressure, 0.9 for both the species and energy equations. A maximum of 50 iterations for the iterative matrix solvers was used to ensure the solution reached a converged state at each time step. The time step was set to which lead to a maximum local CFL number of approximately 2.4. Although these choices do not yield the most accurate results, they enable us to see the differences arising from the choice of an EOS model.

Case 1: Inlet Speed the Same

![Figure 3.10: Non-Reacting temperature contours at 0.5 and 1.0 ms. Same inlet velocity. Top: ideal gas; Bottom: real gas.](image)
Figure 3.11: Temperature contours at 0.5 and 1.0 ms, for a combustion flow of n-heptane showing the effect of EOS. Same inlet velocity.
Top: ideal gas; Bottom: real gas.

(a) Ideal gas, non-reacting.
(b) Ideal gas, reacting.
(c) Real gas, non-reacting.
(d) Real gas, reacting.

Figure 3.12: Q-Criterion iso-surface (Q=5e8). (a) and (b) are ideal gas, (c) and (d) are real gas; non-reacting results are on top, reacting are at the bottom. Colored by temperature in [K] at 1 ms.
The resulting flow field can be compared using scalars such as the temperature and Q-criterion as a measure of vorticity. Fig. 3.10 is the instantaneous temperature profile with non-reacting flow. The spread and penetration depth of the flow are different between ideal gas and real gas with PR EOS predicting further penetrating. Similar flow patterns can be seen in the reacting case, as shown in Fig. 3.11. With combustion model activated, the flow contains higher energy and there is gas expansion, hence, the difference is more pronounced. The temperature fields also reflect differences that align with the mixing field. These fields are affected through the use of the EOS to relate the pressure, density, and temperature, which appear in the conservation equations.

Instantaneous snapshots of the jet dynamics at two different instances in time are shown in Figure 3.12 through iso-surfaces of the Q-criterion colored with temperature. The Q-criterion is an appropriate quantity to visualize coherent structures from LES. Coherent structures in the form of horseshoe vortices are visible at the edge of the jet. These structures contain a major fraction of the energy. As a result of the lower density of the ideal gas, a low momentum is injected into the flow compared to the case of the real gas. This leads to a lower energy content and faster dissipation of coherent structures in the case of the ideal gas.

Similar behavior is observed in reacting flow, where the combustion model generates more turbulent energy and coupled with the higher momentum, the real gas case shows a stronger coherent structure.

Case 2: Flow filed comparison for same inlet mass flow rate

From Fig. 3.11 we see that the choice of EOS in the simulation of high pressure combustion systems, such a fuel injection, is important to the prediction of the flow field. Using a constant velocity boundary condition with the real gas and ideal gas EOS models results in differences in the penetration depth, with the real gas jet going further. This occurs due to the differences in the inlet mass flow rates and momenta of the two jets. One can explore the case where the inlet mass flow rate is the same for the EOS cases.
In Fig. 3.13 and 3.14 we compare the results from real gas and ideal gas EOS simulations in which the inlet jet mass flow rate is held fixed at 0.1 kg/s. Due to higher density of the real gas EOS prediction the inlet velocity is low, requiring more time to reach the same penetration depth.

**Case 3: Flow filed comparison for same inlet momentum**

One can further explore the case where the inlet momentum is the same for both EOS cases. In Fig. 3.15 and 3.16 we compare the results from real gas and ideal gas EOS simulations in which the inlet jet momentum is held fixed. Similar to the fixed inlet mass flow rate case, the higher density of the real gas EOS leads to a lower velocity for the real gas case. This translates to a slower penetration rate. However, the real gas jet is not as slow as in the case of the fixed mass flow rate.
The above discussion brings to light another problem that must be considered in the simulation of physical problems or experiments, that is, the errors that can occur due to interpretation of boundary conditions. For experiments of fuel injection, the injection boundary conditions can be specified either as a measured mass flow rate or a velocity. The boundary condition would then be interpreted by the numerical modeler and adjusted to velocity or mass flow rate to fit with the numerical model of the given experiment. In a high pressure combustion simulation the careful interpretation of these boundary conditions, and the EOS assumptions that have been made during the measurement is important for the proper comparison of experiments and simulations.

The observed differences in the two flows field thus justify the need for real gas models. The real gas model is more physically sound for high density combustion. To use the real gas models, their model parameters are needed. Estimating these real gas model parameters from available resources
would be a convenient solution.

3.3 Real gas EOS parameters estimation from intermolecular potentials

Our goal is to determine for each species in a given mechanism its real gas EOS parameters, i.e. $T_c$, $P_c$, $\omega$. Using an appropriate mixing rule, the EOS parameters for a given combustion gas mixture can be determined from those of the individual species. As mentioned in Section 2.2, for reacting flow simulation, one can reverse-engineer available transport data to obtain the critical state parameters that are needed for the EOS.

To complete chemical kinetic models, estimation rules are adopted for transport properties [187]. These transport properties are given in the form of inter-molecular potential parameters. These
Figure 3.16: Q-Criterion iso-surface (Q=5e5)
Colored by temperature in [K] at 1 ms. Reacting Experiment with Fixed
Momentum Inlet Condition
Top: ideal gas; Bottom: real gas.

are related to the critical state parameters. It appears that the method by Tee et al. [186] performs
better than that of Kee et al. [187] when predicted transport variables are compared with empirical
observations. \( T_c \), \( P_c \), \( \omega \) are observable or experimentally derivable quantities whereas the accuracy
of \( \sigma \), \( \varepsilon \) can only be inferred from their prediction of transport properties. This circularity can lead
to a verification problem. Since the theoretical but unobservable \( \sigma \), \( \varepsilon \) are related to the observable
\( T_c \) and \( P_c \) and transport data, Holley et al. [188] have suggested updated coefficients for the Tee
correlation. This means that with an appropriate correlation, one can obtain \( T_c \) and \( P_c \) from transport
data, as far as consistency is applied in estimating \( \sigma \), \( \varepsilon \) from properties and reverse calculation of
those properties from \( \sigma \) and \( \varepsilon \).

One might check the effectiveness of the proposed approach by comparing predicted critical
state parameters with measured data for some species of relevance to combustion [217, 218]. An
example is shown in Fig. 3.17 for C1-C12 \emph{n}-alkanes, with critical properties from the literature \cite{44}. Intermolecular potential parameters $\sigma$ and $\varepsilon$ are chosen from the JetSurf 2.0 mechanism \cite{219} and LLNL \emph{n}-heptane mechanism \cite{220}. The observed differences in $T_c$ and $P_c$ trace back to differences in the transport data $\sigma$ and $\varepsilon$, which are often not given critical attention in model description and validation.

As shown in Fig. 3.17, Tee’s correlation with LLNL chemical kinetic database provides accurate critical properties. While for large carbon alkanes, Holley’s correlation with JetSurf 2.0 shows good agreement with experimental data, for small carbon alkanes, the correlation results in inconsistency. Kee’s correlation does not require acentric factor but errors increase as carbon number increases due to deviation from spherical shape. Therefore, we recommend using Tee’s correlation with LLNL database. This correlation can still be used with other databases. The method differences are still insignificant compared to using ideal gas models at high density conditions.

![Graphs showing critical properties estimation based on intermolecular constants.](image)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.17}
\caption{Critical properties estimation based on intermolecular constants. (a) and (b) are estimated $T_c$ and $P_c$ based on Tee’s method; (c) and (d) are estimated $T_c$ and $P_c$ based on Kee’s method; (e) and (f) are estimated $T_c$ and $P_c$ based on Holley’s method.}
\end{figure}
Algorithmic description of implementing the method

Figure 3.18: Schematic for estimating real gas parameters from transport and thermodynamic files.

To conveniently estimate real gas EOS parameters from a chemical kinetic model file, the following steps, as also illustrated in Figure 3.18 are recommended:

1. Identify species in model, locate the transport data
2. Locate the thermochemical file carbon number and estimate acentric factor $\omega$
3. Use appropriate correlation to determine $T_c$ and $P_c$
4. Determine the EOS properties $a_i$ and $b_i$ for each species
5. Save $T_c$, $P_c$, $\omega$, $a_i$ and $b_i$ in a file
6. During computation, read in $T_c$, $P_c$, $\omega$, $a_i$ and $b_i$ file for apply mixing rule to code

3.4 Demonstration of method for a LOX/kerosene rocket combustion problem

This section seeks to apply the framework above, to include the real gas effects in a typical rocket combustion problem that uses a detailed chemistry model in a tabulated approach. A model with
31 species and 359 reactions is selected [221]. Most of the critical properties of the species are calculated based on the Kee’s correlation using intermolecular potentials from the combustion model transport data file as outlined above. The Steady Laminar Flamelet model described in Sec. 2.5 is chosen to model the non-premixed combustion of the Liquid Oxygen (LOX)/kerosene propellant.

The problem we consider here consists of a double impinging stream as shown in Fig. 3.19, with LOX and kerosene \( n\text{-C}_{12}\text{H}_{26} \) introduced into a chamber of oxygen. The conditions are such that the chamber is at \( T = 700 \) K, and the subsonic LOX jet with inlet velocity at \( v = 121.30 \text{ m/s} \) and the kerosene jet with a velocity at \( v = 73.16 \text{ m/s} \). Simulations are carried out at 200 atm, with constant injection temperature at \( T = 700 \) K. With an assumption of 45 deg fuel injection angle, the LOX is introduced to the chamber with an angle of 9.82 deg.

In order to properly resolve the flow field, the turbulence model chosen here is LES with the sub-grid-scale (SGS) model, Wall-Adapting Local Eddy (WALE). The mesh consists of 6,050,200 cells with a minimum cell size, \( \Delta x_{\min} = 0.01 \) mm. The simulations are carried out using the CFD solver, STAR-CCM+. The time-step is \( 2.0 \times 10^{-8} \) s with an implicit unsteady scheme. One simulation using 32 cores of a high performance computer took about 90 hours to complete.

The resulting flow field can be compared using scalars such as the temperature and Q-criterion. Figure 3.20 shows the temperature profile and Q-criterion at 0.7 ms, obtained at a pressure of

Figure 3.19: Sketch of standard two impinging jets [222]. Carefully chosen inlet velocity vectors determine the location of the combustion zone.
Figure 3.20: The deviation of density and energy prediction result in further departure in temperature and vortex (colored by temperature), top: ideal gas, bottom: real gas. Length unit in [mm].

200 atm. We see that flow fields are different, since the spread and penetration depth in the case of ideal gas EOS are greater than those of real gas EOS. These differences lead to differences in other dynamical behavior of the reacting flows. Extinction and combustion instability will be differently affected by the flow fields, with the difference originating from the EOS model used. This flamelet simulation thus show how the real gas properties of many species can be conveniently estimated from chemical kinetic model resources.
Chapter Summary

To summarize, this chapter presented simulations of non-reacting and reacting flows at conditions of real gas behavior. It considers a high density N$_2$ flow simulation, non-reacting/reacting $n$-heptane jet injection with different boundary conditions, and proposed a framework to provide real gas parameters. This approach is applied to the simulation of a single element of a rocket chamber combustion problem. The dependence of real gas and turbulence models for high density flow is demonstrated, showing improved results from the combination of real gas and LES models. CFD studies on the $n$-heptane jet highlight the relevance of EOS models. A framework to provide real gas EOS parameters is offered. This framework enables the use of a reduced chemical mechanism to simulate an element of a rocket combustion engine.
Chapter 4

Skeletal chemical kinetic models for spray combustion

In order to simulate spray ignition, a chemical kinetic model is needed. As mentioned in Sec. 1.2.3, the number of differential equations is proportional to the number of species in the kinetic model. This model should not be too large to increase the computational cost substantially but it should be accurate enough to predict ignition. This chapter reviews proposed detailed chemical kinetic models for \( n \)-dodecane. It then obtains reduced chemical kinetic versions of the detailed model using an older reduction technique as well as another technique developed in this work \[141]\.

In combustion analysis, \( n \)-dodecane is used as a surrogate or a surrogate component of Diesel and jet fuel. Selected chemical kinetic models are compared based on their ability to predict ignition phenomena. Measured ignition delay times from the literature are used as references. Both low- and high-temperature ignition simulations are considered.

The detailed models are then reduced using the ASE approach. The resulting skeletal models are compared in terms of their retained species, ranked species sensitivities, and kinetic parameters of the key reactions. Furthermore, another model reduction technique is explored. The aim of this exploration is to further decrease model reduction time since this is often considered as a weakness.

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of the otherwise effective ASE method. The resulting models from this new reduction approach are compared with those obtained from the ASE method in terms of species retained and the accuracy with which combustion properties from the detailed models are predicted. Further chemical kinetic analysis of the reduced models is carried out with the aim of explaining observed similarities and differences.

### 4.1 Validation of \( n \)-dodecane detailed mechanisms at elevated pressure

To determine a reduced model for spray ignition simulation, a detailed model needs to be chosen from several options. We first compare four models with experimental data. Table 4.1 shows the statistics of the four models. The Milano model has the highest reaction-to-species ratio of 39.57, and the CNRS model’s ratio is the lowest, is 4.26. It was optimized for \( n \)-undecane and \( n \)-dodecane. The Milano model has the highest ratio of reactions to species as a result of chemical kinetic lumping of species and duplicate reactions with modified rate constants. For instance, in this Milano model, a species such as \( \text{C}_{12}\text{H}_{25} \) is taken to represent all isomers of the radical obtained by H-abstraction from the fuel. To improve the predictability of the model, however, this species undergoes many duplicate reactions that differ in the assigned reaction rates. The different reaction rates account for radical site-specific reactions that proceed with different degrees of ease. The duplication therefore leads to a higher ratio of reactions to species compared to other models.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>JetSurF</th>
<th>Milano</th>
<th>CNRS</th>
<th>LLNL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>348</td>
<td>451</td>
<td>1377</td>
<td>2755</td>
</tr>
<tr>
<td>Reactions</td>
<td>2163</td>
<td>17848</td>
<td>5865</td>
<td>14314</td>
</tr>
<tr>
<td>Reactions to Species Ratio</td>
<td>6.22</td>
<td>39.57</td>
<td>4.26</td>
<td>5.20</td>
</tr>
</tbody>
</table>

Species in each detailed kinetic model are then examined by their number of carbon atoms, as shown in Figure 4.1. Shown are the percentages of species with a given carbon number plotted
against the carbon number. While JetSurF and CNRS contain carbon atoms up to $C_{12}$, the LLNL and Milano models include species that have up to $C_{19}$. Each mechanism has a peak, which is $C_{12}$ for LLNL and CNRS, and $C_7$, $C_4$ for the JetSurF and Milano models respectively. It is observed that species from $C_0$-$C_{12}$ in the LLNL model increased linearly before dropping. $C_0$-$C_2$ are more popular in the JetSurF and the Milano than in the other two models. The high number of $C_{12}$ in CNRS and LLNL suggests a detailed account of various isomers of $C_{12}H_{25}$ and $C_{12}H_{24}$. The high number of $C_{12}$ species in the CNRS and LLNL models suggests a detailed account of reactions of various structures, including primary fuel radicals, olefins, peroxy, hydroperoxy, and many more intermediate species.

Apart from the species distribution, these models also have different reaction parameters for similar reactions. For example, one of the most important reactions, $NC_{12}H_{26} + OH \rightleftharpoons C_{12}H_{25} - i + H_2O$, is described differently in the detailed mechanisms as shown in Fig. 4.2. Here, $C_{12}H_{25} - i$ is the general name for isomers of $C_{12}H_{25}$. It is noticed that for the Milano model, there is only one $C_{12}H_{25} - i$, $NC_{12}H_{25}$, while the other three detailed mechanisms have six isomers. In the low temperature regime, the reaction rate is lowest for the CNRS model, which might delay the ignition process.

Figure 4.1: Species distribution by carbon number in the selected detailed models.
Figure 4.2: Reaction rates in mechanisms are different as demonstrated in one of the most important reaction here, \( \text{NC}_{12}\text{H}_{26} + \text{OH} \rightleftharpoons \text{C}_{12}\text{H}_{25-i} + \text{H}_2\text{O} \), where \( \text{C}_{12}\text{H}_{25-i} \) are isomers of \( \text{C}_{12}\text{H}_{25} \).

\[ \text{Reaction rate} \ [\text{mole/cm}^3\text{s}] \]

\[ \times 10^{13} \]

\[ \text{JetSurF} \]
\[ \text{Milan} \]
\[ \text{CNRS} \]
\[ \text{LLNL} \]

Figure 4.3: Comparisons of selected detailed models with respect to their prediction of ignition delay times of homogeneous mixtures \( \text{N-C}_{12}\text{H}_{26}/\text{air} \). Experimental data are from Shen et al. [223], Vasu et al. [224] and Kogekar et al.[225].

\[ (a) \phi = 0.5; p=14 \text{ atm} \]

\[ (b) \phi = 0.5; p=20 \text{ atm} \]

\[ (c) \phi = 0.5; p=40 \text{ atm} \]

\[ (d) \phi = 1.0; p=14 \text{ atm} \]

\[ (e) \phi = 1.0; p=20 \text{ atm} \]

\[ (f) \phi = 1.0; p=40 \text{ atm} \]
It is noted that most of these models are for multi-fuel simulations. They are expected to be able to handle \( n \)-dodecane kinetics. Figure 4.3 compares the four models in terms of their ability to predict ignition delay times experimentally determined under lean and stoichiometric conditions. In the simulations, the ignition delay times are determined by the time to maximum gradient of temperature. It is observed that these models generally perform better at higher temperatures than at the lower temperature range. It has to be noted that CNRS model was proposed based on experimental data at \( p = 10 \) bar and temperatures ranging from 550 K to 1150 K [67]. This could explain why the pressure of 14 atm, the CNRS model is closer to experimental data. All mechanisms capture the Negative Temperature Coefficient (NTC) phenomenon at the 20 atm condition, at which the Milano and LLNL models have the longest negative temperature range, but the CNRS and JetSurF models over-predict ignition delay times at low temperatures, indicating much lower reactivity of \( n \)-dodecane. At 14 and 40 atm, ignition delay time predictions of the LLNL and JetSurF models show similar behavior. This comparison therefore shows similar behavior at the high temperature but differ in NTC region, since deviation are observed compared to experimental data.

4.2 Chemical kinetic model reduction methods

Alternative Species Elimination (ASE) Method

The essence of the ASE method is to extract a skeletal mechanism from a detailed chemical kinetic model by identifying the most influential chemical species that contribute to accurate prediction of combustion properties [136–139]. The ASE method is a straightforward and effective reduction process similar to Monte Carlo simulation in statistical physics [136]. First, the ASE reduction process is applied by suppression all reactions involving one species at a time. The influence of removing this species is then assessed by a normalized change in a combustion property of interest. In previous ASE studies and this work, the ignition delay time, \( \tau \), is the property of interest, since it...
encapsulates ignition kinetics. Therefore, the normalized change for species \( i \) would be \( NC_i \):

\[
NC_i = \frac{\tau_i - \tau_0}{\tau_0}
\]  

(4.1)

where \( \tau_0 \) is the ignition delay time obtained with the full detailed model, and \( \tau_i \) is the ignition delay time with all reactions related to the \( i \)th species suppressed.

Kinetic features may be varied in low and high temperature combustion, therefore, in this study the ASE is performed at 1050 K to account for the two regimes. Temperature below 1000K are considered low in the context of combustion kinetics. Fuel-air ratios, \( \phi \), are chosen as 0.5, 1.0, and 2.0 to capture mixture composition effects. Each condition will provide a list of \( NC \) values, then the ASE method ranks the species based on the average \( NC \) value. The number of chemical species in the skeletal mechanism can be determined by imposing a user-defined threshold \( NC \) value.

To ensure accurate prediction of both flame propagation and ignition delay times, it has been observed that a threshold less than or equal to \( 1 \times 10^{-4} \) shows relatively good agreement with detailed models. It has also been observed that a threshold of \( 5 \times 10^{-4} \) can show sufficient agreement between detailed and reduced ignition delay time predictions, with some deviations in flame propagation speed \([135]\). A threshold of \( 5 \times 10^{-4} \) can further reduce the size of chemical kinetic model, with the goal to obtain a compact chemistry for CFD studies. This study therefore selects it as the baseline threshold.

**Species Propensity Method**

While ASE is a simple and accurate reduction approach, the computational cost of this method is relatively high \([139]\). To evaluate each eliminated species, a detailed model simulation has to be performed once at a given condition. Moreover, three conditions need to be evaluated before averaging the sensitivities to obtain the normalized changes.
To address the disadvantage of computational cost associated with the ASE method, a new Species Propensity (SP) method is explored. If successful, the method could reduce the time needed to generate a new skeletal model from a detailed version. This would be convenient since the detailed models are often regularly being updated.

This method relies on postulating a species propensity function, $F_p$, of a given $i$th species:

$$F_p = x_i \cdot \left| \frac{dx_i}{dt} \right|$$

(4.2)

The idea is that we can discover the importance of a species in the simulation of a combustion event by jointly looking at the species concentration and its kinetic rate. It is hypothesized that important species will be marked by high propensity functions. For the kinetic rate of the species, both the rate of production and destruction are considered so that species involved in rapid production and consumption processes can be identified. Hence, the average of the production and destruction rate is selected to represent the reaction rate:

$$\left| \frac{dx_i}{dt} \right| = \frac{1}{2} \left( r_{pi} + |r_{di}| \right)$$

(4.3)

where the rate of production is $r_{pi}$, and $r_{di}$ the rate of destruction. The ranking of the species is based on the normalized species propensity function, $NS_P$. It is the sum of species propensity functions over a simulation event divided by the maximum value among species,

$$NS_P = \frac{\sum_{k=0}^{k=t} F_p}{\max_{i=1}^{n} \left[ \sum_{k=0}^{k=t} F_p \right]}$$

(4.4)

where $k$ is the time step counts, $t$ is the total number of time steps, and $n$ is the number of species in the chemical kinetic mechanism. Skeletal models can be obtained by selecting a user-defined threshold, $NS_{thresh}$, and eliminating species that are below the chosen threshold.
4.3 Reduced mechanisms developed by Alternative Species Elimination method

Figure 4.4: Top 25 chemical species for n-dodecane ignition using the ASE method, whereby the normalized changes $NC_i$ are the averages for n-dodecane/air at a pressure of 15 atm, temperature of 1050 K, and equivalence ratios of 0.5, 1.0 and 1.5.

The four detailed chemical kinetic models are reduced using the ASE method. Using three equivalence ratio 0.5, 1.0, and 2.0 at a temperature of 1050 K and pressure of 15 atm, ignition simulations are performed for each model. The residence time was set to 8 ms for all simulations, while the adaptive time step was decided by the default MATLAB ode solver. Four species, $NC_{12}H_{26}$, $O_2$, $CO_2$ and $H_2O$ are excluded for examination since they are indispensable for the ignition. Simulations are performed using the open-source package, Cantera. The function ”setMultiplier” is used to suppress reactions involving the target species. The absolute values of $NC$ at the three equivalence ratios are averaged before ranking the species.

Figure 4.4 shows the 25 most important species in each reduced mechanism. The averaged $NC$ values are presented against the carbon number of the species. It is found that the top reactive species are from the C0-C3 system. The most sensitive species are of the H2-O2 system. For LLNL this is HO2, while it is H2O2 for the other mechanisms. On the other hand, even the category of C12 does not occupy the highest sensitivities. It should be noted that the fuel, also a C12 species is excluded from the analysis. C12 species do appear among the top 25 species, representing primary radicals.

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Figure 4.5: Comparison of n-dodecane ignition delay predictions using skeletal models and their respective detailed versions for n-dodecane/air mixtures at 20 atm.

Figure 4.6: Comparison of n-dodecane ignition delay predictions using skeletal models and their respective detailed versions for n-dodecane/air mixtures at 40 atm.

and unsaturated C_{12} species. For instance, there are four C_{12} species in JetSurF and CNRS models, while there are only two in the LLNL model and one in the Milano. Four species with a high carbon number, NC_{12}−QOOH, NC_{12}H_{25}−OO, NC_{12}−OOQOOH, and NC_{12}−OQOOH only appear in the Milano model; the first three are radicals and the last is the n-dodecane-keto-hydroperoxide.

By imposing threshold values of NC, the required skeletal models can be derived from the detailed n-dodecane versions. A threshold NC_{thresh} of 5 \times 10^{-4} is first imposed for all the models. However,
it is discovered that for the CNRS, this yields greater deviations in predicting ignition delay times compared to the detailed model. The value for CNRS is thus reduced to \(5 \times 10^{-5}\). Imposing these thresholds results in a skeletal JetSurF model with 115 species and 864 reactions. The Milano model is reduced to 116 species and 1860 reactions. The CNRS skeletal model contains 849 species with 3991 reactions. The LLNL mechanism reduced to 1606 species and 5370 reactions. Compared to detailed mechanisms, these skeletal mechanisms reduced the species and reactions by 55\% and 61\%, on average. Lastly, with the goal to further reduce the LLNL mechanism, we discover that the lean condition dominated the value of \(NC\) in the range from \(1 \times 10^{-4}\) to \(1 \times 10^{-3}\). This behavior was observed in previous study [137]. It was observed that under lean conditions, many oxygenated species appear in the ranking. The exclusion of these, however, does not affect prediction ability. Therefore, by only considering the stoichiometric \(NC\) list, with the same threshold, \(5 \times 10^{-4}\), the LLNL model reduced to a skeletal mechanism with 303 species and 2403 reactions. The ratio of reactions to species is increased to 7.91 in the resulting skeletal LLNL model.

The ignition delay times of reduced and detailed models are compared in Figure 4.5 and 4.6. It is noted that for the conditions investigated, the average deviation for the JetSurF, Milano and CNRS skeletal models, are 1\%, 3\%, and 5\%, respectively. In the case of the LLNL model, at 14 atm and 40 atm, the average deviation for 14 atm and 40 atm is within 5\%. However, the skeletal model slightly over-predicts ignition delay times at 20 atm with an averaged relative error of 7\% but captures the NTC behavior. It could be surmised that essential species have been taken care of, while the exclusion of about 90\% species and 85\% of reactions in detailed mechanism decreases the reaction pathway for ignition, leading to a faster chemical process in general.

4.4 Reduced mechanism based on species propensity method

The proposed SP method is applied to the JetSurF model as a test and to the LLNL model because it is the largest model for which more time is needed using the ASE method. The reduction process
using the SP method is first performed at the 1050 K and 15 atm to assure the same condition as ASE, however, it was found that with a temperature of 800 K and a pressure of 20 atm for n-dodecane/air mixtures lead to a better result. It should be noted that the connectivity in ASE is powerful enough to capture both high and low temperature kinetics. The selection of above condition is decided by the target prediction of ignition delay times. It has been observed that with a higher temperature, the predictions of SP method results in large deviations in the low temperature regime. For further analysis of the two reduction approaches, the number of species in the SP process is first set to be the same as ASE skeletal models. The JetSurF skeletal model using the ASE contains 115 species and 864 reactions. That is, with the same number of species, the SP method reduces the reactions to 769. The computational time of the reduction process is reduced by the order of $3 \times (N - 4)$, where 3 accounts for lean, stoichiometric and rich conditions and $N - 4$ is the number of species evaluated in the ASE process, after excluding four obvious species.

Figure 4.7 shows the distribution of the normalized property after ranking. Selecting the threshold will determine the remaining species and associated reactions in the skeletal model. In this study, with the goal to obtain a minimum size model that is able to accurately predict ignition delay times, we further apply a threshold value as $3.5 \times 10^{-14}$. As a result, skeletal model includes 111 species and 757 reactions with averaged relative error within 4%.

![Figure 4.7: Distribution of the normalized propensity after ranking.](image)
The ignition delay time predictions of the resulting JetSurF skeletal model are compared in Figure 4.8 and 4.9. It is observed that the SP reduced version demonstrates good prediction compared with the detailed model. The average deviations for the SP method are found to be 4% at 20 atm and 6% at 40 atm, whereas the ASE deviations are within 1%.

Figure 4.10 shows the distribution of species in the model, based on their carbon number. The JetSurF detailed mechanism has a peak at C7 with a high percentage of C4 to C10, whereas the
Figure 4.10: Species distribution by carbon number in detailed and reduced versions of the JetSurF model.

ASE version peaked at C₆ and C₁₂, while the SP method has the most C₄. Skeletal models obtained from ASE and the SP method have 109 duplicate species, represents for 98.2% of the total SP skeletal model species. Two isomers of C₇H₁₂ are not in the ASE model but found in the SP skeletal version. Since the fuel is n-dodecane, both skeletal models contains a large number of C₁₂ radicals, indicating a potential to further reduce the model size by lumping together isomeric species. Another observation is that in the two skeletal models, species in the range of C₀-C₅ includes more species than the C₇-C₁₁ range, which is reversed in the detailed model. This highlights the foundational role of C₀-C₄ systems on the kinetics of large fuels such as the n-heptane, n-octane and n-dodecane.

Figure 4.11 shows the distribution of the normalized propensity in the LLNL model after ranking the species. Choosing a threshold value determines the number of species in the skeletal model. The selection standard is decided by the ignition prediction of the obtained model. With a threshold value of 1.12 × 10⁻¹⁹, the SP method results in a skeletal model containing 1200 species and 7864 reactions. This is less than half of the original model in terms of species. It is recognized that this model can be further reduced using ASE.

Figure 4.7 and 4.11 show that species are grouped in a way that shows sharp changes at certain NSₚ. For instance, the NSₚ of the first eight species are of the same order of magnitude. They are H₂O,
OH, CO₂, CO, H₂, O, H, O₂. It is known that OH, O, H are key radicals/atoms, H₂O and CO₂ are major products, CO and H₂ are important intermediates while O₂ is crucial for ignition. The jump of these steps indicates the existence of inwardly connected group or key contribution to kinetic evolution of the system.

The skeletal models reduced from the LLNL detailed mechanism are also compared with two reduced mechanisms found in the literature [226, 227], identified here as SK106 and SK163, with SK for skeletal followed by the number of species. The SK 106 model used the same mechanism as in current study. It was obtained by reducing the detailed version using the DRG with expert knowledge (DRGX), resulting in a 557 species mechanism. The method of DRG sensitivity analysis (DRGASA) was subsequently applied to derive the final version. The SK 163 is derived from two mechanisms, an older version of n-dodecane mechanism with 2885 species [65] and one xylene mechanism [228] using four rounds of reduction methods, including DRGX, DRGASA, isomer lumping, DRGX, and DRGASA. The distribution of the species is analyzed in Figure 4.12. The detailed model has a linear distribution from C₀-C₁₂ with less than 1% of the species in the C₁₃-C₂₀ range. With reduction, the skeletal models have the largest portion of C₁₂, with the majority of the species falling into C₀-C₈. It is observed that all the species from ASE method are found in SP skeletal model.
Figure 4.12: Species distribution by carbon number in detailed and reduced versions of the LLNL model.

Figure 4.13: Comparison of LLNL model and skeletal mechanisms with respect to their prediction of ignition delay time of homogeneous n-dodecane/air, $\Phi = 1, p = 20$ atm.

In Figures 4.13 and 4.14 predictions of ignition delay times by skeletal models are compared to those of detailed mechanisms. The SP skeletal model leads to relative errors that are within 1% in all conditions. The averaged deviation for the ASE skeletal model is 7% with a stoichiometric mixture at 20 atm, while at lean and 40 atm, the deviation goes down to 4%. SK 106 generates about 20% difference, whereas SK 163 averaged to about 30%. The later deviation can be explained by the fact that literature skeletal models are not even in agreement with the original model from which they are reduced. They have been tuned and made more compact by lumping together some
species with the same carbon number.

We next extend our comparison of reaction and species ratio to all the model studied, as shown in Table 4.2. It is found that the reduction process generally increases the reaction to species ratio except for the Milano model. The Milano model has a high ratio due to the species lumping. Overall, the reaction to species ratio is about six for reduced models and about five for detailed mechanisms.

From this model reduction study, in addition to the 111 species obtained by SP process from JetSurf model, with the inert species Ar added, the final skeletal model consists of 112 species and 757 reactions is chosen for use in spray ignition simulation.

Chapter Summary

In this work, skeletal chemical kinetic models of \( n \)-dodecane have been obtained from detailed models after comparing these models with experimental ignition data. Differences in the prediction ability of the detailed models have been noted, especially under lean conditions.

In order to obtain the reduced version of the models, the ASE method has been used. The normalized
Table 4.2: Species and Reactions in Kinetic Models

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Species</th>
<th>Reactions</th>
<th>Reaction to Species Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>JetSurF</td>
<td>348</td>
<td>2163</td>
<td>6.22</td>
</tr>
<tr>
<td>Milano</td>
<td>451</td>
<td>17848</td>
<td>39.57</td>
</tr>
<tr>
<td>CNRS</td>
<td>1377</td>
<td>5865</td>
<td>4.26</td>
</tr>
<tr>
<td>LLNL</td>
<td>2755</td>
<td>14314</td>
<td>5.20</td>
</tr>
<tr>
<td>JetSurF ASE</td>
<td>115</td>
<td>864</td>
<td>7.51</td>
</tr>
<tr>
<td>Milano ASE</td>
<td>116</td>
<td>1860</td>
<td>16.03</td>
</tr>
<tr>
<td>CNRS ASE</td>
<td>849</td>
<td>3991</td>
<td>4.70</td>
</tr>
<tr>
<td>LLNL ASE</td>
<td>303</td>
<td>2403</td>
<td>7.93</td>
</tr>
<tr>
<td>JetSurF SP</td>
<td>111</td>
<td>757</td>
<td>6.82</td>
</tr>
<tr>
<td>LLNL SP</td>
<td>1200</td>
<td>7867</td>
<td>6.56</td>
</tr>
<tr>
<td>SK163</td>
<td>163</td>
<td>887</td>
<td>5.44</td>
</tr>
<tr>
<td>SK106</td>
<td>106</td>
<td>678</td>
<td>6.40</td>
</tr>
</tbody>
</table>

A change threshold of $5 \times 10^{-4}$ has been applied to the rank three of the models and a threshold of $5 \times 10^{-4}$ has been applied to the CNRS model to obtain skeletal models capable of matching the ignition on predictions of the detailed models. The ASE versions are such that JetSurF now has 115 species, Milano 116 species, LLNL 303 and CNRS 849. The last two suffer from many isomers in the model.

Seeing that large models such as the LLNL demands long reduction times, a new method, based on species propensity has been developed and demonstrated on the JetSurF and LLNL models. This method is capable of deducing a JetSurF reduced version that nearly matches the one from the ASE method. The resulting LLNL version from the SP is larger and can be further reduced.

Examining the distribution of the carbon number in the detailed and reduced model gives further insight such as the foundational role of C_0-C_4 chemistry in these models of a C_{12} fuel. The reduced version of the JetSurF model with inert gas Ar added, consists of 112 species and 757 reactions is retained for reacting spray simulation.
Validation of high-density spray combustion

The aim of this thesis is to advance predictive simulation of high density combustion such as found in Diesel engines. We have looked at a convenient approach to invoking real gas behavior and cost-effective means of incorporating chemical kinetic effects through a reduced model. These recommended actions are now tested in this section by validating the flow field of an \textit{n}-dodecane spray from the Engine Combustion Network database. Both non-reacting and reacting cases are simulated. The spray is referred to as Spray A in the ECN nomenclature. To further contextualize the simulations, ideal gas cases are also included in the validation. It might be attempted to ignore real gas effects by assuming that the relatively high temperatures in Diesel engines compensate for the high pressures, so that ideal gas models might still be justified. This additional comparison is intended to refute this simplifying assumptions.

As mentioned in Section 1.2.4, Sandia National Lab initiated the Engine Combustion Network (ECN) to establish a library of well-documented experiments for model validation and improvement at various operating chamber and injection conditions [142, 229]. Among the documented experiments is an \textit{n}-dodecane jet (363K with a speed about 600 m/s) injected into a pre-combustion heated chamber at \( T = 900 \text{ K} \) and at a pressure about 6 MPa. This case is representative of high density combustion and will be used here to validate various physical models that are relevant to spray mixing and ignition.
To be predicted are such aspects of the spray as the liquid and vapor penetration lengths over time. Also, the spray ignition must be captured in terms of auto-ignition time and spatial location. These predictions are possible if the two phase flow, turbulent mixing, and chemical kinetics are properly accounted for.

The fuel is injected into a vessel of compressed air that is heated by pre-combustion of a lean acetylene/air mixture. This two phase problem can be handled using an Eulerian-Eulerian or a Lagrangian-Eulerian framework. Preference here is for the latter.

The Lagrangian-Eulerian framework can be used to simulate various sprays. The Lagrangian transport, break up, and vaporization of the spray needs to be captured with an appropriate spray model. Among these models, the Kelvin-Helmholtz Rayleigh-Taylor (KHRT) model can be adopted for sprays at high density conditions such as the current spray. The parameters, however, must be optimized for reasonable prediction. This KHRT model is therefore chosen for this spray model.

A realistic turbulence model is needed to predict the flow field. This must be chosen with consideration of accuracy and computational cost. While URANS models are cost-effective, their accuracy is not high enough in certain respects. LES models are more accurate but require finer mesh refinements, and a higher computational cost. Hybrid LES and RANS approaches are adopted in some cases to optimize cost and accuracy. These hybrid models help to resolve certain regions of the flow better than RANS models.

In terms of predicting spray ignition events, a validated chemical kinetic model is needed. Considerations of computational costs for reduced chemical kinetic models. These reduced models are preferably generated with ease from the validated detailed models.

Turbulence is modeled using the Wall-Modeled LES (WM-LES) model. A real gas case is considered using the Redlich-Kwong equation of state. The chemistry is represented by a 112 species reduced model, developed in the previous chapter.
5.1 Experimental setups and numerical settings

In this study, the Spray A configuration of the fuel injector and ambient chamber is considered, as described in section 1.2.4. The vessel is cube-shaped (108 mm) with full optical access for line-of-sight or orthogonal optical diagnostics. This is a standard experimental facility at Sandia National Lab for the investigation of spray combustion phenomena. An overview of the specification spray conditions is given in Table 5.1.

Table 5.1: Characteristics of the main combustion vessel and injector for Spray A.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient gas density</td>
<td>22.8 kg/m$^3$</td>
</tr>
<tr>
<td>Ambient gas oxygen conc.</td>
<td>15 vol-%</td>
</tr>
<tr>
<td>Ambient gas temperature</td>
<td>900 K</td>
</tr>
<tr>
<td>Ambient gas pressure</td>
<td>6 MPa</td>
</tr>
<tr>
<td>Ambient gas velocity</td>
<td>less than 1 m/s</td>
</tr>
<tr>
<td>Single hole nozzle outlet diameter</td>
<td>0.090 mm</td>
</tr>
<tr>
<td>Discharge coefficient at 10 MPa</td>
<td>0.86</td>
</tr>
<tr>
<td>Fuel</td>
<td>$n$-dodecane</td>
</tr>
<tr>
<td>Fuel temperature at nozzle</td>
<td>363 K</td>
</tr>
<tr>
<td>Injection duration</td>
<td>1.5 ms</td>
</tr>
<tr>
<td>Injection mass</td>
<td>$\sim$3.5 mg</td>
</tr>
</tbody>
</table>

These simulations can be carried out in 3D or 2D, taking advantage of symmetry. The 2D option permits cost-effective implementation of chemical kinetic aspects of the problem. The computational domain consists of a 2D axisymmetric, uniform mesh with 100 mm in axial direction and 63 mm in the radical direction. Grid dependency was studied by simulating the non-reacting Spray A with three different refinements of the grid along the stream-wise and radial directions: coarse mesh ($73 \times 64$ cells), medium mesh ($81 \times 71$ cells) and fine mesh ($95 \times 85$ cells). These grids are clustered in the region near the injector and stretched at a ratio of 1.05 toward the down-stream and radial directions. The last two resolutions are comparable with those of other high density spray simulations [160].
The computational cost is reduced by implementing the Wall-Modeled LES model \[230\]. The model activates RANS in the inner part of the boundary layer to avoid further mesh refinement and the outer part of a boundary layer is solved using the LES formulation. In the model by Shur et al. \[230\], the eddy viscosity is calculated using:

\[
\nu_t = \min \left[ (\kappa d_w)^2, (C_{\text{Smag}} \Delta)^2 \right] \cdot S \cdot \left\{ 1 - \exp \left[ -\left( y^+ / 25 \right)^3 \right] \right\}
\] (5.1)

where \(d_w\) is the wall distance, \(S\) is the strain rate, \(y^+\) is the normal to the wall inner scaling, \(\kappa = 0.41\) and the Smagorinsky constant is \(C_{\text{Smag}} = 0.2\). These constants are often tuned to match experimental observations if necessary, but are set as default values in this study.

The total computational time for the reacting flow with a finite rate chemistry model is largely determined by the number of species and reactions in the selected chemical reaction model. A reduced \(n\)-dodecane model with 112 species is used \[141\]. This reduced model is derived from a detailed chemistry model, JetSurF 2.0 \[66\], as described in Section 4.1.

The spray simulations are performed using the commercial CFD software, ANSYS Fluent. The PISO scheme is coupled with a second order implicit time discretization to improve the computing speed and accuracy. For spatial discretization, the pressure is second order, the momentum equation uses the bounded central method, while continuity and species equations use the second order upwind scheme. The time step is \(4 \times 10^{-6}\) s with a maximum of 100 inner iteration steps per time step. The Lagrangian phase is injected every 50 iteration and interacts with the continuous phase. The total simulating physical times for the non-reacting and for reacting cases are 3.5 ms and 1.2 ms, respectively. In the later, the time is limited to the time after the observation of the auto-ignition time and location, since the reacting case is more computationally costly.
Figure 5.1: Comparison of detailed and reduced models with respect to ignition delay time prediction for n-dodecane/air mixture, $p = 60$ atm and $\Phi = 1$. Red dashed lines - detailed model and the green dashed line - reduced model.

5.2 Chemistry model validation in a zero-dimension reactor simulation

Simulations are carried out in a zero-dimension reactor, with the goal to further test the reduced model against the detailed one, which cannot be used because of computational cost. Figures 5.1 shows ignition delay times of the detailed and reduced models plotted against inverse temperature. The pressure is 60 atm and the equivalence ratio $\Phi$ is 1. As shown in the Figure 5.1 results from reduced version of chemical model are in good agreement with detailed model.

Further validation of the reduced model is demonstrated in terms of the temperature profile and species mole fractions as shown in the Figure 5.2. Results are obtained from the simulation of the auto-ignition of homogeneous n-dodecane and air mixture. It is seen in Figure 5.2a that the predictions from reduced model agree well with the detailed model. The average percentage error for temperature is 0.75%, and the major species errors are within 5.0%. The ignition time is accurately
Figure 5.2: Comparison of detailed and reduced models with respect to simulation of selected species time histories during ignition of homogeneous n-dodecane/air mixtures at 60 atm and 900 K. Lines - detailed; symbols - reduced.
predicted to within a few microseconds. Figure [5.2b] shows some intermediate species time histories. Predictions of these key intermediate species are shown to be reasonably well.

5.3 Optimization of KHRT and grid independence studies (non-reacting cases)

To assess the quality of the simulation results, mesh dependency study is carried out with grids from coarse to fine identified as Grid 1, Grid 2, and Grid 3, respectively, with the same stretching ratio of 1.05. The minimum grid size is 0.05 mm, 0.10 mm, and 0.15 mm for grid 1, 2, and 3, respectively. Simulations are carried out at 900 K, 6 MPa with 0% oxygen in the chamber. This corresponds to a simple study of spray injection and mixing, without the complexity of chemical reactions. The gases in the chamber are treated as real gases.

![Graph showing mesh dependency study and validation of the liquid and vapor penetration lengths. The liquid core length $L_l$ is defined as $\max[x(LVF = 2\%)]$, while the vapor penetration is $L_v = \max[x(Y_{C_{12}H_{26}}) = 1\%]$.](image)

Liquid and vapor penetration lengths are shown in Figure [5.3]. The liquid penetration length is defined as the location where the liquid volume fraction (LVF) reduces to 2%, and the vapor
penetration is defined as the location where the mass fraction of \( n\text{-C}_{12}\text{H}_{26}, Y_{\text{C}_{12}\text{H}_{26}} \) reduces to 1%. The KHRT model parameters are set to \( C_L = 25.7, B_0 = 0.61, B_1 = 20, C_{RT} = 0.1, \) and \( C_\tau = 0.05, \) based on a prior calibration study. All the grids yield very similar liquid penetration depths. Grid 2 and 3 predict almost the same vapor trajectories, however, the coarsest Grid 1 overestimates the vapor penetration length and the error is magnified at downstream. The above convergence study leads to the choice of Grid 2, with \( 81 \times 71 \) cells yielding a total of 5,600 cells for the flow simulation.

\[
\begin{align*}
\text{Figure 5.4: Simulation of } n\text{-heptane spray with tuned spray model in selected mesh, and validation of the liquid and vapor penetration lengths. The liquid core length } L_l & \text{ is defined as } \max\{x(LVF = 2\%)\}, \\
\text{while the vapor penetration is } L_v & = \max\{x(Y_{\text{C}_7\text{H}_{16}} = 1\%)\}.
\end{align*}
\]

Next, the tuned KHRT model in the selected mesh is examined in a baseline \( n\text{-heptane non-reacting spray from the ECN. The ambient density and temperature for the spray are } 14.8 \text{ kg/m}^3 \text{ and } 1000 \text{ K, respectively. The composition of the initial gas is } O_2 \text{ (0.0%), } N_2 \text{ (89.71%), } CO_2 \text{ (6.52%), and } H_2O \text{ (3.77%). As shown in Figure 5.4, the liquid penetration length predicted by the model is close to the measurement after a short initial transient. Simulation provides overall satisfactory vapor penetration results with a slightly overestimated length at the beginning. The KHRT breakup model and the selected mesh is then used for the reacting flow simulation.}

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5.4 Ignition simulation

The KHRT parameters used in Sec. \ref{sec:flame} are first employed in simulating the reacting case. The auto-ignition delay time is found to be 0.68 ms with a lift-off length of 23.50 mm. These results, compared to the 0.44 ms ignition delay time and 16.5 mm lift-off length observed in experiment, indicate the set of models used predict a longer ignition time and location. This could be linked to the droplet breakup and mixing process or the rate of chemical reactions. It is possible that the chemical kinetic model predicts slower reaction rates than would be observed. However, this thesis is not concerned with the optimization of the chemical kinetic model. Nonetheless, it can be shown that the ignition delay time and location can be influenced by the droplet breakup and mixing process, even to the extent of compensating for the deficiency of chemical kinetic model, since the ignition process is a combination of physical and chemical processes. As shown in Figure \ref{fig:flow_contours}, the gas density (representative of droplet breakup, vaporization, and mixing) is related to the H₂O flow field (representative of ignited zone). Ignition occurs in vaporized and heated combustible gas mixture. Controlling breakup and vaporization can therefore compensate for slow or fast chemical kinetics.

![Density contour](image1.png)

![H₂O mass fraction](image2.png)

**Figure 5.5:** Instantaneous flow contours at 0.8 ms, length in [mm]. (a) Density field. (b) H₂O mass fraction. The interaction between the liquid jet and the ambient gas changed after ignition onset.

This modification of the droplet processes is attempted to improve accordance between simulations and experiments. One of the most effective way is to reduce the length of the liquid core, thus, the
vaporization and mixing could be accelerated, causing the reaction kinetics to set in earlier and shortened the combined ignition time. In KHRT model, the liquid core length $L$ and the KH breakup time $\tau_{KH}$ are proportional to constants $C_L$ and $B_1$, respectively. The magnitude of these two constant are therefore reduced to achieve a faster breakup and mixing process. Parametric studies have been done and the final parameters in KHRT model for this reacting case are set to $C_L = 5.7$, $B_0 = 0.61$, $B_1 = 1.73$, $C_{RT} = 0.1$, and $C_\tau = 0.05$.

Results of the reacting flow simulations are first examined in the early phase before the auto-ignition. In Figure 5.6 Spray A schlieren images at several time reported by Skeen, Manin, and Pickett [231] are compared with simulation results. It can be seen that from the density gradient fields, simulations using the real gas model show a close agreement with experiment in terms of penetration depth and spreading angle. However, results obtained using the ideal gas shows a longer penetration depth. At 700 $\mu$s, the tip of the spray in the experiment and real gas prediction is about 26 mm, but the ideal gas shows that it is about 30 mm. This longer penetration of the ideal gas is also reflected in

Figure 5.6: Early phase of spray comparison based on density gradient fields. The top: Experiment with white line indicating vapor regime [231]; middle is simulation results using real gas model; bottom is simulation results using ideal gas.
the temperature field, not shown here. Because the real gas behavior is more physically sound at these conditions, the results therefore show that the failure of the ideal gas model is because of the physical inaccuracy of the gas model.

After this early phase, the ongoing chemical reactions lead to auto-ignition. The ignition properties can then be compared. Table 5.2 shows a comparison of the determined ignition time and lift-off length. The ignition delay time is defined as the time when the OH mass fraction reaches 2% of the value of quasi-steady state [157]. The lift-off length is consequently calculated as the place where the OH mass fraction reaches 2% of the value of quasi-steady state. After ignition, the burning zone stabilizes such that the base of the flame is near the lift-off location. The real gas predicts a sufficiently close auto-ignition time, but it is shorter by 20 $\mu$s.

As for the flame lift-off, the real gas case shows a flame stabilized further downstream, while the ideal gas is nearer to the injector. The reason for this could be the joint effect of the turbulence and vaporization models. The ignition is controlled by the mixing of the spray tip, heating, and chemical reactions. In this case, there are limited effects of the EOS model. The stabilization of the flame is controlled by the entrainment, mixing, heating and transport of the gases toward the ignition front. The ideal gas appears to have a longer residence time that moves the front upstream.

Table 5.2: Ignition delay time and lift-off length comparisons

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Ideal gas</th>
<th>Real gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ignition delay time [ms]</td>
<td>0.44</td>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>Lift-off length [mm]</td>
<td>16.5</td>
<td>15.1</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Figure 5.7 compares predicted and measured CH$_2$O fields at two different instances. As shown in the figure, some agreement is observed for CH$_2$O. It can be seen that the CH$_2$O is initially more concentrated in the real gas case. At the later time, the CH$_2$O field has a higher magnitude in the ideal gas. The flame propagates faster in ideal gas case, partially due to the lower predicted density which means less amount of mass to be heated up. This discrepancy of the real gas case can be
traced back to turbulence and evaporation models, particularly the mixing zone at the tip.

The simulations also allow us to observe quantities that are difficult to obtain in standard experiments. Figure 5.8 presents velocity vectors along with the temperature contours at two different times. This figure shows the interactions between the liquid phase and the ambient gas after the ignition. At 0.4 ms (as shown in Figure 5.8a), the liquid jet tip displaces the ambient gas, while the exchange of momentum near the injector leads to the gas entrainment on the side of the liquid jet. Therefore, the mixing of fuel and oxidizer is intensified on the shear layers at the side. The mixing process could further explain the ignition location observed in Figure 5.7. After auto-ignition, the flow dynamics between the liquid and the gas is seen to be different, as shown in Figure 5.8b at 1.2 ms. At this moment, the flame kernel is formed and the gas expansion due to combustion changes the flow dynamics at the front. The whole liquid jet can now be categorized in three parts: $x \in [0, 20]$ mm is the liquid core; $x \in [20, 30]$ mm is the mixing zone; and $x \in [30, 45]$ mm is the flame kernel. The combustion process is initialized in the mixing zone, where active intermediate radicals are generated. Later, the mixture and reactive intermediate species travel downstream, generating the flame kernel.
Figure 5.7: CH$_2$O images from experiment compared with simulation results. False-color PLIF images showing ensemble-averaged formaldehyde structures at different times, obtained by IFPEn and Sandia/TUe at Spray A conditions [232]. Displayed dynamic ranges have been adjusted to emphasize the CH$_2$O structure.
Figure 5.8: Instantaneous temperature contours with velocity vectors. (a) Flow field at 0.4 ms. (b) Flow field at 1.2 ms. The interaction between the liquid jet and the ambient gas changed after ignition onset.
Chapter Summary

Simulations of a standard high density \( n \)-dodecane spray has been carried out, examining non-reacting and reacting cases. For the reacting case, a finite-rate chemistry model is employed through a reduced 112 species model developed in previous chapter. The non-reacting cases are performed to evaluate the mesh quality and validate spray results. Comparisons with experiments show good agreement for liquid and vapor penetration lengths.

Simulations of the reacting flow shows that the real gas is closer to experimental Schlieren image than ideal gas before auto-ignition. With respect to the lift-off length, real gas over predict the length while ideal gas underestimate it, showing potential improvement by turbulent and chemistry models. The temporal and spatial examination of intermediate species \( \text{CH}_2\text{O} \) shows close agreement with experiment for early stage and later transition. Ideal gas case appears to be close to experiment in the later combustion process, possibly due to lower density predicted, resulting a fast flame propagation.
Chapter 6

Conclusion and outlook

This thesis sought to contribute to the simulation of high-density combustion, such as found in rocket and Diesel engines. It first demonstrated the need for real gas modeling, provided a framework for conveniently involving this real gas behavior, and proceeded to validating standard experimental measurements of spray characteristics after obtaining a reduced chemical kinetic model. The thesis has established the following main results:

- From the study of high-density N\textsubscript{2} jet simulations, it is found that ideal gas model failed to predict the experimentally observed penetration length and spreading angles, while the real gas case captures the flow dynamics well.

- Studies of \textit{n}-heptane jet with different boundary conditions further demonstrated the necessity of real gas equations of state. Differences in flow fields are more pronounced in reacting cases, due to the gas expansion.

- To address the need for real gas parameters in high-density combustion flow, a convenient framework is proposed. It generates real gas parameters from chemical kinetic models, and is demonstrated in a single element rocket combustion chamber simulation with a reduced chemical mechanism.

- Using \textit{n}-dodecane as a Diesel fuel representative, four detailed chemical models were com-
pared against experimental data. Reduced versions of these models are developed based on ASE methods showing close agreement with detailed models for ignition delay time. A cost efficient reduction method was also developed on the basis of Species Propensity. From this, a reduced chemical kinetic model was chosen for further spray ignition studies.

- The reduced model obtained by SP method and the recommended method of real gas parameter estimation were employed in a Diesel like spray simulation. The simulated ignition delay time is comparable with the measured delay time. Discrepancies are observed for the lift-off length. These differences and those of the ideal gas case are traceable to the spray and turbulence models.

This thesis contributes to the growing knowledge of high density flow combustion, especially for spray simulation with a focus on auto-ignition behavior. The framework developed in this study provides the possibility to account real gas effects for all the species in a chemical mechanism. The chemical reduction methodology explored and reduce models developed will be useful for future fuel combustion modeling.

Outlook

A few directions beyond this work are possible:

- 3D simulations of Spray A need to be attempted to justify the assumption of the present work regarding the 2D versions.

- Further parametric studies of the KHRT and turbulence model combinations are needed.

- With a focused on multi-physics simulation, geometry in this study is simplified. Full engine simulation of the high density spray combustion would help for a general picture of diesel engine auto-ignition phenomena and move the work toward practical engineering design and
development.

- For 3D engine simulations, more cost-effective methods of incorporating chemical kinetic effects need to be explored. One option is the use of unsteady reactor network to reduce the number of chemical reactors that need to be evaluated at each time step. Regions of similar thermodynamic states can be related as a single reactor, with the same chemical kinetic evolution.

- Direct integration of chemistry is used but very costly. The implementation of the ignition based model as a field function for predicting spray ignition is more cost-effective. Ignition-based combustion model has been developed by Akih-Kumgeh and Bergthorson [233] and Zhou, Dong, and Akih-Kumgeh [234].


Vita

Chenwei Zheng received his B.S. in Aircraft Propulsion Engineering from the Nanjing University of Aeronautics and Astronautics in 2013. He graduated with honor for his thesis entitled \textit{Large Eddy Simulation of laminar transition over a flat plate}. He joined the Mechanical and Aerospace Engineering Department of Syracuse University in 2013 to conduct research in areas of computational analysis of combustion and equation of state modeling. He became an NSF NRT Empower fellow in Spring 2016. With a focus on water-energy research, the interdisciplinary program equipped him with skills in science communication, business analysis and project management. He received his Master of Science degree in Mechanical and Aerospace Engineering in May 2015 and the Certificate of Advanced Study in Sustainable Enterprise in May 2017. He is currently a member of the Combustion Institute, the American Institute of Aeronautics and Astronautics, and the American Society of Mechanical Engineers.