

THE UNIVERSITY OF QUEENSLAND

The Computational Modelling of High-Temperature Gas Effects with Application to Hypersonic Flows

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A thesis submitted for the degree of Doctor of Philosophy at The University of Queensland in June 2008

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This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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BRANDIS, A. M., GOLLAN, R. J., SCOTT, M. P., MORGAN, R. G., JACOBS, P. A., GNOFFO, P. A.: 2006. Expansion tube operating conditions for studying nonequilibrium radiation relevant to Titan aerocapture. AIAA Paper 2006-4517

Brandis was responsible for 100% of the gathered experimental data, and 20% of the numerical simulations. The remaining 80% of the numerical simulation work was performed by Gollan. The drafting and editing of the text was undertaken by Brandis (50%) and Gollan (50%). The remaining authors contributed to discussions about the work and final editing of the paper.

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The numerical simulation work was performed by Gollan (70%) and C. Jacobs (20%). C. Jacobs was predominantly responsible for performing the experiments and data collection with minor contributions by Eichmann, Potter, McIntyre and Buttsworth. The text was prepared by Gollan (70%) and C. Jacobs (30%), with the remaining authors providing comments and proof-reading.

Statement of Contributions by Others to the Thesis as a Whole

Chapter 6 of this thesis discusses two simulations of the X2 facility as a demonstration of the application of this thesis work. The two simulations are of the X2 facility operated in: (a) expansion tunnel mode, and (b) nonreflected shock tube mode.

In the section of the thesis which presents the simulations of expansion tunnel mode (Section 6.2), there is a contribution of work made by Aaron Brandis. Specifically, the experimental results and one-dimensional modelling are the work of Aaron Brandis.

Similarly, in Section 6.3 which presents simulations of nonreflected shock tube operation, both the experiments and the one-dimensional simulations are the work of Carolyn Jacobs.

Statement of Parts of the Thesis Submitted to Qualify for the Award of Another Degree

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¹Hey, I prefer S.I. units.

Abstract

During atmospheric entry, a spacecraft's aeroshell uses a thermal protection system (TPS) to withstand severe thermal loads. Heating to the vehicle surface arises as convective, catalytic and radiative heat flux due to the high temperature of the shockwave compressed gases surrounding the aeroshell. The problem for the TPS designer is that the heat load estimates are based on phenomenological models which have questionable validity and, thus, large uncertainty. As an example, recent analyses of heat loads for a proposed aerocapture vehicle designed for Titan differ by up to an order of magnitude. This uncertainty stems from the complexity of the blunt body flow field and the associated physical effects: thermochemical nonequilibrium; ablation and vehicle surface catalycity; and radiating flow. The motivation for this thesis is to develop computational tools that give accurate estimates of vehicle heat transfer as an input for design calculations. With that goal in mind, this thesis work has focussed on one aspect of this problem and that is the modelling of thermochemical nonequilibrium. The longer term goal is to produce tools which can be used to compute the high-temperature, radiating flow fields about aeroshell configurations; the modelling work presented here on thermochemical nonequilibrium effects is a foundation for tackling the radiating flow problem.

The modelling work was implemented in an existing flow solver which solves the compressible Navier-Stokes equations with a finite volume method. As part of this work, the flow solver was verified by two methods: the Method of Manufactured Solutions to verify the spatial accuracy for purely supersonic flow; and the Method of Exact Solutions — the flow problem being an oblique detonation wave — to verify the spatial accuracy for flows with embedded shocks. Validation of the flow solver, without any of the complexity of thermochemical nonequilibrium, was performed by comparing numerical simulation results to experiments which measured shock detachment on spheres fired into noble gases.

A model for chemical nonequilibrium based on the Law of Mass Action and using finiterate kinetics was coupled with the flow solver. The implementation was verified on two test problems. The first treated a closed-vessel reactor of a hydrogen-iodine mixture, and the second computed the chemically relaxing flow behind a normal shock in air. For validation, the implementation was tested by computing ignition delay times in hydrogen-air mixtures and comparing to experimental results. It was found that the selection of a chemical kinetics scheme can complicate validation, that is, a poor choice of reaction scheme leads to poor computational results yet the implementation is correct. As further validation, a series of experiments on the shock detachment distance on spheres fired into air was compared against numerical simulations based on the present work. Two models for species diffusion were also implemented: Fick's first law approximation and the Stefan-Maxwell equations. These models were verified by comparison to an exact solution for binary diffusion of two semi-infinite slabs. The more general problem of thermochemical nonequilibrium was also pursued. A multitemperature model, one translational/rotational temperature and multiple vibrational temperatures, was developed as appropriate for hypersonic flows. The model uses the Landau-Teller expression to compute the rate of vibrational-translational energy exchange and the Schwartz-Slawsky-Herzfeld expression for vibrational-vibrational energy exchange. The time constants for the rate expressions are estimated by a number of methods such as the use of SSH theory and the Millikan-White correlation. The coupling of vibrational nonequilibrium effects with the fluid dynamics was tested by computing the flow of nitrogen over an infinite cylinder. The simplified problem of a vibrationally relaxing flow behind a shock, without reactions, was compared to other calculations in the literature. This case tested the multi-temperature formulation, with oxygen and nitrogen each being ascribed their own vibrational temperatures. The coupling of chemistry and vibrational nonequilibrium uses the model by Knab, Frühauf and Messerschmid. The complete model for thermochemical nonequilibrium was verified by calculating the relaxation of oxygen behind a strong shock.

The models developed provide a basis for computing radiating flow fields, however the radiating flow problem cannot be attempted based on this work alone. Instead, a more immediate application of the modelling work was the simulation of expansion tube operation. It is desirable to simulate an impulse facility to give the experimenters access to aspects of experiment that are not directly attainable by experiment; especially a complete characterisation of the test flow properties. The modelling work and code development, as part of this thesis, addresses this need of experimenters. Two large-scale simulations are presented as a demonstration of the modelling work: (a) a simulation of an expansion tube in expansion mode; and (b) a simulation of an expansion tube in nonreflected shock tube mode.

Keywords

hypersonics, atmospheric-entry vehicles, high-temperature gas effects, nonequilibrium flows, expansion tubes

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List of Symbols

Some symbols which appear in this list have more than one meaning. The specific meaning of the symbol should be clear in the document from the context.

Latin symbols

Α	: coefficient in Arrhenius reaction rate expression
а	: sound speed
C_i	: concentration of species <i>i</i>
C_p	: specific heat at constant pressure
C_v	: specific heat at constant volume
D	: diameter (of sphere or cylinder)
\mathfrak{D}_{AB}	: binary diffusion coefficient for the diffusion of species A into B
Ε	: total energy of the gas (kinetic and internal)
E_a	: activation energy in Arrhenius reaction rate expression
е	: specific internal energy of the gas
$e_{v,i}$: specific vibrational energy of species <i>i</i>
f_i	: mass fraction of species <i>i</i>
f_m	: mass factor in SSH calculations of vibrational relaxation times
G	: Gibbs free energy
h	: specific enthalpy of the gas
	: Planck's constant
h_i	: specific enthalpy of species <i>i</i>
I_{ν}	: radiant intensity at frequency ν
\mathbf{J}_i	: diffusion flux of species i (vector quantity)
K _c	: equilibrium constant based on concentration
K_p	: equilibrium constant based on pressure
k	: thermal conductivity
	: Boltzmann constant
k_b	: backward reaction rate coefficient
	: Boltzmann constant

k_f	: forward reaction rate coefficient
$k_{v,i}$: thermal conductivity in vibrational mode for species <i>i</i>
$k_{v,s}$: same as $k_{v,i}$ but for species s
M	: Mach number
M_i	: molecular weight of species <i>i</i>
\mathcal{M}_i	: same as M_i
m_p	: mass of single particle <i>p</i>
N_r	: number of chemical reactions
N_s	: number of species
N_v	: number of vibrating species (diatomic molecules)
\mathcal{N}_A	: Avogadro's number
п	: exponent in Arrhenius reaction rate expression
	: number density of particles
Pr	: Prandtl number
р	: pressure
$Q_{\operatorname{Chem}-V_i}$: vibrational energy source term due to chemistry interation
Q _{rad}	: energy source term due to radiation
$Q_{\mathbf{rad}_i}$: vibrational energy source term due to radiation involving molecule i
Q_{T-V_i}	: vibrational energy source term due to translational-vibrational transfers
Q_{V-V_i}	: vibrational energy source term due to vibrational-vibrational transfers
q	: heat release when converting from reactants to products
R	: gas constant
	: nose radius
${\cal R}$: universal gas constant
Т	: temperature
T_i	: ignition temperature
T _{ref}	: reference temperature for evaluation of thermodynamic functions
$T_{v,s}$: vibrational temperature of species <i>s</i>
t	: time
u	: velocity (vector quantity)
и	: velocity in <i>x</i> -direction
υ	: velocity in <i>y</i> -direction
$[X_i]$: concentration of species <i>i</i>
x_i	: mole fraction of species <i>i</i>
~ · · ·	

Greek symbols

α	: rate constant for single-step reaction
	: parameter in Knab et al. model for chemistry-vibration coupling
α_i	: stoichiometric coefficient for reactant <i>i</i>

$\alpha_{ u}$: absorptivity coefficient at frequency ν
β	: shock wave angle
β_i	: stoichiometric coefficient for product <i>i</i>
γ	: ratio of specific heats
δ	: shock detachment distance
	: Kronecker delta in conservation equations
e	: energy parameter in Lennard-Jones potential
$\epsilon_{ u}$: emissivity coefficient at freqency ν
Θ_D	: dissociation temperature
Θ_v	: characteristic vibrational temperature
μ	: dynamic viscosity
	: reduced molecular weight
μ_{p-q}	: reduced mass of particles p and q
ρ	: density
$ ho_i$: density of species <i>i</i>
σ	: distance parameter in Lennard-Jones potential
$ au_ u$: optical thickness at frequency ν
$ au_v$: vibrational relaxation time
$\dot{\omega}_i$: chemical source term for species i

Introduction

Ever since Tsiolkovsky wrote his famous work in 1903, *The Exploration of Cosmic Space by Means of Reaction Devices*, human minds have worked on the problem of leaving the confines of this world. The two men who are credited with the greatest role in making Tsiolkovsky's ideas a practical reality are Sergei Pavlovich Korolev and Wernher von Braun. These two men worked independently and never met in their lifetimes yet both shared the goal of building rockets that would allow humans to explore the universe. In the post World War II period, both men found themselves working for governments that desired rockets for terrestrial "defence" applications but they both secretly harboured the desire to create space-faring vehicles.

Almost as soon as engineers began building rockets, they realised that designing a vehicle for reentry through Earth's atmosphere would present new technical challenges. The biggest of those challenges is the design of a vehicle to withstand the severe thermal loads generated by the high-speed flow through the planet's atmosphere. An accurate estimate of the thermal loads is vital input for sizing thermal protection systems for reentry aeroshells. The work in this thesis centres around the specific problem of modelling the gas dynamics that give rise to the vehicle thermal loads.

1.1 Exploration of the Solar System

A recent editorial in *NewScientist*¹ addressed the question of investing money in space exploration when there are so many terrestrial problems to be solved. The arguments for continued space exploration span from the direct and tangible benefits to the more esoteric. The billion-dollar industries based on telecommunications and global-positioning satellites are a direct benefit of investment in space exploration. The more esoteric benefits are the gains in human knowledge and the stimulation of a public interest in science. In any case, the policy makers around the world, and the public that backs them, have endorsed further space exploration into the foreseeable future. This means that engineers will continue to play a pivotal role in making space exploration a reality. With that in mind, we return to the narrative about one specific space engineering endeavour: the design of atmospheric-entry vehicles.

As rocket technology matured and reliable multi-staged rockets were being built, the feasibility of interplanetary travel became a reality. Soon scientists were designing experiments that involved landing on extraterrestrial bodies. This meant that the engineer was tasked with

¹"Space exploration does not come cheap", NewScientist, Issue 2620, p. 5, 8 September 2007

building aeroshells for entry into non-terrestrial atmospheres. Engineers had gained much experience in TPS design for Earth reentry from the late 1950s onwards. The USA and the USSR both developed reentry technologies for intercontinental ballistic missiles. The USSR also claimed a "first" in the space race on April 12 of 1961 when cosmonaut Yuri Gagarin travelled into orbit, leaving the Earth's atmosphere, and successfully returned in a Vostok vehicle. As the desire to explore other planets became a reality, the challenge for the engineers was to apply these lessons of Earth reentry capsule design to new atmospheric conditions, that is, the vehicles would be entering into a new set of gas compositions.

Venera 3, built by the USSR, became the first planetary probe to enter another planet's atmosphere, that of Venus, on 16 November 1965. This capsule crash landed on the surface, becoming the first human-made device on another planet. Its successor, Venera 4, successfully entered and landed on the surface of Venus on October 18, 1967. The USSR also claimed another first with exploration of Mars: Mars 2 survived entry into the Martian atmosphere on 27 November 1961 before crash landing on the surface of Mars, becoming the first human-made object on Mars. Since that time there have been other entry probes sent to both Venus and Mars. The Galileo probe began its descent into the Jovian atmosphere on 7 December 1995. This atmospheric entry into Jupiter at 50 km/s is credited with being the most severe for any human-made aeroshell. We turn our attention now to the recent exploration of Titan, Saturn's largest moon because entry into its atmosphere motivated some of the developments of this thesis.

Titan is the only moon in the Solar System with a substantial atmosphere. This thick nitrogen atmosphere, with small amounts of methane and argon, provides much of the intrigue surrounding Titan. Lebreton et al. [1] state that the origin of the methane in the atmosphere is one of Titan's great mysteries. Another motivation for the scientific study of Titan is that its cold atmosphere (relative to Earth's) provides a planetary-sized laboratory representative of a primitive Earth atmosphere, before life began about 3.8 billion years ago (Owen et al. [2]).

The Huygens probe, sent to investigate Titan, was released from the Cassini orbiter on 25 December 2004 and completed a successful entry, descent and landing on 14 January 2005, impacting with a vertical speed of about 5 m/s [1]. From the time of atmospheric entry, the probe took 2.5 hours to reach the surface of Titan. The scientific objectives for the Huygens mission (detailed by Lebreton and Matson [3] and summarised later by Lebreton et al. [1]) were to: (1) determine atmospheric composition; (2) investigate energy sources for atmospheric chemistry; (3) study aerosol properties and cloud physics; (4) measure winds and global temperatures; (5) determine properties of the surface and infer internal structure; and (6) investigate the upper atmosphere and ionosphere. From the perspective of the vehicle design engineers, the entry heat shield succeeded in performing its intended purpose of payload protection [1]. The aeroshell used tiles made of an ablative material which could provide protection up to a heating load of 1.4 MW/m^2 (Clausen et al. [4]).

The vehicle designer requires a number of inputs in order to design an aeroshell: aerodynamic coefficients and from those, determine stability; surface temperature; heat transfer rate; integrated heat load; shear loads; pressure loads; and ablation rates (Gnoffo et al. [5]). Of these, heating rates and loads are probably the most critical factor and the most difficult to estimate correctly. In the next section, we focus on the heating problem associated with atmospheric-entry vehicles. The work in this thesis focuses on models and tools which contribute to towards providing an estimate of heat loads on aeroshells as part of the aerothermal analysis.

1.2 Atmospheric-entry vehicles: the heating problem

During atmospheric-entry manoeuvres, aeroshell spacecraft experience high thermal loads due to the shock-heated gases around the vehicle. The heat transfer to the vehicle surface comes from frictional convective heating, catalytic effects, and, in some cases, radiative heating. The convective heating is a result of particle collisions and interactions with the vehicle surface. The convective heating scales with the nose radius, R, as $1/\sqrt{R}$; as the nose radius decreases, the heating becomes more severe. Hence there is a tendency towards blunted vehicles (larger radius), particularly for those vehicles subject to convective loads only. The radiative heating is produced by excited particles in the hot shock layer emitting radiation during particle deexcitation processes. The radiative heating scales with the thickness of the shock layer gas, or more simply, it is directly proportional to nose radius. Because of the different ways in which the heat transfer scales, there is a conflict between the requirements on nose radius to minimise heating from the convective or radiative modes. The relative dominance of one component of heat transfer over another varies subject to entry trajectory, entry speed, vehicle configuration and the atmospheric composition. For example, the Galileo probe, entering Jupiter's atmosphere with a relative speed of about 50 km/s, was designed based on an estimated peak heating rate 300 MW/m^2 (Gnoffo [6]) of which radiation was the dominant mode of heat transfer (Anderson Jr. [7]). Gnoffo [6] has collated data on peak heating for various atmospheric-entry vehicles. This data is displayed in Figure 1.1, taken from Gnoffo's review article [6], and distinguishes vehicles whose peak heating was from a purely convective mode with those subject to combined convective and radiative heating.

One of the early stages of vehicle design is the quantification of the aerothermal environment based on a proposed configuration and entry trajectory. The quantities of aerothermal analysis such as surface temperature, peak heating, integrated heat load, shear loads, pressure loads and ablation rates are used in the sizing and selection of the thermal protection system (TPS) (Gnoffo et al. [5]). The simplest means to estimate heating inputs for the TPS design would be to perform a worst-case scenario of heat load by assuming that all of the incoming gas energy (kinetic and internal) captured in the shock layer is transmitted as heat to the vehicle surface. However, this gross oversimplification of the problem would lead to vastly oversized heat shields. Unfortunately, there is little room for safety factors and conservative design of heat shields because a conservative design would require so much mass that there would be no accommodation of any scientific payload, which is the reason for a mission in the first place.

To expand on this point about the importance of heating estimates and their influence on probe design, consider two examples: the Huygens probe and the Galileo probe. The Huygens



Figure 1.1: Peak heating estimates (non-ablative) for various atmospheric-entry vehicles. *Source: Figure 2 from Gnoffo* (1999) [6]

descent probe had a total mass of about 318 kg, of which 79 kg was dedicated to the heat shield mass [4]. Thus, approximately 25% of the total probe mass was made up of the heat shield. For the Galileo probe the heat shield mass component is even larger; at a total mass of 339 kg and a heat shield mass of 152 kg, some 45% of the probe mass is accounted for by the heat shield. These figures, 25% for Huygens and 45% for Galileo, indicate that the design of a heat shield is not a trivial part of the total probe design. They also serve to demonstrate how a "conservative design" of heat shield thickness is out of the question. Green and Davy [8] describe this problem of optimal design in relation to the Galileo probe:

The heat-shield mass requirement is so large that a heat-shield design based on a conservative safety margin, although desirable, is not possible, except at the expense of other subsystems, because the total probe mass is constrained by launch requirement limits. Hence, an accurate heat-shield design is crucial to the success of the mission.

The safety margin, a safety factor of 2, for the Galileo probe was not as conservative as designers would have liked; the probe came close to burning up on entry into Jupiter's atmosphere.

Given the mass constraints in the design of an atmospheric-entry probe, there is strong motivation for an optimal heat shield design: thick enough to protect the payload during descent, not so thick as to take up all of the probe mass in heat shield. An optimal heat shield design relies on accurate estimates for the heating rates and heating loads during atmospheric entry. This leads directly to the motivation for this thesis: a contribution to the modelling of high-temperature gas dynamics, as found in the flow fields around aeroshells, will aid in the

provision of accurate estimates for heating loads on atmospheric-entry vehicles.

There has been great progress in aerothermal analysis over the last 50 years — a number of successful planetary probe entry missions are testament to that — but there are still outstanding problems in the analysis of heat transfer for atmospheric-entry vehicles. Giordano [9] laments the fact that our poor heating estimates are hindering our heat shield design efforts:

Notwithstanding our strenuous efforts, there is a feeling of dissatisfaction among (at least some of) us because, let us face it, the error margins of our thermal-load predictions are too large; and that adds on top of other uncertainties, such as those related to the atmosphere composition, for example. Ultimately, still today the design of thermal-protection shields relies mainly on extensive, and expensive, wind-tunnel testing, last-minute fixes, and safety factors based on the designer's experience. Clearly, this approach constrains the sizing of the shield to compromise with the burden of ample safety margins that penalize payload mass; it is also not viable for missions with extreme (re)entry speeds because the payload mass may turn out to be negative.

The present discussion has brought us to the point where we may make two conclusions. First, the heat shield can be a significant component of the total mass of an atmospheric-entry probe and as such is worthy of some detailed attention in terms of sizing and design. Second, providing an optimal design for the heat shield hinges on reliable estimates of heat transfer — these are not universally available with present methodologies. We turn our attention now to look at the various methods available for the estimation of heat transfer on the forebody of atmospheric-entry vehicles, with a view to identifying areas where improvement may be made.

The methods available to analyse heat loads fall into three classes: (1) analytical techniques; (2) experimental techniques; and (3) computational techniques. Currently, the building of an atmospheric-entry vehicle will employ all three techniques. The quick, easy-to-employ analytical techniques are used in the preliminary design stages. As the design progresses, experimental techniques using subscale models and computational techniques are combined to give more detailed analyses.

1.2.1 Analytical techniques

The analytical techniques used are often (a) derived from detailed theory with simplifying assumptions such as simplified geometry or idealised gas behaviour; and/or (b) empirical correlations from experimental or computational data. As an example, the Fay and Riddell [10] correlation can be used to estimate convective heat transfer at the stagnation point of a blunt body in chemically reacting air. The Fay and Riddell results are derived using a combination of simplifying theory and correlation. Fay and Riddell performed numeric computations using the boundary layer equations applied to the stagnation region of spherical and cylindrical geometries. Thus they used simplified geometries (spheres and cylinders) and based the governing model on the boundary layer equations which are a simplification of the continuum

Navier-Stokes equations. The calculations were performed for a number of conditions and the results were used as the basis for correlations of stagnation point convective heat transfer for an equilibrium boundary layer and reacting boundary layer (both fully catalytic and non-catalytic).

A second example of an analytical method is the stagnation point radiative heating correlations of Tauber and Sutton [11]. Based on a number of detailed numeric computations, the Tauber and Sutton correlations provide results for Earth and Mars entries.

1.2.2 Experimental techniques

The results of experimental data have been an integral part of the aerodynamic design process since the Wright flyer. Experiments provide data where theoretical treatment is too complex or in some cases nonexistent. There are two classes of experiment that may be considered: ground-based tests and flight tests.

Hypersonic flow is difficult to reproduce in the laboratory largely due to the huge energy requirements necessary to accelerate the gas to the requisite speeds. As a result, a number of different types of facilities are used to replicate various aspects of hypersonic flow. Bertin and Cummings [12] identify five classes of facilities to which I add a sixth class (based on my local bias):

- 1. conventional wind tunnels
- 2. shock-heated wind tunnels
- 3. shock tubes/tunnels,
- 4. arc-heated facilities,
- 5. ballistic, free-flight ranges and
- 6. expansion tubes/tunnels.

In ground-based facilities, a number of flow parameters between the experimental model and flight vehicle may be matched such as Mach number, Reynolds number, binary scaling parameter and flow total enthalpy. The problem is that it is almost impossible to match all parameters at once, giving complete similitude. Bushnell [13] notes that major disagreement between wind tunnel testing and real flight of the Space Shuttle was due to a reacting gas effect. At the early stage of reentry, dissociating gas in the shocked flow caused a pitching moment that required twice the body flap deflection to stabilise as compared to predictions from the wind tunnel data (Griffith et al. [14]). The wind tunnel data, in this instance, had not been able to produce the correct flow chemistry in order to observe this effect.

There are some other inherent problems with ground-based testing. The finite boundary of the test sections and the influence of stings and model mounts lead to incorrect flow boundary conditions. In impulse facilities, the available test time may not be sufficient for steady flow over the model. An additional problem with extrapolating ground-based testing to flight lies with the nonequilibrium test flow produced by shock tunnels and expansion tunnels.

Flight tests are a very expensive means of experimental measurement of the heating loads. They are however, as Bertin and Cummings [12] note, "critical to our understanding of the hypersonic aerothermodynamic environment because they provide data that cannot be obtained elsewhere." Flight tests avoid many of the scaling issues and all of the edge effects of ground-based tests. However flight tests suffer from poorly defined test conditions (which can only be inferred), a lack of repeatability, and extreme expense.

The flight test data that addresses forebody heating rates is relatively scarce. For Earth entry, Project Fire (Cornette [15]) of the 1960s still provides the best data for total and radiative heat transfer to an Apollo-like blunt body. Also, during the testing phase of the Apollo program, Apollo 4 and Apollo 6 were flown to gather experimental data on surface heating rates [16]. The Apollo 6 flight suffered from a malfunction of the radiometer and thus no measurements on radiative heating were made. An important conclusion from the Apollo 4 flight is that maximum heating would have occurred when the flow was in chemical equilibrium. Measurements were made of surface regression on the Galileo probe (Milos [17]), and the Pioneer Venus probes contained thermocouples in the heat shield to give some indication about heat shield performance (Pitts and Wakefield [18]). The Mars Pathfinder heat shield also contained instrumentation to measure temperatures during entry (Milos et al. [19]).

1.2.3 Computational techniques

Computational techniques aim to solve a complete set equations which describe the pertinent flow physics. Compared to experimental testing, computational analyses are inexpensive and provide more detailed information about the flow field as only certain quantities are measurable by experiment. Computational analyses are limited in a number of ways: by the validity of a certain model for the flow of interest; by the computational effort required to find a solution (grid resolution issues); and by numerical issues (for example, truncation error).

Presently, the state-of-the-art analysis techniques of the aerothermodynamic heating problem combine experimental testing and computational modelling. The computational modelling is used as an aid in the development of experimental conditions and interpretation of results. In a somewhat co-dependent manner, the results of experimental testing are used as a calibration input for computational models.

Ultimately, computational modelling will be the primary means of flow analysis with experimentation in a support role, though it is hard to say when this will occur. Historically, predictions have been wrong. In 1975, Chapman et al. [20] wrote about computers beginning to supplant wind tunnels within the next decade. However, more than 20 years later, in 1999, Gnoffo et al. [5] still identified a need for "new high-fidelity aerothermodynamic algorithms and implementation strategies" that could be used earlier in the design process of entry vehicles. Finally, after the Space Shuttle Columbia disaster of 2003, two critical "returnto-flight" issues related to the aerothermodynamic environment were identified (Bertin and Cummings [12]). These issues were studied by extensive wind tunnel testing and not exclusively by computational techniques. The point is that the computer has not supplanted the wind tunnel in all areas yet.

On a positive note for the use of computational methods, Anderson Jr. [7] identifies the design of the Galileo probe heat shield as the "first" design having relied on state-of-the-art flow field calculations. Part of the reason for a reliance on computational methods is that, at an entry speed of 50 km/s, it was almost impossible to perform experiments. During the 1970s and early 1980s, Moss' [21] viscous shock layer technique was extended and applied to designs of the Galileo forebody (Green and Davy [8], Moss and Simmonds [8, 22]). The next section gives more detail about the computational approach for aerothermodynamic analysis.

1.3 Computational approach to the blunt body problem

In this section, a brief discussion of the computational approach to the blunt body problem is presented. A detailed review is provided later in Chapter 2. This brief discussion is used to set the context for introducing the aims of this thesis.

In broad terms, a computational approach to the blunt body analysis involves the numerical solution of a governing set of equations. The governing set of equations should try to include all of the physics which is pertinent to the problem. Some examples of governing equation sets are the Boltzmann equations and the Navier-Stokes equations.

In choosing a modelling paradigm, there are often certain trade-offs. If one chooses a detailed physical model, then there is a price to pay — a difficult implementation and computational expense. Conversely, a quick, easy-to-implement model may not come anywhere close to representing the reality of the situation. As engineers, the challenge is to develop and use models that are efficient and appropriate for the task. Hofstadter [23] provides a good example of how various levels of modelling can be "sealed off"² from one another (p.305 of his text):

... one does not have to know all about quarks to understand many things about the particles which they compose. Thus, a nuclear physicist can proceed with theories of nuclei that are based on protons and neutrons, and ignore quark theories and their rivals. The nuclear physicist has a *chunked* picture of protons and neutrons — a description derived from lower-level theories but which does not require understanding the lower-level theories. Likewise, an atomic physicist has a chunked picture of an atomic nucleus derived from nuclear theory. Then a chemist has a chunked picture of the electrons and their orbits, and builds theories of small molecules, theories which can be taken over in a chunked way by the molecular biologist, who has an intuition for how small molecules hang together, but whose technical expertise is in the field of extremely large molecules and how they interact. Then the cell biologist has a chunked picture of the units which the molecular biologist pores over, and tries to use them to account for the ways that cells interact. The point is clear. Each level is, in some sense, "sealed off" from the levels below it.

²Hofstadter actually attributes the use of the phrase "sealed off" to H. A. Simons (see the chapter "The Architecture of Complexity" in Simons, H. A. (1969), *The Sciences of the Artificial*, Cambridge, Mass., M.I.T. Press)

However, Hofstadter goes on to comment that "there is always some leakage between hierarchical levels of science." In the work of this thesis, our attention will be restricted to the use of the continuum Navier-Stokes description of compressible viscous fluid flow. The model contains "leakage" from other levels of abstraction when the treatment of thermochemical nonequilibrium and radiation is introduced. In terms of aerothermodynamic analysis, the peak heating occurs in regions where the Navier-Stokes equations are applicable, and so our attention is focused in this regime.

Figure 1.2 shows the components for a continuum-based solver for the aerothermodynamic heating problem. The levels indicate a certain hierarchy in the modelling with each successive level dependent on inputs from lower levels. For example, the treatment of chemical nonequilibrium takes its input from the flow solver. Similarly, a radiation transport calculation requires data from a nonequilibrium flow field computed by the lower levels. Therefore, the levels also suggest a natural progression in model development: from flow solver, to treatment of thermochemical nonequilibrium, to radiation modelling and surface effects. Of course, all of these physical effects interplay with one another and need to be coupled appropriately in the modelling exercise. The analysis of the aerothermal environment for a blunt body comes from the sum total of all components used in a coordinated manner.



Figure 1.2: Modelling components for a continuum-based aerothermal analysis for flow about an atmospheric-entry vehicle at hypersonic speeds

Some preliminary work in this project began with the radiation modelling problem. The radiating flow about a sphere in equilibrium air was computed in a fully-coupled manner as a proof-of-concept for the project work (Gollan et al. [24]). However, we soon realised that it is

important to correctly account for thermochemical nonequilibrium effects before tackling the radiation problem, especially for missions to Titan where the most severe radiative heating is in the nonequilibrium regime. Therefore, in this thesis, the work has concentrated on the second tier from the bottom of Figure 1.2 — the modelling of thermochemical nonequilibrium. The specific aims and contributions of the thesis are discussed in the following section.

1.4 Thesis aims

The major aim of this thesis is the development and implementation of models to treat the thermochemical nonequilibrium nature of high-temperature gas dynamic flows. The development of this modelling has two direct benefits. The immediate benefit is the application of this work to the computation of nonequilibrium gas flows in expansion tube facilities with a view to better characterisation of the free-stream flow. The longer term benefit is that these models provide a foundation for future work on radiating flow fields and the inclusion of vehicle surface effects.

The specific aims of the thesis are:

- 1. to implement a model for the treatment of gas flows in chemical nonequilibrium,
- 2. to implement a model for the treatment of gas flows in thermal nonequilibrium,
- 3. to implement a model that treats the coupling between chemical and thermal nonequilibrium and
- 4. to use the models of high-temperature gas dynamics to simulate expansion tube operation.

There has been a long-standing concern in the aerospace community about the usefulness of data obtained in impulse facilities for CFD validation. To directly quote Park [25] when referring to shock tunnels and arc-jet wind tunnels:

..., because of uncertainties about the thermochemical state of the flows produced, the data obtained in those tunnels cannot be used presently for the purpose of CFD validation without certain amount of caveats. Characterization of the flows in those tunnels must be carried out to a much greater extent than has been before the data can be considered sufficiently reliable for CFD validation.

It is hoped that one of the contributions of this work is to address this concern of flow field characterisation in impulse facilities. Park goes on to recommend the use of free flight data in which he includes the use of ballistic range data. In this thesis, a careful attempt has been made to use ballistic range data exclusively in the course of validation.³ In this way, the bootstrapping problem of CFD validation against impulse facility data, which in turn requires computation to correctly characterise, is avoided.

³The one exception to this is the validation work using shock tube data of ignition delay in hydrogen/air mixtures. However, shock tube data for the purposes of chemical kinetics is a mature technology. Park's statement refers more to blunt body work in the high-temperature effects regime.

1.5 Outline

- **Chapter 2** provides a discussion about the blunt body flow problem. The governing equations for hypersonic flow over a blunt body are presented and the associated high-temperature physical phenomena are described. The bulk of the chapter serves as a review of computational modelling techniques for the treatment of the blunt body problem. The review sets the context for the computational modelling work presented later in the thesis, namely, Chapters 4 and 5.
- **Chapter 3** introduces the flow solver, mbcns, which provides a basis for the work in this thesis. The development of the base flow solver was not part of this thesis work and was provided "as is" for this project. The remainder of Chapter 3 is dedicated to work done as part of this thesis: verification and validation of the flow solver. The flow solver is verified using the Method of Manufactured Solutions (for purely supersonic flow) and the Method of Exact Solutions (for reacting flow). A validation case of shock detachment in noble gases is also presented.
- **Chapter 4** presents the work on modelling reacting gases in thermal equilibrium. First the thermodynamics of a mixture of thermally perfect gases is presented. Then the formulation and solution methodology to the chemical kinetics problem are given. A novel mass-conserving formulation is also presented. The implementation is then verified on two test problems: a simple hydrogen-iodine reaction and the chemical relaxation of air behind a normal shock. The validation of the model is demonstrated by comparison to two experiments: ignition delay of hydrogen-air mixtures; and ballistic-range experiments of spheres fired into air. The final part of Chapter 4 presents the modelling of species diffusion in a mixture of thermally perfect gases.
- **Chapter 5** describes the modelling of general thermochemical nonequilibrium, thus it treats the thermodynamics of the gas mixture; the energy exchange mechanisms and the computation of their rates; and the influence of nonequilibrium thermal states on chemistry and vice versa. Verification of the implementation is demonstrated by comparison to previously reported calculations of relaxing flows behind shocks and the flow of nitrogen over a cylinder.
- **Chapter 6** demonstrates the application of the thermochemical nonequilibrium modelling to computations of expansion tube operation. There are two calculations presented: one for an expansion tube in normal operation mode; and the other of an expansion tube operated in nonreflected shock tube mode.
- **Chapter 7** concludes the discussion with a summary of the work and contributions, along with recommendations for future directions.

Background for Aeroshell Modelling

You would think that it is a horrible way to enter, you really should have a nice point.

Caldwell Johnson (senior design engineer)

In the above quote, Caldwell Johnson, a design engineer for the Apollo program, is referring to the fact that a blunt body is a better configuration for reentry compared to a vehicle with sharp leading edges. This highlights the change in thinking as engineers began to tackle the hypersonic blunt body problem in earnest in the mid-1950s. Allen and Eggers [26] first demonstrated the benefits of a blunt-nosed entry configuration in a report on the aerodynamic heating of ballistic missiles. Prior to this, aerodynamic design for hypersonic speeds was treated as an extension of supersonic aerodynamics: sharp leading edges produced weaker shocks and thus lower drag. However, as the Mach number increases to the hypersonic regime, the aerodynamic heating increases also. It increases to such an extent that heating becomes a major concern as was noted in Chapter 1. As Anderson Jr. [7] comments (on p.167 of his text), "if a hypersonic vehicle in flight does employ a sharp leading edge, nature will soon blunt it by melting away the surface via intense aerodynamic heating." In order to model this intense aerodynamic heating, a number of important physical phenomena such as thermochemical nonequilibrium and gaseous radiation need to be considered.

In this chapter, the physics of hypersonic flows is discussed in the context of atmosphericentry vehicles. A set of governing equations which includes the physics necessary for the hypersonic blunt body problem is presented in Section 2.1. Next a review of the modelling for treating the blunt body flow problem is presented. The review of models and techniques of solution is divided into sections according to various flow physics phenomena. The purpose of this chapter is set the context and provide the necessary background for the model development work that is discussed in Chapters 4 and 5.

2.1 Physics of atmospheric-entry flows

Figure 2.1 depicts a blunt body flow and includes some of the pertinent physical effects. This section presents the governing equations that describe the high-temperature flow over a blunt body travelling at hypersonic speeds. We will return to some of the flow features identified in Figure 2.1 as the appropriate terms in the governing equations are described. In this section,

and the thesis as a whole, our attention is restricted to the continuum regime; this is the region where intense aerodynamic heating prevails. At rarefied conditions (free molecular flow) — the particle collisions are so few that thermal and mechanical equilibrium are not attained — the negligible aerodynamic heating is not of concern for the TPS designer. Instead, analysis of the rarefied part of the descent trajectory is often focussed on the aerodynamics of the entry vehicle.



Figure 2.1: Schematic of blunt body flow at hypersonic speeds

The high-temperature flow at hypersonic speeds can be described by a set of conservation equations. The conservation equations which appear below are applicable in the continuum regime. These equations are taken from Lee [27] and Gnoffo et al. [28] (with some changes in notation¹). There is one significant change from Lee's set of equations: a conservation of vibrational energy equation has been written for each vibrational degree of freedom, instead of one lumped vibrational energy conservation equation. In the case of a collection of diatomic molecules, there is one vibrational energy conservation equation for each of the molecules. When more complex molecules are present, with multiple degrees of freedom in vibration, it is possible to write multiple vibrational energy conservation equations. For example CO_2 , with

¹I prefer Gibbs notation [29] to the Cartesian tensor notation as used by Lee and Gnoffo et al. Bird, Stewart and Lightfoot [30] give a good discussion providing arguments for and against each of the notation systems in §A.9 of their text.
three characteristic vibrational temperatures, would require three vibrational energy conservation equations. Also note, this equation set does not have an equation for electron/electronic energy; the assumption is that this mode is not appreciably excited for the flows of present interest. This assumption will need to be revised when this work is extended for radiating flows.

Conservation of mass:

$$\frac{\partial}{\partial t}\rho + \nabla \cdot \rho \mathbf{u} = 0 \tag{2.1}$$

Conservation of species mass:

$$\frac{\partial}{\partial t}\rho_i + \nabla \cdot \rho_i \mathbf{u} = \underbrace{-\left(\nabla \cdot \mathbf{J}_i\right)}_{1} + \underbrace{\dot{\omega}_i}_{2}$$
(2.2)

Conservation of momentum:

$$\frac{\partial}{\partial t}\rho \mathbf{u} + \nabla \cdot \rho \mathbf{u} \mathbf{u} = -\nabla p - \nabla \cdot \left\{ -\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^{\dagger}) + \frac{2}{3}\mu (\nabla \cdot \mathbf{u})\delta \right\}$$
(2.3)

Conservation of total energy:

$$\frac{\partial}{\partial t}\rho E + \nabla \cdot (e + \frac{p}{\rho})\mathbf{u} = \nabla \cdot [\underbrace{k\nabla T}_{3} + \underbrace{\sum_{s=1}^{N_{v}} k_{v,s} \nabla T_{v,s}}_{4}] + \underbrace{\nabla \cdot \left[\sum_{i=1}^{N_{s}} h_{i}\mathbf{J}_{i}\right]}_{5} - \left(\nabla \cdot \left[\left\{-\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^{\dagger}) + \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\delta\right\} \cdot \mathbf{u}\right]\right) - \underbrace{Q_{\text{rad}}}_{6} \quad (2.4)$$

Conservation of vibrational energy:

$$\frac{\partial}{\partial t}\rho_i e_{v,i} + \nabla \cdot \rho_i e_{v,i} \mathbf{u} = \nabla \cdot [k_{v,i} \nabla T_{v,i}] - \underbrace{\nabla \cdot e_{v,i} \mathbf{J}_i}_{7} + \underbrace{Q_{T-V_i}}_{8} + \underbrace{Q_{V-V_i}}_{9} + \underbrace{Q_{\text{Chem}-V_i}}_{10} - \underbrace{Q_{\text{rad}_i}}_{11}$$
(2.5)

The first item of interest in Figure 2.1 is the detached bow shock which is created as the blunt body drives into the atmospheric gases at speeds in excess of the local speed of sound. In the shock layer behind the bow shock, the large amounts of kinetic energy of the blunt body are dissipated into the surrounding shock layer gases. This gives rise to a number of high-temperature physical effects: chemical reactions occur, dissociation and ionisation; the gas exhibits thermal nonequilibrium as some internal energy modes lag others during the collisional exchange of energy processes; and, at high enough temperatures, the gaseous emission of radiation becomes significant. Thus a set of conservation equations are written which account for these effects.

Equation 2.1 is the total mass conservation equation, also known as the continuity equation, while Equation 2.2 expands to N_s species conservation equations, where N_s is the number of species in the gas mixture. The production or loss of various species is modelled by term (2), $\dot{\omega}_i$, in the species conservation equations: this models the effect of chemical nonequilibrium

with finite-rate reactions. A large component of Chapter 4 is devoted to the modelling of the chemical nonequilibrium effect. Term (1) in Equation 2.2 describes the molecular diffusion of species in the flow due to gradients in concentration. The exact form of the diffusion flux, J_i , is dependent on the choice of diffusion model. The effect of species diffusion is important in the boundary layer of the vehicle flow where surface catalysis can create substantial gradients in the species concentrations. In Section 4.6, the modelling of the diffusion term is discussed.

The conservation of momentum is given by Equation 2.3. This equation applies to the mixture momentum which is based on the mass-averaged velocity of the component species. In the Cartesian coordinate system, Equation 2.3 expands into three equations, the momenta in the x, y and z directions.

Equation 2.4 is the equation for the total energy conservation. There are some terms in this equation worth noting in this multi-temperature formulation: term (3) represents the conduction of energy in translational/rotational energy modes, which are described by one temperature, T; the conduction of energy in vibrational energy modes are given by term (4); term (5) models the transport of energy bound in the species enthalpies as they diffuse in the mixture; and term (6) is a source term which accounts for the effect of radiative energy transfer.

There is one vibrational energy conservation equation for each vibrational degree of freedom in the gas mixture. Thus Equation 2.5 splits into the N_v conservation equations: one for each vibrational degree of freedom. As an example, for a 5-species model of chemically reacting air, there are three vibrational energy conservation equations, that is, one each for molecular oxygen, molecular nitrogen and nitric oxide. Term (7) in the vibrational energy conservation equation accounts for the movement of vibrational energy as the molecular species diffuse. The vibrational energy conservation equation also includes terms to model the exchange of vibrational energy with other energy modes: term (8) models the exchange of vibrational energy with the translational mode; term (9) accounts for exchange of energy between the various vibrational modes; term (10) describes how the average vibrational energy is changed as chemical reactions proceed; and the influence of molecular band radiation which represents an energy source or sink is given by term (11). The modelling related to the effect vibrational nonequilibrium is the subject of Chapter 5.

2.2 Modelling of atmospheric-entry flows

The equations presented in the previous section are a governing set of equations applicable to the high-temperature flow about atmospheric-entry vehicles when the flow is in the continuum regime. In this section, the development of computational techniques for solving this set (or similar sets) of equations is discussed. This review concentrates on the techniques that are most closely related to the work in this thesis.

2.2.1 Blunt body flow modelling

This discussion on the historical development of solution methods for the blunt body flow problem is brief and aims to highlight the major development steps towards the finite-volume method. This bias towards the finite-volume method is because the remainder of this thesis work uses a finite-volume based flow solver. Also the finite-volume method for the Navier-Stokes equations is sufficiently general such that internal flows may also be treated by the same technique. This is important as the thesis work aims to develop models for high-temperature flows which will be equally applicable to blunt body flows and high-enthalpy impulse facilities. The viscous shock layer technique and coupled Euler/boundary layer equation methods are acknowledged as important techniques for computing blunt body flow, however they are restricted to this problem domain only.

The numerical computation of blunt body flows in supersonic streams can be traced back to the 1950s. One of the early stumbling blocks for a general solution to the blunt body problem was the mixed nature of the governing flow equations. The supersonic region of the flow field is hyperbolic while the subsonic flow is elliptic. The earliest methods, today called inverse methods, used an assumed shock shape and proceeded downstream to calculate the body which supports that assumed shock. An example of blunt body calculations using the inverse may be found in the work of van Dyke [31] — this article is still easily available in the archival literature, whereas the work of van Dyke's contemporaries is not.

There are several limitations of the inverse method. The use of an assumed shock shape means that an iterative technique is required to solve for the flow field of a prescribed body geometry. The inverse method also has problems with numerical stability that requires special care to treat (Marrone [32]). The method is also limited to inviscid flows.

Moretti and Abbett [33] avoided the problem of mixed equation types by solving the timedependent (unsteady) form of the Euler equations. This gave a set of equations that were everywhere hyperbolic (with respect to time) regardless of the flow region being supersonic or subsonic. In effect, Moretti and Abbett had transformed the problem to a time-dependent one where the steady flow solution was just the limit of the unsteady flow computation. This first calculation was also shock-fitting: the outer boundary of the flow domain tracked with the shock and jump conditions were used to calculate the flow inside the domain (across the shock). Additionally, the method solved the governing Euler equations using a finite-difference technique.

At this point in the development of solution techniques, the late 1960s/early 1970s, the computation of the steady-state flow field was very much the focus. A technique which allowed larger time steps and thus quicker convergence to a steady-state was the time splitting technique of MacCormack and Paullay [34]. The technique split the multidimensional finite difference operators into a sequence of one-dimensional operators. The sequence of direction-ally split operators can be shown to be more efficient than a multidimensional operator if one considers the Courant-Friedrichs-Lewy (CFL) condition for both cases; the condition for one-dimensional operators is always less restrictive (Rizzi and Inouye [35]). With the introduction of directional splitting, it was useful to think of small cells in the domain rather than a finite-difference grid of nodes and thus the finite-volume method was born. The first use of the term finite-volume method is often attributed to Rizzi and Inouye [35], yet Morton and Sonar [36] state that the main ideas of the method appear in the literature at least as early as the early

1960s. In any case, the work of MacCormack and Paullay is the beginning of the finite-volume method applied to the blunt body flow problem.

The finite-volume method offers some advantages over the finite-difference method. The finite-volume method is applied directly to the conservation form of the governing equations and so conservation is ensured. It is also more natural, when using the finite-volume method, to solve the equations in physical space. The advantage of using physical space is that complex coordinate mapping is avoided. Finally, the finite-volume method is computationally more efficient as mentioned previously.

The review here of blunt body modelling has drawn our attention to the finite-volume method as this is the basis of the flow solver used in this thesis work. The details of the flow solver, along with its verification and validation, are the subject of Chapter 3.

2.2.2 Thermochemical modelling

As outlined at the beginning of this chapter, one challenging aspect of hypersonic flows — and the aspect of focus in this thesis — is the correct accounting of high-temperature gas effects. The high-temperature effects are included by using an appropriate equation of state and accounting for exchanges in internal energy between the various forms, including chemical energy. The modelling of nonequilibrium phenomena in gases is extensive and extends some way back in the literature. The review in this section focuses on the inclusion of nonequilibrium modelling in the finite-volume technique.

The various models for gases are presented in order from the simple to more complex. Not surprisingly this order also corresponds to their first inclusion as part of blunt body calculations employing the finite-volume method. The more complex gas models usually provide a greater power of description and a broader range of applicability. The trade-offs to using the most general gas models are the increased complexity of implementation and a greater computational expense. Some judgement should be exercised to choose a gas model which captures just enough of the salient physics while still delivering a solution in a reasonable time. Figure 2.2, taken from the review article by Tirsky [37], shows the regions on a velocity-altitude map where various gas models are appropriate for a blunt body analysis. This map of the various regions is applicable to a Shuttle-sized vehicle.

Calorifically perfect gas

The calorifically perfect gas model describes a gas with constant specific heats (no change in internal energy storage with increases in temperature) and perfectly elastic collisions between molecules (which are assumed to occupy no appreciable volume). The second assumption about perfect behaviour is reasonable for the vast majority of flows pertaining to the blunt body flow problem (see p. 379 of Ref. [7]). The first assumption about constant specific heats does not hold, in general, for blunt body flows in terms of performing aerothermal analysis. For a given pressure, the assumption of constant specific heats is violated as temperature is increased. Figure 2.3 shows the change in the ratio of specific heats (isentropic exponent) as the temperature is increased for air in chemical equilibrium at a given pressure of 1 atmosphere. The case for



Figure 2.2: Regions on a velocity-altitude map where various physical and chemical processes are important for the trajectories of: (I) Space Shuttle, Buran vehicles, and (II) aeroassisted orbital transfer vehicles. *Redrawn based on Source: Tirsky* (1993) [37]

chemically reacting air is more complex, being a function of the mixture composition as well as the temperature. With increased temperature, vibrational and electronic excitation along with chemical reactions change the energy distributions among the particles, and the nature of energy storage is changed. Anderson Jr. [7] gives an example for air at a pressure of 1 atm: at 800 K the molecules begin to become vibrationally excited; by 2 000 K the oxygen molecules begin to dissociate; and by 4 000 K the nitrogen molecules begin to dissociate. From this example, the assumption of constant specific heats is questionable from 800 K onwards when some of the energy is first taken up in the vibrational modes in appreciable amounts. This situation is not peculiar to Earth entry: the calorifically perfect gas assumption is not valid for entry into other atmospheres such as those of Mars and Titan.

Sometimes the perfect gas assumption is extended to moderate temperatures, 1 000–2 000 K, by using an effective γ , the ratio of specific heats. This is often useful for ducted flows with heat release (scramjets) but not appropriate for the blunt body problem.



Figure 2.3: Depiction of how the ratio of specific heats varies with temperature for air in chemical equilibrium at a pressure of 1 atmosphere. The data were generated with version 2 of the CEA program [38].

Chemically reacting, thermally perfect gases

The next level of complexity of gas models for hypersonic flow is to treat the mixture of gaseous species as chemically reacting but treat each component species as thermally perfect. Figure 2.2 shows that a portion of the Shuttle trajectory passes though a region of chemical nonequilibrium; this emphasises the importance of modelling chemically reacting flows.

A thermally perfect gas is assumed to have all of its internal energy modes described by one common temperature, that is, the Boltzmann distributions for all internal modes are described by one temperature. The specific heats for the mixture are calculated as a function of the temperature and the composition. The details of this calculation are given in Section 4.1.

The first calculations of chemically reacting flow using the finite-volume method appear to be by Rizzi and Bailey [39] in 1975. Not long after, Reinhardt [40] used the method of Rizzi and Bailey to perform parallel calculations in three-dimensions on the Shuttle orbiter configuration. In these calculations, the calculation of chemical reactions was "split" from the species convection. The advantage of this operator-splitting are that potentially "stiff" chemical sources can be treated by the best numerical methods for that job and the fluid dynamic problem can be computed with the best algorithms for that purpose. The discussion presented later in Section 4.2.3 is about some of the available methods for treating stiffness problems of chemical kinetics.

Eberhardt and Brown [41] presented a general treatment of the hypersonic chemically reacting flow problem in 1987. Their algorithm used operator splitting: a first-order total variation diminishing scheme for the convection and a fourth-order Runge-Kutta scheme for the chemical source terms. Around this time, the late 1980s and early 1990s, a number of researchers began to demonstrate the inclusion of chemically reacting flows with various methods of flux calculation: with van Leer's [42] flux-vector splitting [43–50]; with Steger-Warming [51] splitting [44–50]; with Roe's [52] flux difference splitting [43–50,53,54]; with Osher's [55] scheme [56, 57]; and with Pullin's [58] equilibrium flux method [59]. It appears that Grossman and Cinnella [44] were among the first researchers to fully couple the fluid dynamics and chemistry problem as a means of avoiding stiffness. Their work in 1989 used an Euler-implicit update procedure [44], while their subsequent work in 1990 made use of implicit two-step Runge-Kutta integration [47].

It should also be mentioned that in the limit of fast reactions that rapidly come to equilibrium, an equilibrium gas assumption may be appropriate. When applying an equilibrium gas assumption, the chemical kinetic problem is ignored. The difficulty becomes one of finding the equilibrium gas state at every set of flow conditions in the computational domain. For specific gas compositions there may be curve fits available, for example, Srinivasan et al. [60] provide curve fits for air. Another option is to pre-compute a look-up table of thermodynamic properties for a specific gas composition in equilibrium at a certain density and energy (or any other two state variables). An older method to estimate the properties of an equilibrium gas relied on the use of Mollier diagrams (enthalpy plotted against entropy).

General thermochemical nonequilibrium

Tirsky identifies a region of nonequilibrium flow as indicated in Figure 2.2. In this work, we define thermochemical nonequilibrium as the regime where chemical and thermal modes of the gas are not in equilibrium, that is, the energy distributions of internal modes cannot be described by a single thermodynamic temperature. If we are interested in the combined radiative and convective heating problem in air (Earth reentry), and in particular, the peak heating, this regime of thermochemical nonequilibrium may not be so important. Anderson Jr. [61] notes that, in air, "the flight conditions that generate noticeable radiative heat-transfer rates are the same as those that generate equilibrium shock-layer conditions, namely, high velocities and low altitudes." However, this argument will not hold in general for other atmospheres, for example, Titan entry problems. For Titan, a proper accounting of thermochemical nonequilibrium is a necessary prerequisite for calculations of radiative transfer.

In addition to computing the effect of chemical reactions, a general model of thermochemical nonequilibrium includes the effect of finite-rate relaxation among the internal energy modes, that is, the energy exchange mechanisms. There is an implicit assumption in this treatment that the internal modes may be separated under the Born-Oppenheimer approximation.² When modelling a gas in thermochemical nonequilibrium, there is also a coupling effect between the chemistry and internal energy relaxation: thermal nonequilibrium affects the reaction rates,

²The Born-Oppenheimer approximation was presented in the paper by Born, R. and Oppenheimer, M., "Zur Quantentheorie der Moleküle", *Annalen der Physik, vol. 84, pp. 457–484,* 1941. The approximation is used to facilitate solutions to the Schrödinger equation by separating the motion of the electrons from the nuclear motion. For the aerothermodynamicist, a model of separable energy storage modes described by different temperatures makes the implicit assumption that the Born-Oppenheimer approximation is valid.

and dissociation and recombination affect the average energy in the various pools of internal energy.

The first work to include a general model of thermochemical nonequilibrium in a finitevolume method was that of Candler [62]. Candler gave a description of a multi-temperature formulation and presented calculations using a two-temperature model for hypersonic air flows: a temperature, T_{tr} , for the translational and rotational modes and a separate temperature for the vibrational and electronic modes, T_{ve} . Later Walters et al. [50] generalised the multi-temperature models for various flux schemes and included the work in a production code. Walpot [63] presented work in 2002 that included up-to-date physical modelling for the the various energy exchange processes.

Before concluding this section, it would be remiss of me to ignore the recent comments of Giordano [9] in relation to the use of the Born-Oppenheimer approximation. The Born-Oppenheimer approximation underpins multi-temperature modelling because the modelling implicitly relies on the fact that the various energy modes are separable. Giordano calls the use of the Born-Oppenheimer approximation into question and goes on to argue that there is no physical and rational basis to support a separation of energy modes in hypersonic flows. The repercussions are that heat flux estimates should be viewed with some suspicion. While I agree with Giordano's reasoning and share his concerns about the state of aerothermodynamics with its wildly varying heat predictions, the pragmatic part of me reconciles the use of a flawed multi-temperature model for heat transfer estimates as better than no estimate at all.

Non-Boltzmann gases

At certain conditions toward the more rarefied limit, the gas mixture is so far from equilibrium that a Boltzmann distribution of states, even separated into various temperatures, is a poor assumption. This nonequilibrium effect is captured naturally in rarefied gas simulations using the direct simulation Monte Carlo (DSMC) method. However, if we wish to use continuum solvers, then some attempt should be made to account for this. Candler et al. [64] performed detailed simulations of nitrogen dissociation in flow about a 10 cm sphere using a finite-volume method. Their work used ten conservation equations for the mass of nitrogen species in various vibrational states. They accounted for vibrational transitions of up to four quantum levels and for the rates of transitions they used either the model of Schwartz, Slawsky and Herzfeld [65] or the forced harmonic oscillator model of Adamovich et al. [66]. The work of Candler et al. concluded that there are indeed non-Boltzmann distributions present in the shock layer at low density conditions and that multiple-quantum transitions are an important mechanism for dissociation.

A further conclusion to draw is that this detailed state-to-state vibrational modelling is too computationally expensive for practical aerothermal analyses on present-day computers. Candler et al. needed to highly optimise the grid to reduce the computational burden. If we are striving towards computational aerothermodynamic analysis as part of the design process, then the modelling of non-Boltzmann gases on highly optimised grids presently seems too burdensome.

2.2.3 Radiating flows

As shown in Equations 2.4 and 2.5, the effect of radiative heat transfer appears as a source term in the energy equations. The radiative transfer equation, as presented by Anderson Jr. [7], is

$$\frac{dI_{\nu}}{ds} = \epsilon_{\nu} - \alpha_{\nu}I_{\nu}, \tag{2.6}$$

where ϵ_{ν} is the emissivity coefficient and α_{ν} is the absorptivity coefficient, both at a given frequency ν . The radiative transfer equation describes the change in radiant intensity I_{ν} with distance *s* due to emission and absorption. As explained by Anderson Jr. [7], the term dI_{ν}/ds has units of energy per second per unit solid angle per unit frequency per unit volume. Therefore, to calculate the change in energy of a cell volume due to radiation, one needs to integrate over all frequencies and solid angles. The result of this integration is shown here.

$$\nabla \mathbf{q}_{\mathbf{r}} = 4\pi\epsilon - \int_0^\infty \int_{4\pi} \alpha_\nu I_\nu d\omega d\nu.$$
(2.7)

This is the source term which appears in the conservation of energy equations, that is, $Q_{rad} = \nabla q_r$.

There are a number of limiting cases that make the above equation more tractable. The simplifying assumptions can be divided into two groups: those assumptions that simplify the spectral details, that is, the integration over frequency; and those that simplify the geometric details, that is, the integration of physical space. In the following sections, the various approaches used by researchers in the past are presented; the discussion is split into the approaches to the spectral modelling and the geometric modelling.

Radiative properties: spectral modelling

Spectral modelling refers to the issue of calculating the radiative properties (emissivity and absorptivity) for the gas at its given conditions. As Anderson Jr. [61] states:

... the question quite naturally arises as to how much spectral detail is required for engineering calculations of shock-layer radiative heat transfer.

In attempting to answer this question, a survey of the approaches used by other researchers is presented.

The grey gas approximation ascribes a single value for the absorption coefficient over all frequencies but is no longer used for any serious attempts of calculating radiative transfer about blunt body flows (Hartung [67]). It was first demonstrated by Hoshikazi and Wilson [68] that a grey gas model can be in significant error when calculating shock structure and heat transfer. Despite its shortcomings, Elbert and Cinnella [69] used the grey gas approximation when doing a full axisymmetric calculation of hypersonic flow fields. The authors acknowledge that a better treatment of the spectral detail is required for practical problems of engineering interest.

Multi-band or step models, where the absorption coefficient is constant over several ranges of frequency, have been used by Olstad [70]. Olstad used an eight-step model for radiating air and assumed local chemical and thermodynamic equilibrium. Another approximate model for radiative properties is the Planck-Rosseland-Gray (PRG) model of Sakai et al. [71]. In essence, the model uses three limiting cases of radiative transport: the Planck approximation where the gas is optically thin; the Rosseland approximation where the gas is optically thick; and the grey gas approximation for all cases in between. The details of this model are presented in Ref. [71]. Some calculations of the radiation behind a reflected shock wave in air with the PRG model have yielded good agreement with experiments (Sakai et al. [72]). The model has also been applied with some success to the calculation of flow in high enthalpy arc heaters (Sakai et al. [73]). The advantage of this model is its high computational efficiency while maintaining a level of accuracy desirable for practical reentry problems.

The Langley Optimized RAdiative Nonequilibrium (LORAN) code [67,74] has been developed as an efficient radiation transfer code for coupling to flow field solvers. The code takes temperatures and species concentrations as inputs from a flow field solver. It is able to handle flows in thermal and chemical nonequilibrium. In essence, LORAN is a modern multi-band model with thousands of wavelength points unlike the earlier generations with fewer than 100 points (Olstad [70]). This method can reproduce the results of a detailed line-by-line method to within a few percent [74]. The SPRADIAN code which is the work of Fujita and Abe [75] is also in this class of multi-band models.

The NEQAIR code by Park [76] uses a detailed line-by-line spectral model to calculate radiative properties for flows in chemical and thermal nonequilibrium. It can also treat flows that are in chemical equilibrium as these are just a limiting case of the more general nonequilibrium flow. The NEQAIR code is often used on a converged nonequilibrium flow field solution; this is known as an uncoupled approach. The use of NEQAIR becomes computationally prohibitive in a fully coupled radiating flow field calculation (Sakai et al. [72]). There is also a European code, PARADE, by Bottin [77] which computes radiative properties based on line-by-line modelling.

Radiative transfer: geometric approximations

The other aspect of computing the radiative source term is to calculate the radiative transfer through the gas of the blunt body shock layer. A number of geometric approximations are used to make the problem computationally tractable.

In terms of simplifying the geometric problem, the easiest model considers a transparent gas. The transparent gas assumption neglects self-absorption of the radiating gas element (Anderson Jr. [7]). By defining the optical thickness of a gas as

$$\tau_{\nu} = \int_0^s \alpha_{\nu}(x) dx \tag{2.8}$$

where the distance *s* is the path of interest, then the optical thickness is a measure of a the medium's ability to attenuate the radiation over that path (Oran and Boris [78]). The transparent gas assumption applies when $\tau_{\nu} \ll 1$. The geometric modelling problem is almost non-existent for a transparent gas because this model is tantamount to modelling heat sinks at each point in the flow field where radiation occurs.

Another geometric modelling technique is the tangent-slab approximation. In this model, the distance between the shock and the vehicle is treated as an infinite slab. Analytical methods can be used if the important radiation is considered to occur in the cross-shock layer direction only. This method can give good results near the stagnation region (Anderson Jr. [7]). A number of researchers [74,79,80] have used this model with reasonable success to calculate the radiative heat transfer to the stagnation point of a hypersonic vehicle. It is known that the tangent-slab model is quite erroneous away from the stagnation region (Elbert and Cinnella [69]).

A more complete approach to the geometric problem of radiation transfer is to integrate over all solid angles allowing for emission and absorption from all gas elements in the path. This kind of modelling takes account of the gas as a full participating medium and is the most detailed way of accounting for the actual physics of radiative transfer through gases. In Shah's thesis a three-dimensional technique was developed [81], which has come to be known as the Discrete Radiative Transfer Model. This has been applied to a sphere of radius 1.524 m in an axisymmetric version of the Discrete Radiative Transfer Model by Elbert and Cinnella [69]. Also, Karl [82] used this model when computing the radiating flow field of an argon plasma.

Hartung [67] used the Modified Differential Approach which is an example of a flux method to model three-dimensional radiative transport. The idea is to separate the angular dependence of intensity and the spatial dependence (Oran and Boris [78]). In this way, the governing integro-differential equations for radiative transfer can be reduced to a system of differential equations, hence the name Modified Differential Approach.

Calculations of radiating flow fields about aeroshells

The discussion up to this point of modelling radiating flows looked at the details of calculating the radiative properties and the radiation transport. Now we turn our attention to calculations of radiating flow fields which use a combination of the models and methods just discussed. We restrict our attention to calculations for air and the Titan atmosphere, and, in keeping with the theme thus far, the review focuses on calculations based on the finite-volume method.

Hartung et al. [83] used their modern multi-band model and the tangent-slab approximation to compute the radiative heat transfer based on the nonequilibrium flow field computed by the flow solver LAURA (Gnoffo [84]). The radiation calculation was applied as a postprocessing step to the nonequilibrium flow field calculation. In 1994, Hartung et al. [85] extended their work in air flows by loosely coupling the flow solver and radiation transport calculation: for nonequilibrium flows a radiation calculation was applied every 200 iterations of flow field calculation while for near equilibrium flows, only every 1 000–5 000 iterations. They concluded that the correct coupling of radiation and flow field calculation is important for nonequilibrium situations.

In 2001, Sakai and Sawada [86] presented calculations of radiating air flow which simulated a ballistic range experiment on 0.5 cm and 0.7 cm cylinders. The radiation transport calculation was fully coupled to the implicit flow solver scheme. The spectral detail was modelled with the PRG approximation [71] and the radiation transport was calculated using the tangent-slab approximation. The largest calculation of hypersonic radiating flow in air, to my knowledge,

is the work of Matsuyama et al. [87] in 2003. Their work extended that of Sakai and Sawada by including more sophisticated modelling for the details of radiating flow: a modern multi-band model with on the order of 10³ wavelength points was used for the spectral detail; and the transport was calculated with the tangent-slab approximation, as well 2D and 3D ray-tracing techniques. In order to perform a calculation of such complexity, the code was parallelised by dividing the wavelength range between various processors. In total, 128 processors of an SGI ORIGIN 2000 were used to perform the calculations. This example goes some way to demonstrating that fully-coupled radiating flow field calculations are not yet available as a quick calculation aid for design work.

In terms of entry into Titan, recent calculations have focused on a 3.75 m diameter, 70 degree sphere cone geometry as a proposed aerocapture configuration. In 2003, Olejniczak et al. [88] reported on calculations of a nonequilibrium flow field to which the radiation calculation was applied as a post-processing step. For the spectral modelling, both a modern multi-band code (LORAN [67]) and a detailed line-by-line code (NEQAIR96 [89]) code were used. In both cases, the radiation transport was approximated by using the tangent-slab approach and a correction for surface curvature was included by applying a reduction factor of 0.8. The authors acknowledged that the radiative heating estimate was conservative because of the uncoupled calculation. Nevertheless, they concluded that radiative heating is a significant design issue for a Titan aerocapture mission, with the peak radiative heating rate being up to five times larger than the peak convective heating rate. The authors also found that the radiation field was optically thin for all conditions of interest.

In 2005, Wright et al. [90] extended the analysis of Olejniczak et al. [88] by performing fully coupled radiation flow field calculations for the same proposed Titan aerocapture vehicle. Wright et al. made use of the fact that the radiation field was optically thin; they were able to fully couple the flow field and radiation calculation because the radiation transport problem was reduced to an emitting gas only. In an emitting gas only, no absorption is considered, and thus the radiation problem becomes one of volumetric heat sinks in the flow field calculation. The emissivity properties of the gas were calculated based on curve fits which were constructed from NEQAIR calculations. Only the CN red and CN violet bands were included in the calculation of radiative emission — previous analyses had shown that these bands dominate the radiation for this flow field. Wright et al. found that the fully coupled calculations gave a net radiative heating rate that was a factor of 2 reduction on the value given using the tangent-slab approximation. Also, in the stagnation region, the peak radiative heating was 25% less using the "emission only" model with a view factor calculation instead of the tangent-slab approximation. The authors recommended the use of their approach for optically thin gases, or even just the optically thin portion of a given spectrum, for other atmospheric-entry problems.

2.3 Summary

In this chapter, an introduction to the blunt body problem has been provided with focus on the pertinent high-temperature phenomena: chemical and thermal nonequilibrium, and radiating

flow. A review was provided on some of the methods and techniques available for analysing aeroshell flows. The selection of methods reviewed focused on those most relevant to the work in this thesis. Thus the development of the finite-volume method was discussed, along with its extension to gases in a state of nonequilibrium. Although the modelling of radiating flows is not treated directly in this thesis, the modelling work on thermochemical nonequilibrium flows is intended to provide a foundation for future work on radiating flows. Thus the review on radiating flows was provided to demonstrate how this thesis work can directly contribute towards the radiating flow problem.

Flow Solver

In this chapter, the flow solver used for the simulations presented in this thesis is described. It should be emphasised that the implementation of this flow solver was not part of this thesis work. The remainder of the chapter deals with verification and validation of the flow solver for the types of problems of interest in this thesis. The verification and validation exercises are the work of the author.

3.1 Description of the finite-volume flow solver

The flow solver mbcns [91] was provided as a base to which the modelling work in this thesis — the modelling of high temperature effects in compressible flows — has been added. The code, developed by Jacobs, began its life as a single block integrator of the compressible Navier-Stokes equations, CNS4U [92]. The code treats two-dimensional geometries: planar and axisymmetric. It was later extended to handle multiple blocks, and was renamed mbcns [91,93]¹. In its present incarnation, the "number-crunching" core of mbcns is written in a combination of C/C++, and the pre- and post-processing stages are handled by a suite of Python programs.

The finite-volume formulation and the associated numerical schemes are described in the report by Jacobs [92]. The code integrates the compressible Navier-Stokes equations in a time-accurate manner. An explicit predictor-corrector update is used to advance the solution in time. The time advancement algorithm in mbcns treats each piece of physics in a timestep-splitting (or operator-splitting) approach as advocated by Oran and Boris [78] (see Chapter 11 of their text). Thus the order of operations for a full multi-temperature reacting flow simulation applied over a small timestep, Δt , is:

- 1. compute gas transport due to inviscid flux
- 2. compute gas transport due to viscous flux
- 3. compute change of gas state due to chemical reactions
- 4. compute change of gas state due to thermal relaxation

For the inviscid transport of gas, the properties at the cell interfaces are reconstructed using a so-called piecewise parabolic reconstructor. This is employed for high-order reconstruction.

¹To be pedantic, its exact naming is MB_CNS but I more commonly use mbcns to refer to the code

For low-order reconstruction, the adjacent cell centre properties are taken as the interface values. Based on the flow properties at cell interfaces, the inviscid flux is calculated using a flux calculator. In mbcns there are five flux calculator options: 1) an approximate Riemann problem solver developed by Jacobs [94], 2) the advection upstream splitting method (AUSM) by Liou and Steffen Jr. [95], 3) the AUSMDV calculator by Wada and Liou [96], 4) the equilibrium flux method (EFM) by Macrossan [59], and 5) an adaptive calculator which uses EFM near shocks and AUSMDV elsewhere.

The viscous transport update is based on the calculation of viscous derivatives at the cell centres. The cell-centred derivatives are calculated as an average of the derivatives evaluated at the cell vertices. Those cell-vertex derivatives are calculated by application of Gauss' divergence theorem to convert a surface integral around a secondary volume to the derivative value within that volume, that is, at the vertex.

The remaining pieces of physics in the timestep-splitting algorithm are the subject of this thesis: the change of state due to chemical reactions is presented in Chapter 4; and the change of state due to thermal relaxation is the subject of Chapter 5.

Prior to the development work in this thesis, mbcns had gas models for a variety of gases of interest in hypersonic flows, such as, perfect gases, equilibrium gases (via a look-up table), nitrogen in vibrational equilibrium and some exotic gases for comparison to rarefied gas dynamics calculations. The work in this thesis has contributed the following gas models to the above list: a mixture of ideal gases, a mixture of thermally perfect gases and a mixture of gases with nonuniform internal energy excitement (a multi-temperature gas mixture).

3.2 Verification of the flow solver

As the flow solver, mbcns, is the foundation for the high-temperature modelling presented in this thesis, it was deemed a worthy exercise to verify and validate the code. The terms "verify" and "validate" take on the technical meanings used by Roache [97]. Roache cites Boehm and Blottner when he defines verification as "solving the equations right" and validation as "solving the right equations." In the context of this work, the code solves the set of partial differential equations given in Section 2.1. Verification is the act of testing that this claim is true in a rigorous manner: a check of the solution methodology by assessing the consistency of the order of accuracy as mesh discretisation tends to zero (this can include a temporal mesh). Validation, on the other hand, is the act of assessing if indeed the governing equations (partial differential equations) are appropriate for the problem of interest and how well those equations model the problem. Also in this section, the verification that is referred to is verification of the code. This is distinct from verification of a calculation as pointed out by Roache.

Two verification cases are presented. The first case uses the Method of Manufactured Solutions to generate an analytical solution for a purely supersonic flow field based on "manufactured" source terms. This case is used to demonstrate the formal order of spatial accuracy of the code without the complications of embedded shocks. The Method of Manufactured Solutions is not easily applied to test flows with embedded shocks, that is, the shock-capturing aspect of the numerical methods. For this reason, a second verification case, an analytical solution for an oblique detonation wave, is used to quantify the spatial accuracy when embedded shocks are present.

3.2.1 Method of Manufactured Solutions: Euler flow

The Method of Manufactured Solutions was first proposed by Steinberg and Roache [98]. The method involves choosing an analytical solution to continuum partial differential equations which are solved by the code in question. The analytical solution is then passed through the differential operators of the governing equations to generate analytical source terms. The idea is that with these source terms in place, the code should produce a numerical approximation to the original chosen analytical solution. Roache [99] advises that the solution should be non-trivial but analytical such that cross-derivative terms of the governing equations are tested. The numerical (discretised) solution may then be verified by comparison to the exact analytical solution. For a code which is behaving well, the error between the numerical and analytical solutions should diminish with increased grid resolution. Furthermore, it is possible to evaluate the order of the spatial accuracy by analysing the behaviour of successive grid refinements.

The Method of Manufactured Solutions is best demonstrated by an example. The example presented here was first used by Roy et al. [100] and is applied to mbcns to demonstrate verification. Roy et al. used the Method of Manufactured Solutions to evaluate the order of spatial accuracy for two finite-volume codes which solved the Euler and Navier-Stokes equations. Our attention will be restricted to their application of the method to the Euler equations.

Consider the Euler equations for two-dimensional inviscid flow in differential form:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} = f_m \qquad (3.1)$$

$$\frac{\partial (\rho u)}{\partial t} + \frac{\partial (\rho u^2 + p)}{\partial x} + \frac{\partial (\rho u v)}{\partial y} = f_x \qquad (3.2)$$

$$\frac{\partial (\rho v)}{\partial t} + \frac{\partial (\rho v u)}{\partial x} + \frac{\partial (\rho v^2 + p)}{\partial y} = f_y$$
(3.3)

$$\frac{\partial (\rho E)}{\partial t} + \frac{\partial (\rho u E + p u)}{\partial x} + \frac{\partial (\rho v E + p v)}{\partial y} = f_E$$
(3.4)

As part of the Method of Manufactured Solutions, an analytical solution is chosen as a function of sines and cosines

$$\rho(x,y) = \rho_0 + \rho_x \sin\left(\frac{a_{\rho x}\pi x}{L}\right) + \rho_y \cos\left(\frac{a_{\rho y}\pi y}{L}\right)$$
(3.5)

$$u(x,y) = u_0 + u_x \sin\left(\frac{a_{ux}\pi x}{L}\right) + u_y \cos\left(\frac{a_{uy}\pi y}{L}\right)$$
(3.6)

$$v(x,y) = v_0 + v_x \cos\left(\frac{a_{vx}\pi x}{L}\right) + v_y \sin\left(\frac{a_{vy}\pi y}{L}\right)$$
(3.7)

$$p(x,y) = p_0 + p_x \cos\left(\frac{a_{px}\pi x}{L}\right) + p_y \sin\left(\frac{a_{py}\pi y}{L}\right)$$
(3.8)

The particular values for the constants in Equations 3.5–3.8 appear in Table 3.1. The analytical solution based on the given constants is shown in Figure 3.1. The analytical solution is then

substituted into the Euler equations and the analytical source terms are generated. The generation of source terms is tedious and error-prone to do by hand thus a computer algebra system is recommended for this task.² Contour plots of the source terms are shown in Figure 3.2.

Equation, φ	ϕ_0	ϕ_x	ϕ_y	$a_{\phi x}$	a _{φy}
ρ (kg/m ²)	1.0	0.15	-0.1	1.0	0.5
u (m/s)	800.0	50.0	-30.0	1.5	0.6
v (m/s)	800.0	-75.0	40.0	0.5	2/3
p (Pa)	1.0×10^{5}	0.2×10^{5}	0.5×10^5	2.0	1.0

Table 3.1: Particular constants for the manufactured solution to the Euler equations

The numerical solution was computed on five grids of varying refinement as given in Table 3.2. The flow field for each of the simulations was initialised by the conditions given by the ϕ_0 column of Table 3.1 and extends over the domain

$$0 \le x/L \le 1$$
$$0 \le y/L \le 1.$$

The gas is modelled as a calorifically perfect gas with $\gamma = 1.4$ and R = 287.0 J/(kg K) which are the values for ideal air. Exact Dirichlet values given by the manufactured solution are specified at the west and south boundaries, while the north and east boundaries use an extrapolation boundary condition. The verification exercise was performed with high-order reconstruction for three of the flux calculators which are implemented in mbcns: AUSM, AUSMDV and EFM. The AUSM calculator was also used with low-order reconstruction to assess the effect of spatial reconstruction on the observed order of spatial accuracy. An example input file for the mbcns code which simulates this flow problem is given in Appendix A.1.

Table 3.2: Levels of grid refinement used for the numerical solution to the Manufactured problem

Grid	Cells (nx \times ny)
1	8 imes 8
2	16×16
3	32×32
4	64 imes 64
5	128 imes 128

²In this work, Maxima 5.11.0 released under the GNU Public License was used to compute the source terms and generate C code for inclusion in mbcns. This source is available from the author.



Figure 3.1: Contour plots of primitive variables for the analytical solution based on constants given in Table 3.1.

The transient behaviour of the L_2 error norm based on density for a typical set of numerical solutions is shown in Figure 3.3(a); this set used the AUSMDV flux calculator with high-order spatial reconstruction. The L_2 error norm, an indicator of global discretisation error, is computed using the numerical and analytical solutions and is given by

$$L_{2}\text{norm} = \left(\frac{\sum_{n=1}^{N} \left|\phi_{n} - \phi_{\text{exact}}\right|^{2}}{N}\right)^{1/2}.$$
(3.9)

. ...

As mentioned above, the norm was based on density for these comparisons ($\phi = \rho$). Figure 3.3(a) shows that the error decreases with time as the steady-state solution is approached. Also, for successive grid refinements, the L₂ error norm decreases as should be expected for finer grids. The computed global discretisation errors based on the L₂ error norm for all simulations are shown in Figure 3.3(b) as a function of cell width. The error values plotted in Figure 3.3(b) are taken at steady-state, which was the value at the end of the simulation at 5 ms. The error is seen to decrease with successive grid refinements, and the calculations with high-order reconstruction show a higher order of spatial error convergence than the low-order re-



Figure 3.2: Contour plots of the generated source terms based on constants given in Table 3.1.

construction. By fitting a curve of the form ax^b to the values for L₂ error shown in Figure 3.3(b), the observed order of spatial accuracy can be evaluated. The order of spatial accuracy is given by the exponent *b*. The observed orders of spatial accuracy for the various flux calculators and spatial reconstruction are given in Table 3.3.

The results for the observed order of spatial accuracy, shown in Table 3.3, indicate that the code, mbcns, is verified for supersonic Euler flow. The global discretisation error has been shown to decrease in size with increasing grid resolution in a self-consistent manner. Therefore, in the limit of cell widths of size zero, the numerical solution approaches the continuum analytical solution. Also, the low-order reconstruction has a lower order of spatial accuracy as would be expected. This further demonstrates the internal consistency in the code.

3.2.2 Method of Exact Solutions: Oblique detonation wave

In the purely supersonic flow computed in Section 3.2.1, the shock-capturing capability of the flow solver is not exercised. It is desirable to evaluate the order of spatial accuracy when the reconstruction limiters are employed, as is the case when the flow field contains embedded shocks. It is possible to use the Method of Manufactured Solutions to generate a smooth con-



Figure 3.3: Computed global discretisation error based on L_2 error norm for density: (a) transient convergence for the AUSMDV flux calculator with high-order reconstruction, (b) results of all simulations with error value taken at steady-state

Flux calculator / reconstruction	Observed order of accuracy	
AUSM / high-order	1.619	
AUSM / low-order	0.705	
EFM / high-order	1.651	
AUSMDV / high-order	1.619	

Table 3.3: Observed order of spatial accuracy based on the L₂ error norm

tinuum solution with rapid changes in property such that the solution mimics a shock-like structure [99]. However, an easier and more direct approach to test shock-capturing is to use an exact analytical solution for a flow with an embedded shock. There are several analytical solutions available in the literature for flows with embedded shocks: supersonic blunt body flows [31] and nonequilibrium flow over wedges and slender bodies [101–105]. The term "analytical", in this context, extends to cover solutions given by series expansions, ordinary differential equations or the method of characteristics. The idea is that numerical techniques can solve these solution types to a sufficient degree of accuracy to provide an "exact" reference for the discretised partial differential equation solution. In this section, an exact solution for an oblique detonation wave, by Powers and Stewart [106], is used for code verification purposes.

Powers and Stewart [106], in 1992, first computed the chemically reacting flow over a wedge with a single-step reaction kinetics. This approximate solution is representative of an oblique detonation wave: a shock-induced combustion phenomena. In the work by Powers and Stewart, two solutions were presented: a straight wedge supporting a curved shock and a curved wedge supporting a straight shock. Grismer and Powers [107], used the straight wedge, curved

shock solution to compare a numerical solution algorithm to the analytical solution. Grismer and Powers intent was to demonstrate the use of these analytical solutions to aid in code development. However, over a decade later, Powers and Aslam [108] noted that these solutions "have not been widely utilised in the decade since they appeared." In 2006, Powers and Aslam wrote a paper detailing how the curved wedge, straight shock solution could be used for code verification purposes. This calculation is repeated here as a verification exercise which demonstrates additional aspects of the code not included in the purely supersonic flow: the shockcapturing capability and the treatment of multiple species.

The oblique detonation wave problem is governed by the Euler equations for reacting flow which are given here in differential form

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} = 0$$
(3.10)

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u^2 + p)}{\partial x} + \frac{\partial(\rho u v)}{\partial y} = 0$$
(3.11)

$$\frac{\partial (\rho v)}{\partial t} + \frac{\partial (\rho v u)}{\partial x} + \frac{\partial (\rho v^2 + p)}{\partial y} = 0$$
(3.12)

$$\frac{\partial (\rho E)}{\partial t} + \frac{\partial (\rho u E + p u)}{\partial x} + \frac{\partial (\rho v E + p v)}{\partial y} = 0$$
(3.13)

$$\frac{\partial \rho f_r}{\partial t} + \frac{\partial \left(\rho f_r u\right)}{\partial x} + \frac{\partial \left(\rho f_r v\right)}{\partial y} = -\alpha \rho f_r H(T - T_i)$$
(3.14)

$$\frac{\partial \rho f_p}{\partial t} + \frac{\partial \left(\rho f_p u\right)}{\partial x} + \frac{\partial \left(\rho f_p v\right)}{\partial y} = +\alpha \rho f_r H(T - T_i).$$
(3.15)

where f_r is the mass fraction of reactant; f_p is the mass fraction of product; α is a rate constant for the single-step reaction; and the term $H(T - T_i)$ is the Heaviside function. The use of the Heaviside function acts as a switch to "turn on" the reaction when some ignition temperature, T_i , is exceeded. In this work, T_i is set to 400.0 K so that the reaction begins immediately after the flow is shock processed.³ The form of the source terms for the reactant and product components of the gas ensure that the process is a single-step irreversible reaction; this is due to the dependence on ρf_r only. The notation of these equations differs to that which appears in Powers and Aslam [108]. This choice was made because the equation set shown here corresponds to the implementation of governing equations in the code, mbcns. Powers and Aslam write only one equation for species continuity in terms of a reaction progress variable, λ , because in this system they can rely on the fact that $f_r = 1 - f_p$. In keeping with our notation, the equation set is closed with equation of state relations for a binary mixture of ideal gases (Equations 3.16 and 3.17). The product component has an associated heat release represented by q and its effect is

³Powers and Aslam [108] used a value for T_i of 362.58 K. This discrepancy with the present value of 400.0 K has no practical effect — in both simulations, the reaction first begins immediately post-shock as the post-shock temperature is 423.2 K.

seen in the calculation of internal energy for the mixture.

$$e = \frac{p}{\rho(\gamma - 1)} - f_p q \tag{3.16}$$

$$p = \rho RT \tag{3.17}$$

In Equation 3.17, *R* is the average mixture gas constant (weighted by mass fraction), which is always constant in this problem as both species have a value of R = 287.0.

The analytical solution for the oblique detonation wave given by Powers and Aslam [108] is shown in Figure 3.4. The temperature is increased suddenly across the shock and continues to rise as the exothermic reaction proceeds; this is shown in Figure 3.4(a). Similarly, the progress of the irreversible reaction is demonstrated by the contours of product mass fraction displayed in Figure 3.4(b). The rate of reaction slows as the flow moves further downstream of the shock because less reactant gas is available. The complete derivation of the solution is given in the paper by Powers and Aslam [108]. In Appendix B, the major parts of the analytical solution are repeated, and a computer program for calculating the analytical solution is given. The analytical solution is for an inverse problem: given a straight shock deflection angle as input, the solution gives the curved wedge which supports the shock. In the numerical analysis, the curved wedge (as a wall boundary condition) is part of the input. The numerical solution should then calculate a straight shock structure as part of the flow field.



Figure 3.4: Analytical solution for an oblique detonation wave: (a) contours of temperature (values in K), and (b) contours of mass fraction of product

The simulations were performed on five different grids: from 64×64 cells as the coarsest and doubling in resolution to 1024×1024 cells as the finest. Four of the flux calculator options were tested: AUSM, AUSMDV, EFM and the adaptive calculator (which switches between EFM near shocks and AUSMDV elsewhere). In all simulations, high-order reconstruction with the limiter of van Albada et al. [109] was used. The simulation domain was divided into 20 blocks

Parameter	Unit	Value
R	J/(kg.K)	287.0
α	s^{-1}	1000.0
β	radians	$\pi/4$
γ		6/5
T_{∞}	Κ	300.0
M_{∞}		3.0
$ ho_\infty$	kg/m ³	1.0
q	J/kg	300,000

Table 3.4: Parameters used for the oblique detonation wave verification exercise

and run in parallel, thus the communication routines for the parallel version of the code were also tested. The parameters used in the simulation are those used by Powers and Aslam [108] and appear in Table 1 of their work; they are shown here in Table 3.4. The free stream values are used as the initial condition for the flow field. A supersonic inflow condition is applied to the west face of the domain, while an extrapolation boundary condition is used on the north and east boundaries. The south boundary is specified as a slip wall. The spline describing the curved wedge consists of 71 points. This large number of points ensures that the maximum deviation of the spline from the true analytical curved surface is less than 1.0×10^{-5} m. By specifying such a tight tolerance, any discretisation errors at the surface are a result of the finite grid and not the spline representation. In other words, the errors due to the spline fit of the analytical surface are minimal compared to the grid discretisation. This is important because we seek to assess the spatial effect of finite grid discretisation.

The L_1 error norm is computed as a measure of global discretisation error, as defined in Powers and Aslam [108]

$$L_{1} = \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} \left| \rho_{n,ij} - \rho_{\text{exact},ij} \right| \Delta x \Delta y, \qquad (3.18)$$

Figure 3.5(a) shows the transient convergence towards steady-state for a set of calculations which use the AUSMDV flux calculator. As the grid resolution is increased, the L_1 error norm reduces. It also takes longer (in simulated physical time) for the finer grids to reach a converged solution because they are better able to resolve the transient relaxation process. In Figure 3.5(b), the trend in error is shown for the various flux calculators as the grid is refined. The order of spatial error is shown in Table 3.5.

The results shown in Table 3.5 indicate that the order of spatial accuracy approaches $O(\Delta x^1)$ for all flux calculators, with EFM having the highest order of convergence and AUSM, the lowest. The reduction of spatial accuracy to sub-first order is expected because of the limiter used in the shock-capturing scheme: Roy [110] and Powers and Aslam [108] both cite Godunov as first demonstrating that the capturing of discontinuities without oscillation reduces the spatial



Figure 3.5: Computed global discretisation error based on L_1 error norm: (a) transient convergence for the AUSMDV flux calculator, (b) results of all simulations with error value taken at steady-state

Table 3.5: Observed order of spatial accuracy based on the L_1 error norm for the oblique detonation wave solution

Flux calculator	Observed order of accuracy	
AUSM	0.866	
AUSMDV	0.960	
EFM	0.968	
adaptive	0.960	

accuracy to first order. As a comparison, the code Powers and Aslam verified in their work showed a spatial convergence rate of $\mathcal{O}(\Delta x^{0.779})$ [108]. In the present work, the adaptive flux calculator achieves the same order of convergence as the AUSMDV flux calculator, that is, $\mathcal{O}(\Delta x^{0.960})$. This is not surprising as the adaptive flux calculator, implemented as a switching between EFM and AUSMDV, will be reduced to the accuracy of the least accurate calculator.

The results of this verification exercise demonstrate that mbcns performs as expected for shock-capturing finite-volume codes which employ limiters. Based on this, the claim is made that mbcns is verified for multiple species flows with embedded shocks. Additionally this verification case exercised the parallel implementation, that is, the data exchange routines and parallel algorithm. The finest grid (at 1024×1024) did not fit into the memory of a single workstation and so the flow domain was decomposed into 20 blocks and solved on a cluster. Thus the parallel aspects of the coding were also verified. This verification exercise is important because the remainder of this thesis work, the modelling of high-temperature phenomena, takes this flow solver infrastructure as the starting point for further development.

3.3 Validation of the flow solver: shock detachment in noble gases

In this section, a validation case is presented in which the code is compared against experimental data. Verification showed that the governing partial differential equations were being solved correctly; validation addresses the question about the appropriateness of the equations for the flows of interest. The validation case involves the calculation of shock detachment distances on a spheres fired into noble gases (argon and krypton).

Schwartz and Eckerman [111] performed a series of experiments in a free-flight ballistics range at the U.S. Naval Ordnance Laboratory, White Oak. Ball bearings 7.9375 mm ($\frac{5}{16}$ inch) in diameter, made of various materials, were fired at supersonic speeds into three test gases: argon, krypton and chlorine. Their main purpose was to assess the sensitivity of the shock detachment to "real" gas effects (also known as high-temperature effects). In particular, the vibrational relaxation of the chlorine alters the thermal state behind the shock and thus alters the shock detachment distance. At lower flow speeds and pressures, the vibrational mode is effectively frozen and at higher speeds and pressures, the vibrational mode approaches equilibrium. Between these two limits, there is a nonequilibrium region. Schwartz and Eckerman aimed to measure the effect of this thermal nonequilibrium region on the shock location. As a preliminary study, Schwartz and Eckerman first tested their experimental technique by firing spheres into noble gases. They chose conditions that avoided electronic excitation and significant amounts of ionisation. Therefore, these conditions did not include the effects of any excitation processes. This meant that the validity of the experimental technique could be established by comparing to well-regarded theoretical calculations of shock detachment distance for monatomic gases.

For validation of the code, a simple, ideal gas case is also desirable for the same reason that the experimenters had: the complications of internal excitation and ionisation are avoided. Schwartz and Eckerman performed experiments in the Mach number range of 2–12. Argon was used as the test gas below Mach 6 whereas krypton was used above Mach 6. The free stream pressure was varied over a range of 1 333.22 Pa (10 mm Hg) to 26 664.4 Pa (200 mm Hg). Various optical techniques were used to record the flow field shot to shot: shadowgraph, reversed shadowgraph and Schlieren. There was no observable effect on the shock detachment distance due to the variation of initial pressure, and this is consistent with theoretical expectations.

The numerical simulations were performed over the same Mach number range as the experiments. The Mach number for the numerical simulations was incremented by 0.2 for each successive simulation. Also, three different initial pressures were simulated over the complete Mach number range: 1333.22 Pa, 13332.2 Pa and 26664.4 Pa. Schwartz and Eckerman [111] only reported that the pressure was varied but did not give specifics about the pressures used for the results presented. The initial temperature was taken as 300.0 K for the numerical work. Schwartz and Eckerman state that the temperature of the ballistic range cannot be varied but they do not proceed to report the temperature for their tests. The gas was treated as inviscid as viscous effects have little influence on the shock detachment at these conditions [111]. Schwartz and Eckerman used the work of Homann [112] to demonstrate this point.

The computational domain and a typical grid are shown in Figure 3.6. The boundary conditions are indicated in Figure 3.6(a). The slip_wall shown on the south boundary is equivalent to a symmetry boundary condition for these axisymmetric simulations. The inflow boundary (denoted sup_in) is given by a spline which is based on the correlation by Billig [113] for shock shapes in perfect gases with $\gamma = 1.4$. Note that $\gamma = 1.667$ for these monatomic gases and so the points of the Billig correlation were adjusted so as to encapsulate the flow of the monatomic gas over the sphere. The details of the adjustment can be found in the input script for this case shown in Appendix A.3. At each condition, the solution was performed on three grids to ensure grid independence. The coarsest grid had 60 cells normal to the body and 60 cells around the body. The medium resolution grid used 90×90 and the finest used 135×135. The grid resolution was increased by a factor of 1.5 for each successive grid. Also, to reduce computation time, the converged results on the coarse grid were used as input for the medium and fine resolution computations.



Figure 3.6: A typical setup for a numerical simulation of a D = 7.9375 mm sphere: (a) computational domain and (b) a 60x60 grid (the lines shown actually connect cell centres). This particular geometry corresponds to a krypton case at Mach 8.

Before presenting the results, a comment should be made on how the shock location is determined from the numerical simulations. To locate the shock, a search is performed along the profile of flow field data extracted from the stagnation streamline, beginning from the free stream and working towards the body. The search terminates when a certain pressure level (above the free stream pressure value) is exceeded within a finite-volume cell. In this work, that pressure level is taken as half the value of the post-shock pressure based on the Rankine-Hugoniot shock relations for an ideal gas. Due to the finite resolution of the grid, the true shock location is somewhere between the located cell and the cell immediately preceding it. Therefore, the shock location is reported as the *x*-location midway between the two cells bounding the pressure rise. Upper and lower bounds for the shock location estimate are provided based on the *x*-location of the finite-volume cells enclosing the pressure rise. This procedure for determining the shock location is best illustrated by an example. In Figure 3.7, a pictorial representation of the shock location procedure is shown. The actual data corresponds to the simulation of krypton gas at Mach 8.0 with a initial pressure of 13 332.2 Pa. The "detected cell" is the first cell to exceed the value of the criteria pressure, 5.32×10^5 Pa; this criteria pressure is half of the post-shock pressure based on ideal gas shock relations with M = 8.0 and $\gamma = 1.667$. The "preceding cell" is therefore the cell immediately before the "detected cell". As indicated in Figure 3.7, the location of the shock is reported at midway between these two cells.



Figure 3.7: Pictorial representation of the procedure for determining shock location in the numerical simulations. The profile of pressure is taken along the stagnation streamline for a 7.9375 mm diameter sphere in krypton gas flow at free stream conditions: $M_{\infty} = 8.0$ and $p_{\infty} = 13332.2$ Pa. The grid contained 60 × 60 cells.

The results for the suite of simulations are shown in Figure 3.8. A comparison to the experimental results of Schwartz and Eckerman [111] is presented in Figure 3.8(a). The numerical values for shock location are based on the finest grid and the case when $p_{\infty} = 13332.2$ Pa. The agreement, for the most part, is very good. Unfortunately, Schwartz and Eckerman do not provide uncertainty bounds for their experimental results. They state that, "the error involved cannot be estimated because of the complexity of the optical problem and the uncontrollable variations in optical conditions." [111]

An attempt was made to provide error bars for the numerical results by applying the grid

convergence error analysis for mixed-order schemes presented by Roy [110]. This error analysis is not shown here because I do not believe that it is an appropriate means of estimating shock detachment distance. The error analysis, based on Roy's work, proceeds by calculating an extrapolated "exact" value if the grid discretisation tended to zero for some quantity. Normally that quantity would be a surface pressure or an integrated value like coefficient of lift. The idea behind the analysis is that the value of interest, in this case shock detachment distance, should asymptote towards some value as the grid is refined, but not necessarily monotonically. Based on the grid refinement factor and the order of spatial accuracy, Roy provides extrapolation techniques that allow one to estimate the "exact" value for the quantity of interest. There are two difficulties in applying Roy's error estimation technique when the value of interest is the shock detachment distance: (1) the shock detachment distance is not only a function of grid refinement but also the grid location; and (2) the method does not work well in the vicinity of shocks where the order of spatial accuracy is affected by reconstruction limiters - unfortunately, we are attempting to extract the location of the shock by this method. To expand on the first point, consider Figure 3.9 which shows the reported shock location (using the method from Figure 3.7) based on three grid refinements: coarse, medium and fine. In this artificial example, but entirely plausible, the shock location "extracted" from the coarse grid is closer to the "actual" shock than that given by the medium grid. The problem is not that the medium grid provides less resolution but rather that the extracted quantity, shock detachment, is inextricably linked to the grid position as well as the grid refinement. In summary, without a standard means of reporting shock detachment distance, I have chosen to present the results from the finest grid $(135 \times 135 \text{ cells})$.

In lieu of a standard for reporting grid convergence index for a quantity like shock detachment, a visual representation of grid independence for these results is shown in Figure 3.8(b). The results for the three grid resolutions are given in Figure 3.8(b) for the case when $p_{\infty} = 13332.2$ Pa. It may be noted that the values for shock detachment are virtually indistinguishable, thereby giving confidence in a grid-independent result. Finally, Figure 3.8(c) displays the results for the finest grid at the three different free stream pressures used. These results demonstrate that the numerical simulation is consistent with the experimental and theoretical expectation: for an ideal gas, the shock detachment distance is a function of Mach number only and independent of free stream pressure.

As mentioned earlier, the agreement between the experiment and numerical simulations is very good. However, at the highest Mach number value, there is some discrepancy as shown in Figure 3.8(a). Schwartz and Eckerman [111] claim that in their test conditions "the excitation of electronic states and (significant amounts of) ionisation in the gas were avoided." The present numerical results dispute that claim. To investigate the possibility of any electronic excitation or ionisation, a simulation of the krypton gas in equilibrium (thermal and chemical) was performed at a Mach number of 12 and free stream pressure of 13 332.2 Pa. The result (see Figure 3.8(a)) shows that this equilibrium calculation agrees better with the experimental value than the perfect gas calculation. This suggests that there is some electronic excitation or ioni-



(a) Numerical values for the case when $p_{\infty} = 13332.2$ Pa on the fine grid (135×135)



(b) Numerical values for the case when $p_{\infty} = 13332.2$ Pa: various grid resolutions



(c) Numerical values on the fine grids for various free stream pressures.

Figure 3.8: Results of shock detachment distance for a 7.9375 mm diameter sphere fired into noble gases (argon and krypton)



Figure 3.9: Demonstration of the dependency on the extracted value of shock location based on various levels of grid refinement.

sation of the krypton gas at the highest Mach numbers. The excitation of the gas was further investigated by considering the composition at the stagnation point. The gas at the stagnation point has an approximate pressure of 2.8×10^6 Pa and a temperature around $12\,000$ K. These values were input into the CEA program [38] to compute the equilibrium composition (these values are not available directly from the flow solver). This computation showed that no ionisation had occurred, as Schwartz and Eckerman had claimed, but there was some electronic excitation — the value of γ , the ratio of specific heats, is approximately 1.6 instead of the frozen value of 1.667. This difference in γ gives rise to a different shock detachment distance when comparing the perfect gas and equilibrium gas simulations.

The results of these simulations compared against experiment provide a convincing demonstration that the code, mbcns, is valid for blunt body inviscid flows. In the remainder of this thesis, the use of experimental measurements of shock detachment as a means of validating the modelling of high temperature gas effects will be a recurring theme. Thus, the validation provided here for perfect gases is a useful result and a necessary precursor step before introducing more complicated physics into the numerical simulations.

3.4 Summary

This chapter was used to present the flow solver mbcns which is used as the basis for the development work in this thesis. As the flow solver is an integral part of the modelling, some checks of its integrity were performed; specifically, verification and validation.

The flow solver was verified by two techniques: the Method of Manufactured Solutions and the Method of Exact Solutions. The Method of Manufactured Solutions used a purely supersonic Euler flow to establish the order of spatial accuracy without the complications of embedded shocks. It was found that the order of spatial accuracy was greater than about 1.6 for the various flux calculators with high-order reconstruction. This positive value for order of convergence indicates that the code will asymptote to the continuum solution, thus it is said to be verified.

For the case of embedded shocks (a discontinuity) it is difficult to use the Method of Manufactured Solutions. Instead, the Method of Exact Solutions was used to establish the order of spatial accuracy when the flow field has embedded shocks. The exact solution to an oblique detonation wave was compared to the numerical solution and an order of spatial accuracy of between 0.87–0.96 was established for the various flux calculators. This verification case tested several aspects of the coding implementation including: the shock-capturing method; the treatment of multiple species; and the parallel algorithm.

In order to validate the code, numerical simulations were compared to experiments that measured the shock detachment distance on spheres fired into noble gases. The results from the numerical simulations compared favourably to the experiments. In the remainder of the thesis, the sensitivity of shock detachment to the thermochemical state is used as means to validate the modelling for thermochemical nonequilibrium. Thus it was important to demonstrate that the base flow solver could estimate shock detachment distance for the relatively simple noble gases.

Chemical Nonequilibrium

Chemical nonequilibrium flows, also called flows with finite-rate chemical effects, are an important class of flows in the study of gas dynamics. In this chapter, the discussion is restricted to chemical nonequilibrium only and assume that all of the gases are in thermal equilibrium. The details of more general thermochemical nonequilibrium flows are treated later in Chapter 5. On a kinetic level, chemical nonequilibrium exists in the gas when there have not been sufficient particle collisions to facilitate the exchange of chemical energy. From a modelling perspective, the influence of chemical nonequilibrium effects is only important when the time for completion of the chemical reactions is of the same order of magnitude as some characteristic flow time scale. Consider τ_f as a characteristic transit time for the flow and τ_c as a characteristic chemical relaxation time; this leads to a convenient classification of types of flows:

frozen flow the time taken for chemical relaxation is much longer than the flow transit time of interest

$$\tau_c \gg \tau_f$$

nonequilibrium flow the time taken for chemical relaxation is comparable to the time for flow transit (and influential on that flow)

$$\tau_c \approx \tau_f$$

equilibrium flow the time taken for chemical relaxation time is much quicker than the flow transit time

$$\tau_c \ll \tau_f$$

As an example of nonequilibrium flow, consider the hypersonic flow field of a planetary entry vehicle during atmospheric descent. Gnoffo et al. [28] explain the presence of nonequilibrium flow (in blunt body flow fields) as follows:

The combination of low density in the upper atmosphere (which lowers collision frequency) and high vehicle velocity (which lowers transit time) creates the conditions which make nonequilibrium phenomena an important aspect of the shocklayer flow.

During atmospheric entry, the large kinetic energy of the vehicle is dissipated into the surrounding gases. From the perspective of a gas particle, the flow time of interest is the time it takes for the gas particle to pass through the bow shock and transit the vehicle shock layer. After passing the shock, the thermally perfect gas particle has an excess of sensible internal energy¹ and during subsequent collisions the gas particle will seek to redistribute that energy among other modes, including chemical energy if available. In particular, molecules will seek to break chemical bonds as a means of absorbing the excess internal energy. For certain flow conditions, often associated with flows tending towards the rarefied limit, the amount of time required for sufficient collisions for equilibrium is of the same order as the time required for a gas particle to transit the shock layer. In these cases, the modelling of chemical nonequilibrium is important to correctly characterise the flow field about the vehicle. On a more practical note, the correct modelling of nonequilibrium phenomena is required for accurate estimates of heat loading on the vehicle surface. Sutton and Gnoffo [114] have reported that a little more than half of the stagnation point heating rate for entry into air at 10.9 km/s is due to recombination of atomic species of O and N. This effect on heat transfer estimates can only be reliably modelled by including finite-rate chemistry effects.

The influence of chemical nonequilibrium phenomena in gas dynamics is not limited to blunt body flows. Its influence extends to combustion processes, detonation waves and nozzle flows to name a few examples and the same basic theoretical treatment can be applied to each of theses types of flows.

In this chapter, a computational model for calculating the finite-rate chemical evolution of reacting gas in nonequilibrium flows is described. In essence this chapter is dedicated to the term

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as it appears in Equation 2.2; its theory, implementation, verification and validation is reported. The theory behind the coding implementation is presented in two sections: the model for a mixture of thermally perfect gases is presented in Section 4.1 and the model for the chemical kinetics is described in Section 4.2. The numerical methods for solving the chemical kinetic rate equation are presented in Section 4.2.3. An oft encountered problem in the numerical solution of the chemical rate equations is that numerical inaccuracies can lead to problems ensuring that mass is conserved in the system. In Section 4.3, an original treatment — to the best of my knowledge — to the numerical solution of the chemical kinetics equations is presented; this method directly addresses the problems of mass conservation. The implementation is verified by comparison with an analytical solution to a hydrogen-iodine system in Section 4.4, and, finally, some validation cases for gas dynamic flows in chemical nonequilibrium are shown in Section 4.5.

¹This is a result of shock processing, or consider this a result of indirect transferal of vehicle kinetic energy to the gas.
4.1 A mixture of thermally perfect gases

4.1.1 A single thermally perfect gas

The assumed behaviour of a thermally perfect gas is that all internal energy modes are in equilibrium at a single temperature. For atoms this means that the Boltzmann distributions for translational and electronic energy are governed by one temperature value. Similarly for molecules, the Boltzmann distributions for translational, rotational, vibrational and electronic energy are described by a single temperature value.

To model a thermally perfect gas requires a knowledge of how the gas stores energy as a function of temperature. It is convenient to have available the specific heat at constant pressure as a function of temperature, $C_p(T)$. From this, specific enthalpy of the gas can be computed as

$$h = \int_{T_{ref}}^{T} C_p(T) dT + h(T_{ref})$$
(4.1)

and entropy is given as

$$s = \int_{T_{ref}}^{T} \frac{C_P(T)}{T} dT + s(T_{ref}).$$
(4.2)

The transport properties, viscosity and thermal conductivity, can be calculated as a function of temperature for a single component of the gas mix. The transport properties for a single component can be combined by an appropriate mixing rule to give a mixture viscosity and thermal conductivity.

In the implementation as part of this thesis work, a thermally perfect gas is characterised by five curve fits all of which are functions of temperature:

1. specific heat at constant pressure, $C_p(T)$,

```
2. enthalpy, h(T),
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- 3. entropy, s(T),
- 4. viscosity, $\mu(T)$, and
- 5. thermal conductivity, k(T).

The form of these curve fits follows that used by McBride and Gordon [38]. The curve fits for thermodynamic properties in non-dimensional form are as follows:

$$\frac{C_p(T)}{R} = a_0 T^{-2} + a_1 T^{-1} + a_2 + a_3 T + a_4 T^2 + a_5 T^3 + a_6 T^4$$
(4.3)

$$\frac{H(T)}{RT} = -a_0 T^{-2} + a_1 T^{-1} \log T + a_2 + a_3 \frac{T}{2} + a_4 \frac{T^2}{3} + a_5 \frac{T^3}{4} + a_6 \frac{T^4}{5} + \frac{a_7}{T}$$
(4.4)

$$\frac{S(T)}{R} = -a_0 \frac{T^{-2}}{2} - a_1 T^{-1} + a_2 \log T + a_3 T + a_4 \frac{T^2}{2} + a_5 \frac{T^3}{3} + a_6 \frac{T^4}{4} + a_8$$
(4.5)

The coefficients for these curve fits are available for a large number of gaseous species in the CEA program [38] (and associated database files). Each of these curve fits are only valid over a

limited temperature range. For example, the thermodynamic curve fits for molecular nitrogen (N₂) are comprised of three segments: 200.0–1000.0 K, 1000.0–6000.0 K and 6000.0–20000.0 K. Beyond this range the values are extrapolated in this work. The extrapolations are based on a crude assumption of constant C_p outside of the range. Thus the extrapolations are as follows:

$$\frac{C_p(T < T_{low})}{R} = \frac{C_p(T_{low})}{R}$$

$$\frac{C_p(T > T_{high})}{R} = \frac{C_p(T_{high})}{R}$$

$$\frac{H(T < T_{low})}{RT} = \frac{1}{T} \left\{ H(T_{low})T_{low} - C_p(T_{low})(T_{low} - T) \right\}$$

$$\frac{H(T > T_{high})}{RT} = \frac{1}{T} \left\{ H(T_{high})T_{high} + C_p(T_{high})(T - T_{high}) \right\}$$

$$\frac{S(T < T_{low})}{R} = S(T_{low}) - C_p(T_{low}) \log \left(\frac{T_{low}}{T}\right)$$

$$\frac{S(T > T_{high})}{R} = S(T_{high}) + C_p(T_{high}) \log \left(\frac{T}{T_{high}}\right)$$

These extrapolations do not cause much concern for the calculations presented in this thesis as the temperature rarely exceeds the range of the various curve fits.

The curve fits for viscosity and thermal conductivity are also in the same form as that used by the CEA program [38]. The curves are as follows.

$$\log \mu(T) = a_0 \log T + \frac{a_1}{T} + \frac{a_2}{T^2} + a_3$$
$$\log k(T) = b_0 \log T + \frac{b_1}{T} + \frac{b_2}{T^2} + b_3$$

4.1.2 Mixing rules for a collection of thermally perfect gases

The thermodynamic state for a mixture of thermally perfect gases is uniquely defined by two state variables and the mixture composition. The internal energy is computed as a mass fraction weighted sum of individual internal energies,

$$e = \sum_{i=1}^{N} f_i e_i = \sum_{i=1}^{N} f_i \left(h_i - R_i T \right).$$
(4.6)

Pressure is computed from Dalton's law of partial pressures,

$$p = \sum_{i=1}^{N} \rho_i R_i T.$$
 (4.7)

The specific gas constant for the mixture is defined as

$$R = \sum_{i=1}^{N} f_i R_i.$$
 (4.8)

The calculation of C_p is based on a mass fraction weighted sum of component specific heats,

$$C_{p} = \sum_{i=1}^{N} f_{i} C_{p_{i}}.$$
(4.9)

The specific heat at constant volume is then computed as

$$C_v = C_p - R. (4.10)$$

The ratio of specific heats, γ , is given by its definition,

$$\gamma = \frac{C_p}{C_v}.\tag{4.11}$$

The frozen sound speed for the mixture, *a*, is calculated as

$$a = \sqrt{\gamma RT}.\tag{4.12}$$

During a compressible flow simulation, the values of ρ and e are most readily available from the conserved quantities that are solved for during each time increment. This leads to the specific problem of solving for the thermodynamic state of the gas mixture given ρ , e, and the mixture composition, \overrightarrow{f} . However, the formulae previously presented are all explicit in temperature. We solve for temperature using the Newton iteration technique for zero solving,

$$T_{n+1} = T_n - \frac{f_0(T_n)}{f_0'(T_n)},$$
(4.13)

where the zero function, $f_0(T)$, is based on the given internal energy, *e*, and a guess for internal energy based on temperature,

$$f_0(T) = e_{guess} - e = \sum_{i=1}^N f_i \left(h_i - R_i T_{guess} \right) - e.$$
(4.14)

Using the fact that $C_{vi} = \frac{de_i}{dt}$, we can conveniently find the derivative function for the Newton technique by computing the mixture C_v ,

$$\frac{df_0(T)}{dT} = \sum_{i=1}^N f_i \frac{de_i}{dT} = \sum_{i=1}^N f_i C_{vi} = C_v.$$
(4.15)

The Newton iteration is set to converge when the accuracy of the temperature value is within $\pm 1.0 \times 10^{-6}$ K. Personal experience has shown that this kind of error tolerance is required when temperature is used in a finite-rate chemistry calculation to compute rates of composition change.

The calculation of mixture transport properties is not as straight forward as the thermodynamic properties. A mixing rule is required to compute the mixture viscosity and thermal conductivity. Palmer and Wright (2003) [115] compared three mixing rules against a detailed multicomponent treatment for mixture viscosity based on the Boltzmann equation: Wilke's mixing rule [116], Armaly-Sutton mixing rule [117], and Gupta et al.-Yos mixing rule [118]. The multicomponent treatment is considered exact but is also far too expensive for inclusion in CFD calculations. Palmer and Wright compared the three mixing rules in terms of accuracy and efficiency, and found that the Gupta et al.-Yos rule was the most efficient and gave reasonable accuracy provided the gas was only weakly ionising. The study also concluded that the Armaly-Sutton rule gives good accuracy over a wide range of temperatures and is only 15% more expensive than the Gupta et al.-Yos. The Wilke's mixing method was the least accurate and in Palmer and Wright's words [115], "should be the method of last resort."

Despite the warnings of Palmer and Wright [115], the Wilke's mixing rule [116] has been implemented in the work presented here. The choice of the Wilke's mixing rule can be defended on two grounds: 1) the region of flow where transport effects are most dominant are near the cold walls, and 2) the species data is more readily available for this rule. To expand on these points further, in the flows of interest for this work, blunt body flows and expansion tube flows, the important viscous features of the flow are near the wall region where the boundary layer develops. Therefore, the region where it is most crucial to compute the correct mixture transport properties is in the cold near-wall flow and it is in this region that the Wilke's mixing rule performs just as reliably as any of the other more complex mixing rules. In further defence of choosing Wilke's mixing rule, the required input data is more readily obtained compared to the collision integral data required by the Gupta et al.-Yos formula. The finding of appropriate data is further complicated by the study of the Titan gas mix which has not been studied as extensively as terrestrial air.

The mixing rules used by Gordon and McBride [119] in the CEA program are used for calculating mixture transport properties in this work; these rules are a variant of Wilke's original formulation [116].

$$\mu_{mix} = \sum_{i=1}^{N} \frac{x_i \mu_i}{x_i + \sum_{j=1}^{N} x_j \phi_{ij}}$$
(4.16)

and

$$k_{mix} = \sum_{i=1}^{N} \frac{x_i k_i}{x_i + \sum_{j \neq i}^{N-1} x_j \psi_{ij}}$$
(4.17)

where x_i is the mole fraction of species *i*.

The interaction potentials, ϕ_{ij} and ψ_{ij} , can be calculated a number of ways. Again, the formulae suggested by Gordon and McBride [119] have been used,

$$\phi_{ij} = \frac{1}{4} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4} \right]^2 \left(\frac{2M_j}{M_i + M_j}\right)^{1/2}$$
(4.18)

and

$$\psi_{ij} = \phi_{ij} \left[1 + \frac{2.41(M_i - M_j)(M_i - 0.142M_j)}{(M_i + M_j)^2} \right]$$
(4.19)

where M_i and M_j refer to the molecular weights of species *i* and *j* respectively.

Once the mixture viscosity and thermal conductivity have been computed, it is possible to compute the mixture Prandtl number from its definition

$$Pr = \frac{\mu C_p}{k}.$$
(4.20)

Section 4.2

4.2 Calculation of chemical source terms

4.2.1 Rates of species change due to chemical reaction

By assuming a collection of simple reversible reactions, the chemically reacting system can be represented as,

$$\sum_{i=1}^{N} \alpha_i X_i \rightleftharpoons \sum_{i=1}^{N} \beta_i X_i, \tag{4.21}$$

where α_i and β_i represent the stoichiometric coefficients for the reactants and products respectively. The case of an irreversible reaction is represented by setting the backward rate to zero. For a given reaction *j*, the rate of concentration change of species *i* is given as,

$$\left(\frac{d[X_i]}{dt}\right)_j = \nu_i \left\{ k_f \prod_i [X_i]^{\alpha_i} - k_b \prod_i [X_i]^{\beta_i} \right\},\tag{4.22}$$

where $v_i = \beta_i - \alpha_i$. By summation over all reactions, N_r , the total rate of concentration change is,

$$\frac{d[X_i]}{dt} = \sum_{j=1}^{N_r} \left(\frac{d[X_i]}{dt}\right)_j.$$
(4.23)

For certain integration schemes it is convenient to have the production and loss rates available as separate quantities. In this case,

$$\frac{d[X_i]}{dt} = q_i - L_i = \sum_{j=1}^{N_r} \dot{\omega}_{app_{i,j}} - \sum_{j=1}^{N_r} \dot{\omega}_{va_{i,j}}$$
(4.24)

The calculation of $\dot{\omega}_{app_{i,j}}$ and $\dot{\omega}_{va_{i,j}}$ depends on the value of ν_i in reach reaction *j* as shown in Table 4.1.

Table 4.1: The form of the chemical production and loss terms based on the value of v_i

	$ u_i > 0 $	$ u_i < 0 $
$\dot{\omega}_{app_i}$	$ u_i k_f \prod_i [X_i]^{\alpha_i}$	$-\nu_i k_b \prod_i [X_i]^{\beta_i}$
$\dot{\omega}_{va_i}$	$-\nu_i k_b \prod_i [X_i]^{\beta_i}$	$ u_i k_f \prod_i [X_i]^{\alpha_i}$

The calculation of the reaction rate coefficients, k_f and k_b , is described in Section 4.2.2 and the solution methods for the ordinary differential equation system of species concentration changes is presented in Section 4.2.3.

4.2.2 Reaction rate coefficients

The reaction rate coefficients for a reaction can be determined by experiment (often shock tube studies are used) or from theory. In a great number of cases, estimates of the reaction rate from theory can vary by orders of magnitude from experimentally determined values. For this reason, fits to experimental values are most commonly used.

For the single-temperature gas model discussed in this chapter, the forward reaction rate coefficients are calculated using the generalised Arrhenius form,

$$k_f = AT^n \exp\left(\frac{-E_a}{kT}\right) \tag{4.25}$$

where k is the Boltzmann constant and A, n and E_a are constants of the model.

The backward rate coefficient can also be calculated using a modified Arrhenius form,

$$k_b = AT^n \exp\left(\frac{-E_a}{kT}\right) \tag{4.26}$$

or it can be calculated by first calculating the equilibrium constant for the reaction,

$$k_b = \frac{k_f}{K_c}.\tag{4.27}$$

If the backward rate coefficient is calculated from the equilibrium constant, then a method of calculation of the equilibrium constant is required. The equilibrium constant for a specific reaction can be calculated from curve fits or, as is done in this work, using the principles of thermodynamics. The equilibrium constant based on concentration is related to the equilibrium constant based on pressure by,

$$K_c = K_p \left(\frac{p_{atm}}{\mathcal{R}T}\right)^{\nu} \tag{4.28}$$

where p_{atm} is atmospheric pressure in Pascals, \mathcal{R} is the universal gas constant, $\nu = \sum_{i}^{N_S} \nu_i$ and

$$K_p = \exp\left(\frac{-\Delta G}{\mathcal{R}T}\right). \tag{4.29}$$

The derivation of the formula for K_p , the equilibrium constant based on partial pressures, can be found in any introductory text on classical thermodynamics which covers chemical equilibrium. The differential Gibbs function for the reaction, ΔG , is calculated using

$$\Delta G = \sum_{i}^{N_s} \nu_i G_i \tag{4.30}$$

where each G_i is computed from the definition of Gibbs free energy,

$$G_i(T) = H_i(T) - T \times S_i(T)$$
(4.31)

and G_i is in units of J/mol. H_i and S_i can be computed in the appropriate units by using the CEA polynomials and multiplying by $\mathcal{R}T$ and \mathcal{R} respectively.

Some caution should be exercised in the selection and use of reaction rates for a specific flow problem. In many cases, a set of reaction rates may only be "tuned" for a specific problem domain. This problem of "tuned" sets of reaction rates and an explanation for why it arises is described by Oran and Boris (p. 38 of Ref. [78]):

A problem that often arises in chemical reactions is that there are fundamental inconsistencies in a measured reaction rate. For example, there may be experimental measurements of both the forward and reverse rate constants, k_f and k_r . Nonetheless, when either is combined with the equilibrium coefficient for that reaction, the other is not produced. This appears to represent a violation of equilibrium thermodynamics. The explanation is usually that k_f and k_r have been measured at rather different temperatures or pressures, and so there are inconsistencies when they are extrapolated outside the regime of validity of the experiments.

4.2.3 Solving the chemical kinetic ordinary differential equation

The system represented in Equation 4.23 is a system of ordinary differential equations (ODEs) which can be solved by an appropriate method. For certain chemical systems, the governing ODEs form a stiff system due to rates of change varying by orders of magnitude for certain species. For these systems, special methods for stiff ODEs are required. In this work, four methods for the numerical solution of the ODE system have been implemented.

- 1. Euler method
- 2. modified Euler method
- 3. alpha-QSS method, and
- 4. Runge-Kutta-Fehlberg method

The Euler method and modified Euler method are standard techniques for solving ODEs and the details can be found in any text dealing with numerical methods and numerical analysis. The fourth-order Runge-Kutta method uses a fifth-order error estimate as a means for controlling the timestep used for integration as proposed by Fehlberg [120]. This is particularly efficient for non-stiff systems.

alpha-QSS method

The alpha-QSS (quasi-steady-state) method was proposed in Mott's thesis [121]. It is an ODE solver aimed specifically at the problem of stiffness in chemical systems. This ODE solver makes use of the forward and backwards rates of concentration change as calculated by Equation 4.24. This is a predictor-corrector type scheme in which the corrector is iterated upon until a desired convergence is achieved. The predictor and corrector are,

$$[X_i]^1 = [X_i]^0 + \frac{\Delta t q_i^0}{1 + \alpha_i^0 \Delta t L_i^0}$$
(4.32)

$$[X_i]^{n+1} = [X_i]^0 + \frac{\Delta t \left(\bar{q}_i - [X_i]^0 \bar{L}_i\right)}{1 + \bar{\alpha}_i \Delta t \bar{L}_i}.$$
(4.33)

In the above equations,

$$\bar{L}_i = \frac{1}{2} \left(L_i^0 + L_i^n \right)$$
(4.34)

and

$$\bar{q}_i = \bar{\alpha}_i q_i^n + (1 - \bar{\alpha}_i) Q_i^0.$$
(4.35)

The key to the scheme is calculating α correctly. This α parameter controls how the update works on a given species integration. Note that α is defined as

$$\alpha(L\Delta t) \equiv \frac{1 - \left(1 - e^{-L\Delta t}\right) / (L\Delta t)}{1 - e^{-L\Delta t}}.$$
(4.36)

Using Pade's approximation,

$$e^{x} \approx \frac{360 + 120x + 12x^{2}}{360 - 240x + 72x^{2} - 12x^{3} + x^{4}}$$
(4.37)

it is possible to write a form of the expression for α which is more amenable to computation as the expensive exponential function evaluation is avoided. The approximation for α becomes,

$$\alpha(L\Delta t) \approx \frac{180r^3 + 60r^2 + 11r + 1}{360r^3 + 60r^2 + 12r + 1}$$
(4.38)

where $r \equiv 1/(L\Delta t)$.

4.2.4 Coupling chemistry effects to the flow solver

It was stated in Section 3.1 that a timestep-splitting approach is used in the flow solver to incorporate the various component physics. Some details about the coupling of the chemistry effects are provided here.

In an unsteady, time-accurate flow simulation, the allowable timestep is constrained by the Courant-Friedrichs-Lewy (CFL) criterion. In a viscous compressible flow, the CFL criterion allows one to select an appropriate timestep and limit the propagation of flow information to distances less than one cell-width. The speed at which flow information propagates is a function of inviscid wave speeds and viscous effects.

When the effects of finite-rate chemistry are 'split' from the flow simulation, the chemical update is solved in a separate step in which the flow is held frozen. (In fact, in true timestep-splitting, *all* other contributing physics is frozen during the chemistry update.) Thus the chemistry problem is to find the updated species composition at the end of the flow timestep.

It may be, and is quite likely, that the flow timestep is not an appropriate timestep to solve the chemical kinetic ODE problem. When the timestep for the chemistry problem is smaller than the flow timestep, the chemistry problem is subcycled a number of times until the total elapsed time equals that of the flow timestep. It is common in the problems presented in this work to have a chemistry timestep which is 100–1000 times smaller than the flow timestep, that is, 100-1000 subcycles are required to solve the chemistry problem. When the timstep for the chemistry problem is larger than the flow timestep, it is simply set to the value of the flow timestep.

During the simulation process, the chemistry timestep is tracked for each finite-volume cell in the simulation. Although the flow 'moves on' in subsequent timesteps, if the change of flow conditions is not large, then the previous chemistry timestep will be a good estimate to begin the new chemistry problem in the subsequent timestep. An exceptional case is when a shock passes through the cell: the change of flow conditions does become large. In this instance, the old chemistry step is disregarded and a new step is selected. The selection procedure for a new step is discussed in the next paragraph. When using either the Runge-Kutta-Fehlberg or the alpha-QSS methods, an estimate of the new chemistry timestep is provided as part of the ODE update routine.

So, during a simulation, the old chemistry step at one iteration is used to begin the new chemistry problem in the next iteration. What is needed is a means to select the chemistry step on the initial iteration, or whenever the old suggestion is not reasonable (as in the case of a shock passing through the cell). In this work, the initial step for the chemistry problem is selected based on the suggestion by Young and Boris [122],

$$dt_{\text{chem}} = \epsilon_1 \min\left(\frac{[X_i](0)}{[\dot{X}_i](0)}\right) \tag{4.39}$$

where ϵ_1 is taken as 1.0×10^{-3} in this work, and the expression is evaluated at the initial values for the chemistry subproblem.²

4.3 A mass-conserving formulation and solution to the chemistry problem

One of the numerical difficulties faced in reacting flow simulations is ensuring that mass is conserved during the chemical update. For complex kinetic systems, numerical errors during the solution to the ODE describing the evolution of species concentrations can introduce errors in the the total mass of the reacting system. One common way to overcome this difficulty is to solve the ODE for N - 1 species and then compute the fraction of the last species by using the conservation of mass principle. It is the author's opinion and experience, that this method hides errors from the code user and, as the errors accumulate, can lead to grossly wrong results. Furthermore, it is conceivable that a reaction scheme with unbalanced equations could be solved in this way and the error would be very difficult to detect as, to all outward appearances, the mass would be conserved. A second approach to the problem is to scale the mass fractions of the participating species at the end of each ODE timestep to ensure that mass is conserved. Oran and Boris [78] suggest a scaling (which they call renormalization) as follows:

$$f_i^{\text{new}} = f_i^{\text{old}} \left(\frac{1}{\sum_m f_m^{\text{old}}} \right)$$
(4.40)

for each species *i*, and m = 1...N. The equation here in terms of mass fraction is a rewritten form of Equation 11.32 from Ref. [78].

In Section 5.4, the problem of chemistry and vibration coupling is considered. In this problem, it is desirable to have a record of how much a given species changed due to each individual reaction. For example, if a nitrogen molecule is formed in a third-body recombination

²Young and Boris [122] suggest that ϵ_1 be scaled from the convergence criteria. I have found that the fixed value is adequate for the problems of interest in this work.

then there is some effect on the vibrational energy content of the mix. However, if the nitrogen molecule is formed from an ion reclaiming an electron then the effect on the vibrational energy content may be different. Therefore, it is important to differentiate the mechanisms by which the nitrogen was formed so that the coupling to vibrational energy is treated correctly. In order to record the change for each species from each reaction, the governing ODE for the kinetic system was reformulated. This had the pleasant side effect of leading to a mass-conserving ODE system that describes the evolution of species due to chemical reactions. The development of the reformulated ODE system is described in what follows.

Consider the simple dissociation reaction of molecular nitrogen,

$$N_2 + N_2 \rightleftharpoons N + N + N_2.$$

We wish to solve for the molar change in the forward and backward directions, γ_f and γ_b , over some time increment. An ODE system is sought of the form:

$$\frac{d\gamma}{dt} = f(\gamma). \tag{4.41}$$

We begin by writing,

$$\dot{\gamma_f} = k_f C_{N_2}^2$$
 (4.42)

$$\dot{\gamma}_b = k_b C_N^2 C_{N_2} \tag{4.43}$$

but this is not in the form of Equation 4.41. Combining the molar change in the forwards and backwards direction with the stoichiometric coefficients gives:

$$C_{N_2} = (1-2)[\gamma_f - \gamma_b] + C_{N_2}|_0$$
(4.44)

$$C_N = (2-0)[\gamma_f - \gamma_b] + C_N|_0.$$
(4.45)

Where the values, $C_{N_2}|_0$ and $C_N|_0$, are the initial concentrations at the beginning of the time increment. Finally by substituting the expressions for C_{N_2} and C_N into the equations for the molar rates of change, the ODE can be written as:

$$\dot{\gamma}_{f} = k_{f} \left\{ (1-2) [\gamma_{f} - \gamma_{b}] + C_{N_{2}} |_{0} \right\}^{2}$$
(4.46)

$$\dot{\gamma_b} = k_b \left\{ (2-0) [\gamma_f - \gamma_b] + C_N |_0 \right\}^2 \left\{ (1-2) [\gamma_f - \gamma_b] + C_{N_2} |_0 \right\}$$
(4.47)

The general form for the *j*-th reaction in a set reactions,

$$\dot{\gamma_f}_j = k_{f_j} \prod_i [X_i]^{\alpha_i} \tag{4.48}$$

$$\dot{\gamma_{bj}} = k_{bj} \prod_i [X_i]^{\beta_i} \tag{4.49}$$

where the instantaneous values for concentration, $[X_i]$, are based on the degree of change for each reaction,

$$[X_i] = \sum_j \nu_j \left(\gamma_{f_j} - \gamma_{b_j}\right) + [X_i]|_0, \qquad (4.50)$$

where $[X_i]|_0$ is the concentration at the beginning of the time interval. In implementation in a compressible flow simulation, the value $[X_i]|_0$ is set at the beginning of each call to the update due to chemical kinetics.

Section 4.4

4.4 Verification of the model for chemical nonequilibrium

4.4.1 An isothermal, constant volume reactor

In this verification exercise, a constant-volume, constant-temperature batch reactor is considered. The reacting system comprises of molecular hydrogen and molecular iodine, and one reaction is considered:

$$H_2 + I_2 \rightleftharpoons 2HI. \tag{4.51}$$

While the hydrogen-iodine system is not of direct interest to the aerospace community, it has been a favourite study for chemical kineticists as an example of a bimolecular gas phase reaction [123]. At moderate temperatures (below about 600 K), the reaction system is completely bimolecular and hence its behaviour can be treated analytically. The relative simplicity of the system made it attractive for early experimentalists. Likewise, this bimolecular system with an analytical solution is ideal as a verification exercise for the numerical implementation.

The analytical solution for the hydrogen-iodine system is presented in the book by Williams [124] (see Appendix B of Williams' book). For the case where the initial concentrations of hydrogen and iodine are equal ($C_0 = C_{I_2} = C_{H_2}$), the concentration of hydrogen iodide (HI) as a function of time is given implicitly as

$$\sqrt{k_f k_b} = \frac{1}{4C_0 t} \ln \left[\frac{2C_0 + C_{HI} \left(2\sqrt{k_b/k_f} - 1 \right)}{2C_0 - C_{HI} \left(2\sqrt{k_b/k_f} + 1 \right)} \right].$$
(4.52)

In what follows, the analytical solution for C_{HI} has been computed by rearranging Equation 4.52 such that is equals zero and using the secant method for zero finding.

The conditions for the test exercise were chosen from amongst the many sets of conditions used in the experiments by Graven [123]. The initial conditions in the batch reactor were chosen as

$$C_{H_2} = C_{I_2} = 4.54 \,\mathrm{mol}/\mathrm{m}^3, \quad T_0 = 700.0 \,\mathrm{K}.$$

This condition can be found in Table III of Graven's article. From this the derived values for the other properties are

$$p_0 = 52846.8 \,\mathrm{Pa}, \quad \rho_0 = 1.161 \,\mathrm{kg/m^3}, \quad f_{H_2} = 0.00788, \quad f_{I_2} = 0.99212.$$

The reaction rate used for the calculations, both analytical and numerical, is taken from Baulch et al. [125]

$$k_f = 1.94 \times 10^{14} \exp(-20620.0/T).$$
 (4.53)

The numerical simulations presented here were computed by four different methods in order to test the implementation. The various numerical methods used were:

- 1. Mott's [121] α-QSS integrator,
- 2. Euler method,

- 3. fourth-order Runge-Kutta method with the Fehlberg method of timestep selection based on a fifth-order extrapolation, and
- 4. the mass-conserving formulation of the ODE system presented in Section 4.3 again using the Runge-Kutta-Fehlberg integration technique.

The first three methods were applied to the standard ODE system describing the chemical kinetics as given in Equation 4.23, whereas the fourth method was applied to the mass-conserving system described in Section 4.3.

The results of the simulations are presented in Figure 4.1 which shows the concentration of HI as it develops with time. The agreement for each of the numerical solutions to the analytical solution is excellent. This provides confidence that the implementations of the chemical rate evaluations and the solution of the resulting ODE are correct.



Figure 4.1: Evolution of *C*_{*HI*} as a function of time

4.4.2 Chemical relaxation behind a normal shock in air

This verification case is a weaker form of verification: comparison to calculations made by others. This test case computes the chemically reacting subsonic flow of air behind a strong normal shock. This calculation was performed by Marrone [32] in his report on nonequilibrium flow behind shock waves. Marrone first calculated the case where the flow is in thermal equilibrium and then proceeded to the more complicated case of including the effects of vibrational nonequilibrium. In the present section, the discussion is restricted to the case where the flow is in thermal equilibrium.

Before detailing the specific conditions of interest, the solution methodology for calculating the post-shock flow is outlined as it differs significantly from the approach used by Marrone [32]. We begin by writing the equations for an inviscid, one-dimensional flow which includes chemical reactions (that is, continuity equations for each component species):

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} = 0 \tag{4.54}$$

$$\frac{\partial \rho u}{\partial t} + \frac{\partial \rho u^2}{\partial x} = \frac{\partial p}{\partial x}$$
(4.55)

$$\frac{\partial \rho E}{\partial t} + \frac{\partial \rho u E}{\partial x} = \frac{\partial p u}{\partial x}$$
(4.56)

$$\frac{\partial \rho_i}{\partial t} + \frac{\partial \rho_i u}{\partial x} = \dot{\omega} \tag{4.57}$$

The flow is treated as steady so each of the partial derivatives with respect to time may be eliminated.

$$\frac{\partial \rho u}{\partial x} = 0 \tag{4.58}$$

$$\frac{\partial \rho u^2}{\partial x} = \frac{\partial p}{\partial x} \tag{4.59}$$

$$\frac{\partial \rho u}{\partial x} = \frac{\partial p u}{\partial x} \tag{4.60}$$

$$\frac{\partial \rho_i u}{\partial x} = \dot{\omega} \tag{4.61}$$

After introducing constants, *A*, *B* and *C*, the set of equations describing the flow behind a strong normal shock are:

$$\rho u = A \tag{4.62}$$

$$\rho u^2 + p = B \tag{4.63}$$

$$\rho u E + p u = C \tag{4.64}$$

$$\frac{\partial f_i}{\partial x} = \frac{\omega}{A} \tag{4.65}$$

where $\rho_i = \rho f_i$. This set of equations is comprised of an ordinary differential equation describing the evolution of species and a system of nonlinear equations which couple the effect of the chemical reactions to the remaining flow field variables. The solution methods consists of solving the ODE over some small increment, dx, updating the thermodynamic state assuming pressure and temperature are constant (or frozen) during the chemical increment and finally solving the system of nonlinear equations to get new values for the flow field variables. This algorithm is repeated until the desired distance downstream of the shock is reached.

The following free stream conditions were used by Marrone in his calculation:

$$M_{\infty} = 12.28$$
 $p_{\infty} = 1.0 \,\mathrm{mm} \,\mathrm{Hg}(133.32 \,\mathrm{Pa}),$ $T_{\infty} = 300.0 \,\mathrm{K}.$

Though not directly reported by Marrone, it has been assumed that the free stream composition of the air is

$$f_{O_2} = 0.22; \quad f_{N_2} = 0.78.$$

Marrone's kinetic scheme included 7 species (O_2 , N_2 , NO, O, N, NO^+ and e^-) and six reactions. This reaction scheme is presented in Appendix C in Section C.1.1. Marrone states that the reaction rates used for the calculation differed slightly from those that appear in the report [32].

The initial attempt to verify the present work by comparison to Marrone's calculation is shown in Figure 4.2. In Figure 4.2(a), the temperature ratio and density ratio behind the shock are plotted. The assumption of frozen reactions in the shock leads to high translational temperatures immediately behind the shock. As the molecular oxygen and nitrogen have sufficient time to dissociate, the temperature lowers and there is a corresponding rise in density. The calculations made with the present work agree well with Marrone's calculation of temperature and density ratio. Also shown in Figure 4.2(a) is the post-shock equilibrium values for temperature and density ratio which have been calculated independently by the CEA program [38]. It is not surprising that the present work matches identically the calculation of the CEA program at equilibrium because the same thermodynamic data have been used as input.

There is an alarming discrepancy between the amount of ionisation calculated by Marrone when compared to the present work. The present work using Marrone's kinetic scheme shows no ionisation and this is shown in Figure 4.2(b). The only major difference between the two calculations is the thermodynamic input data. Upon closer investigation, it seemed that the current thermodynamic data for NO⁺ differed significantly from the data available in 1963. Indeed later in 1979, the electron levels for NO⁺ were still the object of enquiry. Albritton et al. [126] note that, "the NO⁺ ion had only grudgingly given up information about its structure." The repercussion is that the reaction rates in Marrone's scheme were tuned against an equilibrium constant based on different thermodynamic data to that used currently. It seemed that the use of current thermodynamic data and "older" reaction rate data caused the problem with regards to calculating the level of ionisation.

To test this idea further, a modern set of reaction rates by Gupta et al. [118] was used with the reactions listed in Marrone's scheme [32] (see Section C.1.2). The ideal situation would be to repeat the present calculation with Marrone's thermodynamic data. This was decided against because it would not be trivial to change the code base to include old data. Furthermore, there was little to be gained by demonstrating that old data and old reaction rates could compute this particular set of conditions when the real interest is in using the latest available (and presumably most correct) data. The next best situation then was to repeat the calculation with modern thermodynamic data and modern reaction rate data. The results of this calculation are shown in Figure 4.3.

The temperature and density ratio calculated using the modern kinetic scheme agree well with the calculations made by Marrone. This is demonstrated in Figure 4.3(b). The pleasing result here is that the use of the modern kinetic scheme with the modern thermodynamic data has given the correct computation of ionisation as shown in Figure 4.3(b). This supports the idea that the problem with the initial attempt at comparison to Marrone's calculation was hampered by the use of incongruous thermodynamic and reaction rate data.

This verification case has demonstrated the application of the finite-rate chemistry imple-



Figure 4.2: Chemically relaxing flow behind a strong normal shock using Marrone's [32] kinetic scheme. The free stream conditions are: $M_{\infty} = 12.28$, $p_{\infty} = 133.32$ Pa, $T_{\infty} = 300.0$ K.



Figure 4.3: Chemically relaxing flow behind a strong normal shock using the reaction rate data proposed by Gupta et al. [118]. The free stream conditions are: $M_{\infty} = 12.28$, $p_{\infty} = 133.32$ Pa, $T_{\infty} = 300.0$ K.

mentation to the types of reactions that are of interest to atmospheric-entry vehicle flows.

4.5 Validation of the model for chemical nonequilibrium

4.5.1 Ignition delay times in hydrogen/air combustion

The calculation of ignition delay times in a hydrogen-air system provides a useful validation case for the finite-rate chemistry implementation. The calculation of species evolution in a hydrogen-air combustion system is challenging for any numerical scheme for solving the ODE. The numerical scheme needs to accurately calculate trace species during the build-up of radicals before the onset of ignition. After ignition, the numerical scheme then faces the stiffness problem presented by the approach to chemical equilibrium.

In the study of hydrogen-air ignition times related to scramjet combustors, Rogers and Schexnayder [127] validated their chemistry model against the experimental data of Slack and Grillo [128]. Slack and Grillo were interested in the effect of NO_x compounds on the ignition times of a hydrogen-air system. As part of their experiments, they measured the ignition delay time of pure hydrogen-air systems without the addition of NO or NO_2 . It is this data that was used by Rogers and Schexnayder. As the validation exercise here, the calculations of Rogers and Schexnayder are repeated. However, a number of other reaction rate sets are tested.

Slack and Grillo [128] performed their measurements of ignition delay in a shock tube. The hydrogen-air mixture in stoichiometric ratios was heated by a reflected shock wave. The ignition delay was measured over a range of temperatures at four different pressures: 0.27, 0.50, 1.0, and 2.0 atm. Ignition delay was determined by the time between the reflected shock signal and the maximum positive rate of change of the OH emission signal. In the numerical work, Rogers and Schexnayder [127] took the ignition delay as the time for the concentration of OH to reach 5×10^{-9} mol/cm³. This definition of ignition time has been adopted in this work also.

During the course of validating the finite-rate chemistry model, it became apparent that deficiencies in the sets of reaction rates can confuse the issue of validation. In other words, a perfectly reasonable numerical implementation can be obscured by a poor choice of reaction schemes. To demonstrate this point, a number of reaction schemes that are available in the literature have been used to compute the ignition delay times in a hydrogen-air mixture. The reaction schemes are given in Table 4.2.

A simulation was performed for each of the reaction schemes listed in Table 4.2 and at the four pressures investigated by Slack and Grillo [128]. At each pressure, a number of simulations was performed over a temperature range of 800–1400 K in increments of 10 K. The simulation was terminated if ignition had not been detected by 1500 μ s. Thus, some of the lines in Figure 4.4 do not extend to the full range of the y-axis.

The results of the simulations, for various reaction schemes, are displayed in Figure 4.4. For each pressure, the reaction scheme of Rogers and Schexnayder [127] agrees most closely with the experimental measurements. This is hardly surprising as the Rogers and Schexnayder scheme is the most detailed and thus better models the build-up of radicals in the reacting

Case	Reaction Scheme	Notes
а	Rogers and Schexnayder (1981) [127]	detailed scheme,
		16 species and 49 reactions
b	Evans and Schexnayder (1980) [129]	full scheme,
		12 species and 25 reactions,
		k_b from rate coefficients
с	Evans and Schexnayder (1980) [129]	as (b) but k_b from equilibrium constant
d	Evans and Schexnayder (1980) [129]	reduced scheme with inert N ₂ ,
		8 species and 16 reactions,
		k_b from rate coefficients
e	Evans and Schexnayder (1980) [129]	as (d) but k_b from equilibrium constant
f	Frenklach, Wang and Rabinowitz (1992) [130]	subset of methane system,
		9 species and 19 reactions
g	Jachimowski (1988) [131], Oldenborg et al. (1990) [132]	modified Jachimowski,
		13 species and 32 reactions
h	Warnatz, Maas and Dibble (1999) [133]	9 species and 19 reactions

Table 4.2: Hydrogen-air reaction schemes used for ignition delay validation case

system. The largest discrepancy between experiment and the numerical simulations occurs at the low-temperature values at a pressure of 0.27 atm (see Figure 4.4(a)). However, the low pressure data is the least reliable as these conditions favour boundary layer growth in the shock tube [128].

It is interesting to compare the results from the full scheme and reduced scheme of Evans and Schexnayder [129] — in the reduced scheme nitrogen is treated as inert and acts as a diluent only. For each of the simulations, the calculated ignition delay times from the full and reduced schemes are virtually indistinguishable. This result suggests that the treatment of N₂ as an inert diluent is appropriate at the conditions of this study. Also note the poor performance of the Evans and Schexnayder scheme when the backwards rate coefficients are calculated from the equilibrium constant rather than using the empirically determined backwards rate coefficients. This is an example of a scheme where the given backwards and forwards reaction rate coefficients do not combine to give the correct equilibrium constant. Oran and Boris [78] state that the inconsistencies in the reaction rates usually arise from k_f and k_b having been measured at different conditions. The problem of incorrect equilibrium constant is most prominent when these reaction rate coefficients are used outside of their range of validity as determined by the experiments. This point was further elaborated in the final paragraph of Section 4.2.2.

4.5.2 Shock detachment distance on spheres in air flow

In 1964, Lobb [134] reported on a series of experiments performed in a ballistic range facility involving nylon spheres fired into air. The experiments aimed to measure the shock detachment distance by optical means (the use of Schlieren shadowgraphs) as this distance is sensitive to the thermodynamic state of the gas. At the higher densities, the shock detachment measurements could be used to check the thermodynamic data used for equilibrium air at that time.



Figure 4.4: Ignition delay times for hydrogen combustion in air. The legend corresponds to the reaction scheme listed in Table 4.2.



Figure 4.4: (*continued*) Ignition delay times for hydrogen combustion in air. The legend corresponds to the reaction schemes listed in Table 4.2.

At lower densities, Lobb states that "the shock detachment distance becomes a measure of the lag in the exchange between the energy of translational motion and the internal modes and chemical reactions" (see p. 519 of Ref. [134]). It is these measurements, at lower densities, and their sensitivity to chemical reactions that make this experiment a useful validation case for the finite-rate chemistry work. Indeed J. D. Teare makes a comment to this effect, about using Lobb's data as a check on chemical kinetic models at the end of Lobb's paper (see p. 527 of Ref. [134]). It should be noted that these experiments are sensitive to thermal nonequilibrium effects also whereas the calculations in this present section only model chemical nonequilibrium with thermal equilibrium assumed. We will bear this in mind as we interpret the results.

The data of Lobb [134] have been popular among researchers as a validation case for modelling flows in chemical nonequilibrium (single temperature) and the more general thermochemical nonequilibrium (multi-temperature). Candler [135], Gnoffo [136] and Zhluktov and Smekhov [137] all performed calculations of one of the Lobb experimental conditions using single temperature models. Computations using multi-temperature models have also been performed: Candler [135], Gnoffo [136], Zhluktov and Smekhov [137], Schall and Zeitoun [138], Schall et al. [139], Furudate et al. [140], and Tchuen et al. [141]. The present calculations will be compared to the work of these other authors where appropriate.

More recently, in the late 1990s, Nonaka et al. [142] performed a similar set of experiments to Lobb's [134]. The aim of this newer work was to investigate flow conditions in the intermediate hypersonic regime, that is, conditions more conducive to general thermochemical nonequilibrium behaviour. Some of the experimental conditions studied by Nonaka et al. overlapped with the conditions investigated by Lobb. In this region of overlap, Nonaka et al. did not obtain good agreement with Lobb's results. To investigate this discrepancy, Nonaka et al. introduced oil contaminants into the test gas, the kind of contaminants expected to have been present in Lobb's work based on the technology of the 1960s. Nonaka et al. found that the contaminated flow produced a reduced shock detachment distance between 7–15% compared to that of the uncontaminated flow, thereby bringing the results into better agreement with those of Lobb. The ramification this has for the use of Lobb's data for CFD validation will be discussed in the section entitled "Discussion of results" presented shortly.

Description of experiments

Lobb [134] performed experiments using $\frac{1}{4}$ in. and $\frac{1}{2}$ in. nylon spheres as his test models. Four different ambient pressures were used: 2.5, 5, 10, and 20 mm Hg. The velocity was varied from about 8 000 ft/s to 21 000 ft/s. Lobb did not report the ambient temperature; in this work a value of 293 K is assumed following the work of Gnoffo [136]. In terms of the binary scaling parameter based on radius, ρR , Lobb's experiments were at: 2.5×10^{-5} , 5.0×10^{-5} , 1.0×10^{-4} , and $2.0 \times 10^{-4} \text{ kg/m}^2$. The velocity range in S.I. units was 2400–6400 m/s.

The experiments by Nonaka et al. [142], as mentioned earlier, targeted the intermediate hypersonic regime. They used hemispherical models with nose radii of 7, 14 and 15 mm. In these experiments, the gas had an ambient temperature of 293 K and the ambient pressures were varied between 5.6×10^2 Pa to 2.0×10^4 Pa. This gave four conditions of varying binary

scaling parameter: 1.0×10^{-4} , 2.0×10^{-4} , 4.0×10^{-4} , and 1.7×10^{-3} kg/m². The flight velocity was varied from 2 400 to 3 900 m/s.

Description of numerical simulations

An extensive set of numerical simulations was performed that cover the range of conditions used by both Lobb [134] and Nonaka et al. [142]. Thus, simulations were performed at conditions corresponding to the following binary scaling parameters: 2.5×10^{-5} , 5.0×10^{-5} , 1.0×10^{-4} , 2.0×10^{-4} , 4.0×10^{-4} , and $1.7 \times 10^{-3} \text{ kg/m}^2$. The free stream velocity was varied from 2 000 to 8 000 m/s in increments of 200 m/s. In total, 186 different free stream conditions were simulated. These independent simulations were performed on a cluster computer in an "embarrassingly" parallel manner.

The computational domain is very similar to that used for the noble gas simulations (see Figure 3.6) with a radius, in this case, of 6.35 mm (corresponding to Lobb's $\frac{1}{2}$ in. diameter spheres). The difference being that the Billig correlation [113] was used directly to define the inflow boundary as opposed to the adjustments that were made for the noble gas simulations. The Billig correlation is based on $\gamma = 1.4$ and gives the shock shape for a frozen flow. As the flow of interest here is relaxing — the temperature drops behind the shock and density increases — the shock detachment distance should be shorter than the equivalent frozen case. Thus, use of the Billig correlation will guarantee an inflow boundary which stands off farther than the captured shock. As was done with the simulations of the noble gases, three grids of varying resolution were used: 60×60 , 90×90 and 135×135 cells. A typical input file is given in Appendix D.1.

The air was modelled as a mixture of 5 species with 6 reactions:

$$O_2 + M \rightleftharpoons O + O + M$$

$$N_2 + M \rightleftharpoons N + N + M$$

$$N_2 + N \rightleftharpoons N + N + N$$

$$NO + M \rightleftharpoons N + O + M$$

$$NO + O \rightleftharpoons O_2 + N$$

$$N_2 + O \rightleftharpoons NO + N$$

The reaction rates are taken from Gupta et al. [118] and are shown in Appendix C.1.3. The species are treated as being in thermal equilibrium; the data for thermodynamic properties are taken from the values used by Gordon and McBride [38] in their CEA program. Finally, the gas was treated as inviscid. Lobb comments that the displacement thickness of the boundary layer at the conditions in his experiment is practically zero. Thus, neglecting the viscous boundary layer in the simulations by performing an inviscid calculation should not effect the estimate of shock detachment distance.

Discussion of results

The results, in terms of non-dimensional shock detachment distance (δ/D) , for the present numerical simulations are displayed in Figure 4.5. The numerical results are taken from the finest grid of 135×135 cells. The experimental results of Lobb [134] and Nonaka et al. [142] are also plotted for comparison. For the case when $\rho R = 5.0 \times 10^{-5} \text{ kg/m}^2$ and the velocity is 5280 m/s, there are also computational results available from Candler [135] and Gnoffo [136] which also use a single temperature model; these are shown in Figure 4.5(b).

First, a general statement may be made by considering the six graphs in Figure 4.5 as a whole: the agreement between the numerical simulations and the experiments is satisfactory. This agreement provides a reasonable validation of the finite-rate chemistry model and the chosen set of reaction rates. Second, the data of Lobb [134] displays some trends over the velocity range that appear suspicious, particularly at the lower densities (see Figure 4.5(a) and 4.5(b)). It is because of these trends that some of the Lobb data should be treated with a certain amount of caution with regards to its reliability.

To expand on the point about the reliability of the Lobb data, consider Figure 4.5(b) which includes the computational results from Candler [135] and Gnoffo [136] also. The experimental result at 5 280 m/s with its large error margin supports the validation of all three calculations: Candler's, Gnoffo's and the present work. If one stopped one's investigation at this point, after a comparison to this isolated data point, then a likely conclusion is that the modelling is valid. But now consider the experimental data point at 6 000 m/s on that same graph (Figure 4.5(b)). When the experimental value is compared with the numerical result, it is hard to claim that the numerical model is valid. Indeed it was this data point that prompted the present work to study the entire range of velocities. In this instance, I believe the experimental result is suspect. Furthermore, this example highlights the danger in choosing one data point from the experiment to use as a validation case. It is my opinion that the value in Lobb's data comes from a comparison of general trends over the entire velocity range.

There is a clear discrepancy between the numerical results and the data from Nonaka et al. [142] for the case when $\rho R = 1.0 \times 10^{-4} \text{ kg/m}^2$ (see Figure 4.5(c)). There is also a marked difference between the Lobb [134] results and those of Nonaka et al. This is mostly likely due to the presence of contaminants in the experiments performed by Lobb as explained in the article by Nonaka et al. If we argue that the Nonaka et al. results are more reliable, then it leads to the conclusion that the good agreement between the numerical work and Lobb's data is purely fortuitous. In that case, the discrepancy between the numerical results and the data from Nonaka et al. can be explained by the fact that the numerical model is invalid. At this low velocity region of the conditions, the gas exhibits a larger degree of thermal nonequilibrium. This suggests that the present model, of chemical nonequilibrium with thermal equilibrium, is not valid at the low velocity region. Similar comments may be made about the discrepancies in Figure 4.5(d).

The discrepancy between the numerical results and the data of Nonaka et al. [142] in Figure 4.5(e) is again attributed to the use of an inappropriate model at those conditions. Finally,



Figure 4.5: Shock detachment distance for spheres fired into air. Simulations model chemically reacting air in thermal equilibrium. Experimental results are taken from Lobb (1964) [134] and Nonaka et al. (2000) [142]. Also shown for $\rho R = 5.0 \times 10^{-5} \text{ kg/m}^2$ are the results of calculations by Candler (1989) [135] and Gnoffo (1990) [136].



Figure 4.5: (*continued*) Shock detachment distance for spheres fired into air. Simulations model chemically reacting air in thermal equilibrium. Experimental results are taken from Lobb (1964) [134] and Nonaka et al. (2000) [142].

when $\rho R = 1.7 \times 10^{-3} \text{ kg/m}^2$, the higher density favours a rapid approach to thermal equilibrium; in this instance the single temperature model is valid and the results compare favourably to experiment as shown in Figure 4.5(f).

In summary, the numerical results compare well to the experimental results within the range of validity for the single-temperature model. It is my opinion that the benefit of this type of data, from Lobb [134] and Nonaka et al. [142], for CFD validation comes from comparison over the entire range of conditions. In other words, a fair degree of caution should be exercised if using an isolated data point for validation.

4.6 The inclusion of diffusive species transport

Once multiple species are introduced into the flow modelling, it is important to assess the effect of species diffusion. When modelling the flow in impulse facilities, for example, molecular diffusion is often neglected because the entire flow process is of such a short duration that no appreciable diffusion occurs. This is not the case if we are interested the heating problem associated with aeroshell vehicles. As an example consider the reentry of the Stardust capsule into Earth's atmosphere.

Sutton and Gnoffo [114] provide a calculation of the Stardust forebody flow field when the free stream velocity is 10.9 km/s. They report that 600 W/cm² of the total 1100 W/cm² stagnation point heating rate comes from the recombination of the atomic oxygen and nitrogen. This physical effect can only be correctly accounted for with accurate multicomponent diffusion models and appropriate catalytic wall boundary conditions. This example serves to demonstrate the importance of modelling species diffusion to the atmospheric-entry vehicle problem.

There are a number of models available that may be used to calculate the species diffusive fluxes. Sutton and Gnoffo [114] reviewed and compared several models for multi-component diffusion and applied them to the blunt body heating problem. There is a detailed equation for diffusive fluxes in a multi-component mixture given by Curtiss and Hirschfelder [143] which is considered to be exact but its computational expense is prohibitive for use in CFD calculations. The Stefan-Maxwell equations are an approximation to the detailed equations for multicomponent diffusion. Curtiss and Hirschfelder showed that for gases at low density the Stefan-Maxwell equations are a very good approximation. The crudest approach to multicomponent diffusion is an approximation using Fick's law. Fick's law is used for the binary diffusion of two gases but is sometimes extended to multicomponent flows by introducing an effective binary diffusion coefficient which models the diffusion of species *i* into the mix. Sutton and Gnoffo compared the detailed equation for multicomponent diffusion and various forms of the approximate models over a range of gas mixture conditions. Their results were able to quantify to what extent the various models are accurate and to clarify when various modelling assumptions are violated. Sutton and Gnoffo's work continued by using the approximate models in the aforementioned Stardust calculation. Their results suggested that the "corrected" forms of the Fick's law approximation may be adequate for Earth entry problems. They also demonstrated that an iterative scheme for the Stefan-Maxwell equations can be an efficient and accurate method for inclusion in CFD calculations.

Following the work in Sutton and Gnoffo's paper [114], two models have been selected for implementation in this work: the approximate Fick's law with an effective binary diffusion coefficient (see Section 4.6.2); and the Stefan-Maxwell equations (see Section 4.6.3). Before proceeding to detail these models, first the method of calculating binary diffusion coefficients is presented; both methods require the binary diffusion coefficients for the interacting species as input.

4.6.1 Calculation of binary diffusion coefficients

The calculation procedure used to compute the binary diffusion coefficients follows the treatment of Bird, Stewart and Lightfoot [30] given in §17.3 of their text. The equation for binary diffusion of species A into B, \mathfrak{D}_{AB} , in m²/s is:

$$\mathfrak{D}_{AB} = 1.8583 \times 10^{-7} \sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B}\right)} \frac{1}{p \sigma_{AB}^2 \Omega_{\mathfrak{D},AB}}$$
(4.66)

where *T* is the temperature in K, σ_{AB} is the distance parameter in the Lennard-Jones potential in Å, *p* is the partial pressure of species A and B in atm, and $\Omega_{\mathfrak{D},AB}$ is the collision integral for diffusion, a dimensionless quantity.

The collision integral for diffusion may be calculated on the basis on the curve-fits provided by Neufeld et al. [144].

$$\Omega_{\mathfrak{D},AB} = \frac{1.06036}{T^{*0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$
(4.67)

where $T^* = kT/\epsilon_{AB}$ and k is Boltzmann's constant. Thus both Lennard-Jones parameters, σ_{AB} and ϵ_{AB} , are required for the calculation of \mathfrak{D}_{AB} .

The combining rules given by Hirschfelder, Curtiss and Bird [145] are used to estimate the Lennard-Jones potential parameters. The form of the combining rules changes based on the nature of the interacting species, that is, based on their polarity or otherwise. For the collision of nonpolar gas pairs or polar gas pairs:

$$\sigma_{AB} = \frac{1}{2} \left(\sigma_A + \sigma_B \right); \quad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$
(4.68)

When a polar gas A collides with a nonpolar gas B, a correction is applied to the estimates:

$$\sigma_{AB} = \frac{1}{2} \left(\sigma_A + \sigma_B \right) \xi^{-1/6}; \quad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \xi^2$$
(4.69)

The following formula is used to calculate ξ :

$$\xi = 1 + \frac{1}{4} \frac{\alpha_B {\mu_A^*}^2}{\sigma_B^3} \sqrt{\frac{\epsilon_A}{\epsilon_B}}$$
(4.70)

where α_B is the polarizability of molecule B in Å³ and μ_A^* is the reduced dipole moment of molecule A, that is, $\mu_A^* = \mu_A / \sqrt{\epsilon_A \sigma_A^3}$.

4.6.2 Fick's approximate law for multicomponent diffusion

Fick's first law applies to the ordinary diffusion (or mass diffusion) of binary mixtures of gases or liquids. When computing the diffusive flux of species A into a binary mixture of A and B, Fick's first law may be written in terms of mass fraction gradient as:

$$\mathbf{J}_{\mathbf{A}} = -\rho \mathfrak{D}_{AB} \nabla f_A \tag{4.71}$$

Buddenberg and Wilke [146] used an expression for the "effective" diffusion coefficient of one species, A, into a mixture.³ Wilke showed a derivation of this expression in Ref. [147] which calculates the effective diffusion coefficient as a harmonic mean. The effective diffusion coefficient for species A diffusing through a mixture is:

$$\mathfrak{D}_{A,mix} = \frac{1 - x_A}{\sum_{j \neq i} \frac{x_j}{\mathfrak{D}_{Aj}}}$$
(4.72)

This effective diffusion coefficient may then be used in an approximate form of Fick's first law:

$$\mathbf{J}_{\mathbf{A}} = -\rho \mathfrak{D}_{A,mix} \nabla f_A \tag{4.73}$$

The correct implementation of this is demonstrated in Section 4.6.4.

4.6.3 Stefan-Maxwell equations for multicomponent diffusion

The Stefan-Maxwell equations are presented in the text by Bird, Stewart and Lightfoot [30], and are given here in a form amenable to calculating the mass fraction gradient. Sutton and Gnoffo [114] rewrote the equations to give the diffusive flux of species *i* in a mixture as:

$$\mathbf{J}_{\mathbf{i}} = -\rho \mathfrak{D}_{i,mix} \nabla f_i + \frac{f_i}{(1-x_i)} \mathfrak{D}_{i,mix} \sum_{j \neq i} \left(\rho \frac{\mathcal{M}_i}{\mathcal{M}} \nabla f_j + \frac{\mathcal{M}}{\mathcal{M}_j} \frac{\mathbf{J}_j}{\mathfrak{D}_{ij}} \right)$$
(4.74)

Equation 4.74 represents a system of $(n_s - 1)$ equations and as such a closure equation is required. The iterative scheme suggested by Sutton and Gnoffo has been adopted. In this scheme, Equation 4.74 is used to solve for all J_i diffusive fluxes at iteration count N. Then the fluxes are corrected at iteration count N + 1 by applying:

$$\mathbf{J}_i^{N+1} = \mathbf{J}_i^N - f_i \sum \mathbf{J}_j^N \tag{4.75}$$

The procedure for calculating the fluxes is as follows:

- 1. Calculate J_i^0 using the leading term of Equation 4.74
- 2. Apply the correction at level N = 1 using Equation 4.75
- 3. Calculate J_i^N using Equation 4.74

³Buddenberg and Wilke [146] actually cite a presentation of Wilke's as first introducing the expression for diffusion of a species into a multicomponent mixture.

4. Apply the correction at level N + 1 using Equation 4.75. If the change between values at level N and N + 1 is less than some tolerance, then stop, otherwise repeat from Step 3.

The iteration procedure is stopped if it has failed to converge after a certain number of steps. The values for the iteration procedure are based on those used by Sutton and Gnoffo; they suggest a tolerance of 1×10^{-6} , and an upper limit on iterations of 40. A calculation using this implementation is given in the following section.

4.6.4 Verification of diffusive transport terms

In this section, the implementation of the diffusive flux calculation is verified by comparing to an exact solution for the binary diffusion of two gases. Both the approximate Fick's law and the Stefan-Maxwell equations were used in the flow solver, mbcns, to compute a numerical solution to the problem.

Sánchez et al. [148] have derived exact solutions for the transient mixing of gases at different densities. They provide solutions in one-dimension for spherical, cylindrical and planar configurations. For the verification case, the planar solution is used which treats the interdiffusion of two semi-infinite gases with densities ρ_a and ρ_b . A schematic of the problem arrangement, in its initial condition, is shown in Figure 4.6. At t = 0, the initial density field is $\rho = \rho_a$ for x < 0 and $\rho = \rho_b$ for $x \ge 0$.



Figure 4.6: Schematic of the problem arrangement for the interdiffusion of two semi-infinite slabs of gas

In the case of isothermal mixing, Sánchez et al. [148] give the self-similar solution for this binary diffusion problem as:

$$\frac{\rho - \rho_a}{\rho_a - \rho_b} = \frac{1}{2} \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{\mathfrak{D}_{ab}t}}\right) \right]$$
(4.76)

The mass fraction of species *a* is:

$$f_a = \frac{\rho_a(\rho_b - \rho)}{\rho(\rho_b - \rho_a)} \tag{4.77}$$

and in a binary mixture it follows that:

$$f_b = 1 - f_a. (4.78)$$

To compare against a numerical solution, a specific set of conditions are chosen. Those conditions are: a mixture of nitrogen (species *a*) and oxygen (species *b*), at T = 273.2 K and $p = 100.0 \times 10^3$ Pa. At these conditions, the value for the binary diffusion coefficient, $\mathfrak{D}_{N_2O_2}$, is 1.77522×10^{-5} m²/s. The binary diffusion coefficient was computed using the Lennard-Jones

 Table 4.3:
 Lennard-Jones potential parameters for nitrogen and oxygen used to compute the binary diffusion coefficient

	<i>σ</i> , m	<i>ϵ</i> , J
N_2	$3.798 imes 10^{-10}$	$9.86 imes 10^{-22}$
O ₂	3.467×10^{-10}	$1.47 imes 10^{-21}$

parameters for nitrogen and oxygen shown in Table 4.3 and Equations 4.66, 4.67 and 4.68. The parameters which appear in Table 4.3 are taken from Table 1 of Ref. [149], the data collection compiled by Svehla.

The computational domain extended from $[-2.0 \times 10^{-5}, 2.0 \times 10^{-5}] \times [0, 0.1]$ m in the x-y plane. An adiabatic wall boundary condition was used on each of the four boundaries. The domain was discretised with 100 cells in the x-direction and 10 cells in the y-direction, though the discretisation in the y-direction is not important for this one-dimensional problem. The flow solver was used to compute the transient solution up to $t = 1.0 \times 10^{-6}$ s with both the Fick's first law approximation and the Stefan-Maxwell equations for the diffusive flux terms.

The results of the numerical simulations along with the comparison to the exact solution are shown in Figure 4.7. This figure displays the profiles of mass fractions for the nitrogen and oxygen gas at the final simulation time of 1.0×10^{-6} s. The numerical results are in excellent agreement with the exact solution. Additionally, the numerical results for the Fick's first law approximation and the use of the Stefan-Maxwell equations are identical.⁴ This is not surprising as both methods for diffusive flux calculation should reduce to the same formulation, and be exact for the case of binary diffusion. The results of this test case are a preliminary and encouraging step towards verifying the implementation of the diffusive transport terms.

The future work in this area of diffusive transport terms will concentrate on further verification and validation of the implementation. The implementation should be tested with more interacting species ($N_s > 2$). Tied closely with this work is the implementation of catalytic boundary conditions. This was not pursued in this thesis as it was considered a large job to implement and rigorously test boundary conditions for the treatment of wall catalycity. Furthermore, while catalytic boundary conditions are important for the overall atmospheric-entry vehicle problem, that work on catalytic boundary conditions does not contribute directly towards providing a foundation for radiating flow calculations.

4.7 Summary

This chapter has focussed on the modelling work related to chemical nonequilibrium effects as they apply to hypersonic flows. The work was presented broadly in three parts: a) theory and background for the modelling; b) verification of the implementation; and c) validation of the

⁴In the output files, 7 significant figures are recorded. The results from the two simulations, one with Fick's law and the other with the Stefan-Maxwell equations, do not differ in any of those 7 significant figures.



Figure 4.7: Profiles for the mass fractions of nitrogen and oxygen in the binary diffusion verification problem. The profiles were taken at $t = 1.0 \times 10^{-6}$ s.

implementation.

The model for chemical nonequilibrium begins with the assumption that the gas can be described as a mixture of thermally perfect gases. The thermodynamic relations for a single component of the gas mixture and for the gas mixture as a whole were presented in Section 4.1. The other aspect to the model is the calculation of rates of species concentration change. In this work, the Law of Mass action is used to calculate rates of species concentration change. The rate constants are computed using the generalised Arrhenius equation, and in some cases, from the equilibrium constant. It was noted that care should be exercised when choosing between calculating rate constants based on Arrhenius parameters or from the equilibrium constant. This problem was further demonstrated in Section 4.5.1 which showed that poor estimates of ignition delay times are made when the wrong choice is made. The recommendation is that if an author provides both forward and reverse rate parameters then these should be favoured over use of the equilibrium constant to calculate reverse rates.

As an operator-splitting approach is employed, we are able to use the best methods available to solve the ODE problem which describes the changes of species concentration. Alongside standard integration techniques such as the Euler method and the Runge-Kutta method, the alpha-QSS method of Mott [121] was implemented as this exploits some structure of the chemical kinetic ODE that makes it an efficient method for stiff systems. Section 4.3 showed an alternate formulation of the ODE problem which ensures mass conservation. In deriving the alternate formulation, the goal was not to ensure mass conservation but rather provide a means of tracking species changes within particular reactions. This information is important later in accounting for the effect various reactions have on the vibrational energy content of the mixture (see Section 5.4); that mass is conserved is a beneficial side-effect. The implementation of the models and their solution methods was verified by considering two test cases: a) a hydrogen-iodine batch reactor; and b) the chemical relaxation of air behind a normal shock. The hydrogen-iodine system has an analytical solution for the concentration as a function of time; this was used to compare to the numerical solutions and the comparison was in excellent agreement. The post-shock air relaxation problem was first treated by Marrone [32] and provides a good test case for comparison as it treats high temperature air chemistry appropriate for the reentry problem. Initial attempts to compare the present work to Marrone's calculations highlighted the difficulty with blind use of reaction rate data. The reaction rate data of Marrone was tuned against the thermodynamic data of his day, and in particular the equilibrium constants. However, using modern day thermodynamic data (and as such, computing different equilibrium constants) changed the reaction rates such that very little ionisation was computed in the present work. When modern thermodynamic data was used with modern data reaction rate parameters, the agreement with Marrone's work was much more satisfactory.

Validation of the model, as opposed to verification, assesses how well the model represents the physical system. The model was validated by computing ignition delay times in a hydrogen-air mixture and comparing to experimental measurements. A valuable lesson was learnt about the importance of reaction rate data when trying to validate the implementation of a finite-rate chemitry model: a perfectly good implementation may be obscured by a poor choice of reaction rate data. This point is demonstrated in Figure 4.4 which shows varying degrees of success at estimating the ignition delay times by using various reaction schemes, even though the underlying implementation and solution methodology are the same. The other validation case used the experimental measurements of Lobb [134] and Nonaka et al. [142] of shock detachment distance on spheres fired into air to compare to numerical simulations. On the whole the agreement was good and the assertion was made that the value of this type of data is in considering the full range of pressures and velocities. The discrepancies, where they exist, were attributed to use of the finite-rate chemistry model beyond its domain of validity, that is, thermal nonequilibrium effects come into play at the lower densities.

Finally, as a step towards the implementation of catalytic wall boundary conditions, the modelling of multicomponent diffusion was presented. Two models were discussed: Fick's first law approximation for mixtures, and the Stefan-Maxwell equations. The implementation was verified by comparing the numerical models to an exact solution for the binary diffusion of two semi-infinite slabs of gas. It is acknowledged that this verification case is only a preliminary step towards complete verification because it only treats the case of binary diffusion and not general multicomponent diffusion. Future work hopes to further test the diffusive transport terms, leading to the implementation of catalytic wall boundary conditions.

Vibrational Nonequilibrium

The term vibrational nonequilibrium, in the context of hypersonic flows, refers to a gas state in which the energy in the vibrational mode is not in equilibrium with translational and rotational energy modes. Considering the compressive flow field of a blunt body, the process by which vibrational nonequilibrium arises is as follows. Across the strong bow shock, the translational temperature of the gas is raised considerably due to collisions within the shock. The rotational mode relaxes very quickly to the translational temperature as it requires on the order of 10s of collisions. The vibrational temperature, which is frozen at the pre-shock temperature, lags the translational temperature as the vibrational mode requires on the order of 10 000s of collisions to equilibriate (see p. 483 of Anderson Jr. (1989) [7]). It is this lagging of the vibrational temperature that leads to a zone of vibrational nonequilibrium in the shock layer. The extent of vibrational nonequilibrium is dependent on the flow conditions, such as density and velocity of the gas. The graph by Tirsky [37] which appears as Figure 2.2 (and is repeated here on p. 84 for convenience) shows the conditions for entry into Earth's atmosphere where vibrational nonequilibrium is important.

The vibrational energy content of the gas is changed during particle collisions and due to radiation; these will be referred to as energy exchange mechanisms. In order to model vibrational nonequilibrium in the flow, the conservation equation for vibrational energy requires the correct accounting of these energy exchange mechanisms. The energy exchange mechanisms include vibrational-translational energy exchange when a molecule collides with other particles in the mixture and gains or loses some vibrational energy; vibrational-vibrational energy exchange which occurs between two molecules during a collision; change in vibrational energy due to chemical reactions; and radiation processes. The chemistry affects the average vibrational energy of the mixture because chemical reactions are not guaranteed, indeed not likely, to remove or produce molecules at the exact average vibrational temperature of the species in the mixture. During dissociation, for example, a molecule in a high vibrational state is more likely to dissociate than one in a lower state. If on average, molecules in a high vibrational state dissociate more often, then the average vibrational energy is reduced by these dissociation reactions.

This chapter begins by discussing the equations which describe the thermodynamic nature of a gas mixture in vibrational nonequilibrium. The assumption is applied that the electronic energy is in equilibrium with the vibrational energy throughout this chapter. The modelling



Figure 2.2: Regions on a velocity-altitude map where various physical and chemical processes are important for the trajectories of: (I) Space Shuttle, Buran vehicles, and (II) aeroassisted orbital transfer vehicles. *Redrawn based on Source: Tirsky* (1993) [37]

for the vibrational-translational (V-T) and vibrational-vibrational (V-V) energy exchange mechanisms are presented next, Section 5.2. In order to model these energy exchange mechanisms, the calculation of an appropriate vibrational relaxation time is required; the models for vibrational relaxation time used in this thesis are given in Section 5.3 and some example calculations are shown. The effect of chemistry, mentioned in the previous paragraph, is treated in Section 5.4 which deals with the coupling of chemistry and vibrational nonequilibrium. The coupling refers to the fact that the presence of vibrational nonequilibrium also affects the chemistry: the reaction rates need to be modified to account for the vibrational nonequilibrium. The implementations of all of the submodels that contribute towards the vibrational nonequilibrium effect are verified in Section 5.5. The verification test cases include the chemically inert, vibrationally relaxing flow of nitrogen over an infinite cylinder; the chemically inert, vibrationally relaxing flow of air behind a normal shock; and the general thermochemical relaxation of dissociating oxygen behind a normal shock.

5.1 A mixture of perfect gases with nonequilibrium thermal state

This section discusses the thermodynamic model for a mixture of gases with nonequilibrium thermal states, in particular, vibrational nonequilibrium. The thermodynamic relations are needed for coupling to the flow solver, that is, certain parts of the flow field calculation require an evaluation of an equation of state. This section is in two parts: the first looks at the models for single components of the gas mixture and the second part presents the expressions for a mixture of gases.

5.1.1 Components of the gas mixture

We will consider two components in the gas mixture: atoms and diatomic molecules. The treatment can be extended to polyatomic molecules (exhibiting more than one characteristic vibrational temperature) and electrons but these are not of immediate interest for this work. In this section the relations are stated but not derived; the derivations, along with the attendant statistical mechanics theory, are given in the texts by Anderson, Jr. [7] (see Chapter 11) and Vincenti and Kruger, Jr. [150] (see Chapter IV). In what follows, the Born-Oppenheimer assumption is applied, that is, each of the internal energy modes are treated as separable.

The internal energy for an atom is composed of translational and electronic modes:

$$e_{atoms} = e_{trans} + e_{el} + e_{ref} \tag{5.1}$$

For the purposes of the current work, it is assumed that there is no significant excitation of the electronic energy. Thus the term e_{el} may be ignored henceforth. The absolute value of energy is arbitrary unless tied to some reference value. In this work, the reference energy is taken as the value for the enthalpy of formation at 298.15 K; it is a measure of the chemical energy, that is, energy in chemical bonds (or the absence of chemical bonds). The energy stored in translation when the gas has a Boltzmann distribution at temperature, *T*, is

$$e_{trans} = \frac{3}{2}RT\tag{5.2}$$

It follows that the specific heat at constant volume, $C_v = \partial e / \partial T$ is:

$$C_v = \frac{3}{2}R\tag{5.3}$$

For diatomic molecules, there are four modes of internal energy storage: translational, rotational, vibrational and electronic. The internal energy for a diatomic molecule is:

$$e_{molc} = e_{trans} + e_{rot} + e_{vib} + e_{el} + e_{ref}$$

$$(5.4)$$

The expression for translational energy remains the same as for atoms (Equation 5.2); there are still only three spatial dimensions available for translation. Assuming that the characteristic temperature is very small for most molecules gives the following expression for the rotational energy:

$$e_{rot} = RT \tag{5.5}$$

Again, e_{el} is neglected in the present treatment.

In this work, two related models are used to model the energy in the vibrational mode: the harmonic oscillator model and the truncated harmonic oscillator model. For a harmonic oscillator with frequency, ν , the allowable energy states are $\epsilon_i = (i + \frac{1}{2})h\nu$; this frequency can be related to a characteristic vibratonal temperature for the diatomic molecules, Θ_{ν} . This gives the average vibrational energy for a collection of like molecules in a Boltzmann distribution at temperature *T* as:

$$e_{vib} = \frac{R\Theta_v}{e^{\Theta_v/T} - 1} \tag{5.6}$$

For the truncated harmonic oscillator, only the energy states, ϵ_i , less than the dissociation energy for the molecule are considered. Thus, based on a dissociation temperature, Θ_D , the vibrational energy for a collection of truncated harmonic oscillators is:

$$e_{vib} = \frac{R\Theta_v}{e^{\Theta_v/T} - 1} - \frac{R\Theta_D}{e^{\Theta_D/T} - 1}$$
(5.7)

There are two expressions for C_v for the molecule dependent on the choice of model for the vibrational energy term. For the harmonic oscillator, the total specific heat at constant volume is:

$$C_{v} = R \left\{ \frac{5}{2} + \frac{(\Theta_{v}/T)^{2} e^{\Theta_{v}/T}}{(e^{\Theta_{v}/T} - 1)^{2}} \right\}$$
(5.8)

For the truncated harmonic oscillator, the expression for C_v is:

$$C_{v} = R \left\{ \frac{5}{2} + \frac{(\Theta_{v}/T)^{2} e^{\Theta_{v}/T}}{(e^{\Theta_{v}/T} - 1)^{2}} - \frac{(\Theta_{D}/T)^{2} e^{\Theta_{D}/T}}{(e^{\Theta_{D}/T} - 1)^{2}} \right\}$$
(5.9)

5.1.2 Thermodynamic properties of the mixture

The mixture of gases is assumed to behave as a collection of perfect gases; the same assumption was made in Section 4.1 for the gas mixture in the thermal equilibrium. Thus the expressions for the mixture are similar to those presented in Section 4.1. The difference here is the calculation of internal energy and the corresponding specific heats. For this mixture of gases exhibiting vibrational nonequilibrium, the gas is characterised by multiple temperatures: there is one temperature for translation/rotation, *T*, and one temperature for each vibrating molecule, $T_{v,M}$. This implies the assumption of a Boltzmann distribution amongst the various energy modes each described by an appropriate temperature.

The energy for the gas mixture is based on the average energy of the component particles:

$$e = \sum_{i=1}^{N} f_i e_i = \sum_{ia=1}^{N_{atoms}} f_{ia} e_{ia} + \sum_{im=1}^{N_{mole}} f_{im} e_{im}$$
(5.10)

The pressure for the mixture, based on Dalton's law of partial pressures, and assuming each component exhibits perfect behaviour, is:

$$p = \sum_{i=1}^{N} \rho_i R_i T \tag{5.11}$$
The gas constant for the mixture is:

$$R = \sum_{i=1}^{N} f_i R_i.$$
 (5.12)

The specific heat at constant volume is computed using a mass fraction weighted average of the component species:

$$C_{v} = \sum_{i=1}^{N} f_{i}C_{v,i} = \sum_{ia=1}^{N_{atoms}} f_{ia}C_{v,ia} + \sum_{im=1}^{N_{mole}} f_{im}C_{v,im}$$
(5.13)

From this, the "frozen" properties for the mixture follow: the specific heat at constant pressure,

$$C_p = C_v + R; (5.14)$$

the ratio of specific heats,

$$\gamma = \frac{C_p}{C_v};\tag{5.15}$$

and the sound speed,

$$a = \sqrt{\gamma RT}.$$
(5.16)

5.2 Energy exchange mechanisms

5.2.1 Vibrational-translational energy exchange

The exchange of energy between vibrational and translational modes can be modelled by the Landau-Teller equation. The Landau-Teller equation is derived on the assumption that jumps in only one level of vibrational quantum number are possible; Anderson Jr. [7] shows this derivation in §13.2 of his text. The rate equation for change of vibrational energy for molecule, p, due to collisions with all other particle types c (including the case when p = c), is:

$$\frac{de_{v_p}}{dt} = \sum_{c=1}^{n_s} x_c \frac{e_{v,p}^* - e_{v,p}}{(\tau_v^{p-c})_{V-T}}$$
(5.17)

where x_c is the mole fraction of particle type c, $e_{v,p}^*$ is evaluated at the mixture translation/rotational temperature and $e_{v,p}$ is evaluated at the vibrational temperature for molecule p, $T_{v,p}$. The calculation of the vibrational relaxation time, $(\tau_v^{p-c})_{V-T}$, is discussed in Section 5.3.

Note in Equation 5.17, the value de_{v_p}/dt is not equal to the source term for the vibrationaltranslational energy exchange, Q_{T-V} , in Equation 2.5. These two terms differ by a factor of ρ_p , that is, $Q_{T-V} = \rho_p de_{v_p}/dt$. In the operator-splitting method employed here, the rate equation is solved separately and so it is easy to write and solve it in terms of de_{v_p}/dt as shown in Equation 5.17.

5.2.2 Vibrational-vibrational energy exchange

In this work, the rate of vibrational-vibrational energy exchange is calculated using the equation derived by Schwartz, Slawsky and Herzfeld (1952) [65]. This model is recommended by various authors for use in CFD calculations [151–153]. Gilmore et al. [153] presented a paper comparing the model of Schwartz et al. to a simplified model which is popular in the aerospace CFD community. The simplified models for vibrational-vibrational energy exchange transfer average amounts of vibrational energy between two molecules which is not physically correct. The model of Schwartz et al. accounts for the exchange of vibrational quanta between two molecules; any deficit in energy between the quanta is absorbed by the translational mode, as would physically occur. Thus the Schwartz et al. model is truer to the physics than the simplified models. Gilmore et al. have this to say about use of the simplified models (p. 5 of Ref. [153]):

These models, often used in multi-temperature CFD programs, should be abandoned. They should be abandoned for failing to respect first principles, as opposed to arguments concerning rates and agreement with data.

Thivet et al. [151] provide a correction to the equation of Schwartz et al. [65] which uses the truncated harmonic oscillator assumption. The difference between the equation of Thivet et al. and the original becomes more important at higher temperatures [151]. The equation of Thivet et al. is also generalised for arbitrary mixtures of vibrational species; Schwartz et al. treated a binary mixture only. This more recent formulation has been adopted in this work. The Thivet et al. model for the rate of vibrational energy change due to vibration-vibration collisions of molecule p with other molecules, q, is:

$$\frac{de_{v_p}}{dt} = \sum_{q=1,q\neq p}^{n_v} \frac{x_q}{(\tau_v^{p-q})_{V-V}} \left(\frac{1 - \exp(-\Theta_{v,p}/T)}{1 - \exp(-\Theta_{v,q}/T)} \frac{e_{v,q}}{\hat{e}_{v,q}} (\bar{e}_{v,p} - e_{v,p}) - \frac{e_{v,p}}{\hat{e}_{v,q}} (\bar{e}_{v,q} - e_{v,q}) \right)$$
(5.18)

where Θ is the characteristic vibrational temperature, *e* is the current vibrational energy, \hat{e} is vibrational energy evaluated at the translational temperature based on the harmonic oscillator assumption and \bar{e} is the vibrational energy evaluated at the translational temperature based on the truncated harmonic oscillator assumption.

5.3 Calculation of vibrational relaxation times

A number of formulae are available in the literature to calculate the vibrational relaxation times of both vibrational-translational transfers and vibrational-vibrational transfers. In this section, the formulae which have been used in this thesis are presented.

5.3.1 Millikan and White empirical correlations (for V-T transfers)

Millikan and White [154] collated a large amount of experimental data for the vibrational relaxation times of various gas systems. From this data, they found an empirical correlation for the vibrational relaxation times that was dependent on the molecular constants of the molecule in question. It was suggested that this empirical equation could be used, with some caution, on systems for which vibrational relaxation data had not been measured. The Millikan and White formula for the vibrational relaxation time of particles p colliding with particles q is (Eq.(3a) of Ref. [154]):

$$\ln(p(\tau_v^{p-q})_{V-T}) = (1.16 \times 10^{-3})\mu^{1/2}\Theta^{4/3}(T^{-1/3} - 0.015\mu^{1/4}) - 18.42$$
(5.19)

where *p* pressure of the colliding species in atmospheres, μ is the reduced molecular weight in g/mole and computed as $\mu = \mathcal{M}_p \mathcal{M}_q / (\mathcal{M}_p + \mathcal{M}_q)$, and Θ is the characteristic vibrational temperature of *p* in K.

5.3.2 Approximate formula from Landau and Teller theory (for V-T transfers)

Giordano et al. [155] give an expression for the vibrational relaxation time which is an approximate form of that given in Landau and Teller's theory:

$$(\tau_v^{p-q})_{V-T} = (A/p) \exp[(B/T^{1/3} + C]$$
(5.20)

The constants A, B, and C are found by fits to experimental data. Equation 5.20 is given in equivalent forms in other references [7, 150].

5.3.3 Schwartz-Slawsky-Herzfeld relaxation time model (for V-T and V-V transfers)

The model proposed by Schwartz, Slawsky and Herzfeld in 1954 [156], commonly known as SSH theory, may be used to calculate both V-T and V-V relaxation times. Thivet et al. [151] note that the SSH theory is not valid for V-T interactions between a molecule and an open shell atom. In this work, SSH theory is used to compute the V-T and V-V relaxation times for interactions between the following molecules: N_2 , O_2 and NO. The formulae for computing the relaxation times based on SSH theory are given in the following paragraphs; they follow the presentation given by Thivet et al. in whose paper a more complete description can be found. No attempt is made to give a derivation of these equations as this was not part of the present work.

The relaxation times for V-T and V-V transfers are expressed as a function of the collision frequency and the transition probabilities:

$$(\tau_v^{p-q})_{V-T} = \left\{ Z_{\text{coll}}^{p-q} P_{10}(A_p, A_q) \left[1 - \exp(-\theta_v^p / T) \right] \right\}^{-1}$$
(5.21)

$$(\tau_v^{p-q})_{V-V} = \left[Z_{\text{coll}}^{p-q} P_{01}^{10}(A_p, A_q) \right]^{-1} \exp(-(\theta_v^p - \theta_v^q)/T)$$
(5.22)

The transition probabilities, P_{10} and P_{01}^{10} are described in more detail below. The collision frequency, Z_{coll}^{p-q} , is computed based on the formula by given in the text by Chapman and Cowling [157] and is

$$Z_{\text{coll}}^{p-q} = 2n\sigma_{p-q}^2 \sqrt{2\pi k_b T/\mu_{p-q}}$$
(5.23)

where *n* is the number density in number of particles/m³, μ_{p-q} is the reduced mass computed as $\mu_{p-q} = m_p m_q / (m_p + m_q)$ in kg, and σ_{p-q} is one of the Lennard-Jones parameters in m. The number density, *n*, is computed based on the partial pressure of the colliding species, ignoring others in the mixture. Thus when $p \neq q$, $n = \mathcal{N}_A(C_p + C_q)$ where \mathcal{N}_A is Avogadro's number and C_p is the concentration of species *p* in mole/m³. When the colliding species are the same, p = q, Chapman and Cowling indicate that the collision frequency is twice that given by Equation 5.23, however when accounting for energy transfer in a certain direction, for example from vibration to translation, only half of those collisions effectively exchange the energy. Based on this, the number density used to compute the collision frequency when p = q is $n = N_A C_p$. Also note that the symbol μ refers to the reduced mass used in Equation 5.23 and not the reduced molecular weight as appeared earlier in the Millikan and White formula [154], Equation 5.19: the reduced mass in Equation 5.23 is in kg based on m_p and m_q as the mass of a single molecule of species p and q. The parameter σ_{p-q} is calculated in the same manner when computing input for the binary diffusion calculations; see Section 4.6.1 and Equations 4.68 and 4.69.

The transition probability for a change in quantum vibrational number from i to j for species p due to collisions with species q is

$$P_{ij}(A_p, A_q) = \mathcal{A}/(Z_0^p Z_V^p Z_T^{p-q} Z_+^{p-q})$$
(5.24)

This equation represents the transition probability for a V-T transfer. When considering V-V transfers, the transition probability for a change in vibrational quantum number from i to j for species p with an accompanying change from states k to l for species q is

$$P_{ij}^{kl}(A_p, A_q) = \mathcal{A} / (Z_0^p Z_0^q Z_V^p Z_V^q Z_T^{p-q} Z_+^{p-q}).$$
(5.25)

The *Z* factors represent the influence of various physical phenomena in the collision process. In these equations (5.24 and 5.25), A is the collision cross-reference factor and is given by $A = (r_{p-q}^{c^*}/\sigma_{p-q})^2$. The calculation of $r_{p-q}^{c^*}$ is given later in Equation 5.32.

To account for the orientation of the molecules during the collision process, the steric factors Z_0^p and Z_0^q are used. Thivet et al. [151] cite the expression of Herzfeld and Litovitz to compute the steric factor:

$$Z_0^p = \delta_{p-q}^* r_p + \frac{5}{2} \left[1/(\delta_{p-q}^* r_p)^2 \right]$$
(5.26)

In Equation 5.26, r_p is the interatomic distance of molecule p at the lowest vibrational level. The calculation of δ_{p-q}^* appears in Equation 5.33.

The vibrational factors, Z_V^p and Z_V^q , are given by the following formula when only monoquantum transitions are considered:

$$Z_V^p = \frac{f_m^p}{(i+1)\pi^2} \frac{\mu_{p-p}}{\mu_{p-q}} \frac{\alpha_{p-q}}{\theta_v^p} \left(\frac{k_b \theta_v^p}{\Delta E}\right)^2$$
(5.27)

The mass factor f_m^p is given by $f_m^p = (m_p \bar{C}_p^2)^{-1}$ and $\bar{C}_p^2 = (m_X^2 + m_Y^2)/2m_X m_Y (m_X + m_Y)$. The subscripts *X* and *Y* refer to the individual atoms composing the molecule. The expression for α_{p-q} is

$$\alpha_{p-q} = \frac{16\pi^4 \mu_{p-q} \Delta E^2}{(\delta_{p-q}^*)^2 h^2 k_b}$$
(5.28)

where *h* is Planck's constant and ΔE is dependent on treating V-T or V-V transitions — this is given in Equations 5.35 and 5.36.

The translational factor is calculated using

$$Z_T^{p-q} = \pi^2 \left(\frac{3}{2\pi}\right)^{1/2} \left(\frac{\Delta E}{k_b \alpha_{p-q}}\right)^2 \left(\frac{T}{\alpha_{p-q}}\right)^{1/6} \exp\left[\frac{3}{2} \left(\frac{\alpha_{p-q}}{T}\right)^{1/3} - \frac{\Delta E}{2k_b T}\right]$$
(5.29)

The effect of attractive forces on the transition probability is included in the Z_{+}^{p-q} which is given by the expression

$$Z_{+}^{p-q} = \exp\left[-\frac{4}{\pi} \left(\frac{\epsilon_{p-q}\chi_{p-q}^{*}}{k_{b}T}\right)^{1/2} - \frac{16}{3\pi^{2}}\frac{\epsilon_{p-q}}{k_{b}T}\right]$$
(5.30)

where ϵ_{p-q} is also calculated using Equation 4.68 or 4.69 (see Section 4.6.1). Thivet et al. [151] attribute Equation 5.30 to Shinn. The expression for χ^*_{p-q} is

$$\chi_{p-q}^{*} = \frac{1}{2} \left(\frac{\alpha_{p-q}}{T}\right)^{1/3}$$
(5.31)

At this point, expressions are still required for $r_{p-q}^{c^*}$ and δ_{p-q}^* in order to compute the transition proabilities and from that, the vibrational relaxation times.

Thivet et al. [151] provide the following first-order expressions for $r_{p-q}^{c^*}$ and δ_{p-q}^* :

$$\sigma_{p-q}/r_{p-q}^{c^*} = \left[1/(2\beta)^{1/6}\right] \left[1 + \frac{2}{19}\beta\right]$$
(5.32)

$$\delta_{p-q}^* \sigma_{p-q} = \left[\frac{12}{(2\beta)^{1/6}} \right] \left[1 + \frac{21}{19} \beta \right]$$
(5.33)

where β is

$$\beta = \left[\frac{1}{2} \left(2\epsilon_{p-q}/\mu_{p-q}\right)^9 \left(3h\mu_{p-q}/(\pi^2 \sigma_{p-q} k_b T \Delta E)\right)^6\right]^{1/19}$$
(5.34)

Finally, the expressions for transition probabilities required in Equations 5.21 and 5.22, are:

$$P_{10}(A_p, A_q) = \mathcal{A} / (Z_0^p Z_V^p Z_T^{p-q} Z_+^{p-q}), \quad \text{with} \qquad \Delta E = k_b \theta_v^p$$
(5.35)

and

$$P_{01}^{10}(A_p, A_q) = \mathcal{A}/(Z_0^p Z_0^q Z_V^p Z_V^q Z_T^{p-q} Z_+^{p-q}), \quad \text{with} \qquad \Delta E = k_b (\theta_v^p - \theta_v^q)$$
(5.36)

5.3.4 The curve fit form of Thivet, Perrin and Candel (for V-T transfers)

Thivet et al. [151] found a curve fit to experimental data for vibrational relaxation times for V-T transfers by assuming that the temperature dependence would have the same form as that given by SSH theory. Their curve fit is

$$p(\tau_v^{p-q})_{V-T} = T^{2/3} \exp(BT^{-1/3} - C)$$
(5.37)

where *B* and *C* are constants.

5.3.5 Example calculations of vibrational relaxation times

In this section some example calculations of vibrational relaxation times are provided. These examples make use of the models and formulae introduced in the earlier part of this section. The intent of these examples is to demonstrate the correct implementation of the models previously discussed. No critique is given about the suitability or otherwise of various models for a given problem. Again, the purpose of this section is to verify the implementation; nothing more, nothing less.

N_2 - N_2 V-T relaxation time

Figure 5.1 shows measurements of the relaxation time for V-T transfers in nitrogen gas. These measurements have been made in shock tube studies by Blackman [158], Lukasik and Young [159], and Millikan and White [154]. Four calculations of relaxation time, using the present implementation, are also shown; these employ three different methods. The curve labelled "SSH theory" uses the theory of Schwartz, Slawsky and Herzfeld [156], as shown in Section 5.3.3, to compute the V-T relaxation time. The appropriate input values for the calculation based on SSH theory are given in Table 5.1. Note that the Lennard-Jones distance parameter for the N₂-N₂ potential is adjusted from its actual value to a value of 4.2 Å to give a better fit to the experimental data as suggested by Thivet et al. [151]; the actual value is reported as 3.798 Å by Svehla [149] and 3.749 Å by Hirschfelder, Curtiss and Bird [145]. The approximate curve fit used by Giordano et al. [155] is plotted for two different sets of coefficients: the first is based on fitting the data of Millikan and White, and the second, Blackman's data. The coefficients are shown in Table 5.2. The last curve is the empirical relation given by Millikan and White. The input is based on molecular constants and empirical values which are part of the formula.



Figure 5.1: Relaxation time for N₂-N₂ V-T exchanges. Experimental measurements are from Blackman [158], Lukasik and Young [159], and Millikan and White [154]. The calculations are based on formulae and models by Schwartz, Slawsky and Herzfeld [156], Giordano et al. [155] and Millikan and White [154].

N_2 - O_2 V-V relaxation time

In Figure 5.2, the transition probability for vibrational energy exchange between N_2 and O_2 is shown. Specifically, it is the transition probability for nitrogen to change from its first vibrational state to its ground state while oxygen goes in reverse, from its ground state to its

Interaction parameters					
Colliders	$r_{pq}^0, \text{\AA}$	ϵ_{pq}^{0} , J			
N ₂ -N ₂	4.200	1.102×10^{-21}			
N ₂ -O ₂	3.645	1.157×10^{-21}			
Molecular parameters					
Molecule	N_p	$\Theta_{v,p}$, K	$r_p, Å$		
N ₂	34	3354	1.10		
O ₂	27	2240	1.21		

 Table 5.1: Interaction and molecular parameters for relaxation time calculations using the theory of Schwartz, Slawsky and Herzfeld [156]

Table 5.2: Parameters in approximate formula based on Landau and Teller theory (Equation 5.20) used to compute N_2 - N_2 V-T relaxation times

Fit to data	А	В	С
Blackman [158]	7.12×10^{-9}	124.07	0.0
Millikan and White [154]	1.0	221.35	-24.84

first excited state. The transition probability is plotted instead of relaxation time because it is easy to compare to the available experimental measurements. One can calculate the relaxation time from the transition probability by using Equation 5.22; the relaxation time has a pressure dependency which comes in with the collision frequency term, Z_{coll}^{p-q} . The experimental measurements in Figure 5.2 were made by Breshears and Bird [160], White [161], and Kamimoto and Matsui [162]. The calculations were made using SSH theory as presented in Section 5.3.3. The input parameters for this calculation are displayed in Table 5.1. The Lennard-Jones potential parameters for the N₂-O₂ interaction were computed using the combining laws in Equations 4.68 with the value for $r_{N_2-N_2}^0$ taken as 3.749 Å; the adjustment to 4.2 Å is only needed to N₂-N₂ (as in the previous example).

O₂-O V-T relaxation time

The final example, the calculation of relaxation times for O₂-O V-T exchanges, demonstrates the use of Thivet, Perrin and Candel's curve fit [151]. Thivet et al. introduce this curve fit because the SSH theory is not applicable for interactions involving open shell atoms. Figure 5.3 shows the experimental measurements of Kiefer and Lutz [163] and Breen et al. [164] compared to the curve fit. The parameters for Equation 5.37 are B = 55.2 and C = 26.95, giving the formula for $\tau_v^{O_2-O})_{V-T}$ as:

$$p(\tau_v^{p-q})_{V-T} = T^{2/3} \exp(55.2T^{-1/3} - 26.95)$$
(5.38)



Figure 5.2: Transition probability, $P_{0,1}^{1,0}(N_2, O_2)$, for V-V exchange. Experimental measurements are from Breshears and Bird [160], and White [161], and Kamimoto and Matsui [162]. The calculations are based on the model by Schwartz, Slawsky and Herzfeld [156].

5.4 Coupling of chemistry and vibrational nonequilibrium

As mentioned in the opening of this chapter, one of the mechanisms of vibrational energy change is due to a chemistry effect. As vibrational species are depleted or replenished by various chemical reactions, there will be a tendency to alter the average vibrational energy of that vibrational species. This is because the selection of molecules that react will tend to have a different average vibrational energy compared to the entire collection. For example, dissociation of molecules will preferentially occur from higher vibrational energy levels, thus leaving a lower average vibrational energy among the unreacted molecules. At the same time, the presence of thermal nonequilibrium affects the rate of chemical reactions. When the vibrational temperature and translational temperature are different, chemical reactions tend to occur at a different rate than if the temperatures were in equilibrium at the translational temperature. This is because the average vibrational state of the collection of molecules affects their propensity to undergo a successful reaction during a collision process. Consider again a compressive flow field and molecules undergoing dissociation. Immediately behind the shock, the translational temperature is high but the vibrational temperature is still frozen at the pre-shock value. It is more difficult to dissociate these molecules with low vibrational energy than the equivalent collection of molecules with a vibrational temperature equal to the translational temperature. If it is more difficult, then the reaction proceeds slower. This slowed reaction rate can be modelled by an appropriate modification to the equilibrium reaction rate. In this section, the modelling of this chemistry-vibration coupling phenomena is discussed.

There are a number of models available in the literature which treat the general problem



Figure 5.3: Relaxation time for O₂-O V-T exchanges. Experimental measurements are from Kiefer and Lutz [163] and Breen et al. [164]. The calculations use the curve fit proposed by Thivet et al. [151].

of chemistry-vibration coupling and the more restricted problem of vibration-dissociation coupling (see Chapter 4 in Volume I of Chernyi et al. [165]) but only a smaller subset are commonly used in CFD for hypersonic flows. Olejniczak and Candler [166] provide a review and comparison of three models: Park's [167] model, the CVDV model of Marrone and Treanor [168], and the model of Macheret and Rich [169]. Olejniczak and Candler found that by comparing the experimental shock detachment distance in a flow of nitrogen it was not possible to assess the validity of the various models; all models accurately computed the shock detachment distance. Their paper concluded with no clear consensus on which model to adopt for hypersonic flows. Knab, Frühauf and Messerschmid [170], in 1995, presented a general model for chemistry-vibration coupling. Their model extended the work of Marrone and Treanor [168] by including the coupling effect for reactions other than just dissocations, that is, it was extended for exchange reactions also. Knab et al. called their model the CVCV model. This model has been used in this thesis work as it arguably has a better physical basis than other models, for example Park's two-temperature model [167], and it treats both dissociation and exchange reactions in a consistent manner.

5.4.1 Influence of vibrational nonequilibrium on reaction rates

In 1963, Marrone and Treanor [168] presented a model that treats the influence of vibrational nonequilibrium on the reaction rates for dissociation. Their model uses the assumption that dissociation reactions are more likely to occur from molecules in higher vibrational levels. Their model uses a parameter, U, which they call the characteristic probability temperature. This parameter, U, is an indicator of the tendency towards preferential dissociation from higher levels; at $U = \infty$, there is an equal probability of dissociation from all levels. Using the model

of Marrone and Treanor, the equilibrium value for the dissociation rate is modified by a factor which accounts for the nonequilibrium, Ψ (in Marrone and Treanor's paper they notate this value as *V*), thus the modified rate is:

$$k = k^{EQ}(T)\Psi(T, T_{v,i})$$
(5.39)

where $k^{EQ}(T)$ is calculated based on the translational temperature and using some model for the reaction rates at thermal equilibrium; in this work, the generalised Arrhenius form is used (see Equation 4.25). Marrone and Treanor give the following expression for the nonequilibrium factor Ψ :

$$\Psi(T, T_{v,i}) = \frac{Q_{v,i}^{D_i}(T)Q_{v,i}^{D_i}(\Gamma_i)}{Q_{v,i}^{D_i}(T_{v,i})Q_{v,i}^{D_i}(-U_i)}$$
(5.40)

where U_i is a parameter of the model, and the pseudo-temperature Γ_i is:

$$\frac{1}{\Gamma_i} = \frac{1}{T_{v,i}} - \frac{1}{T} - \frac{1}{U_i}$$
(5.41)

In Equation 5.40, *Q* is the vibrational partition function which in general form is:

$$Q_{v,i}^{Y}(T) = \frac{1 - \exp(-Y/(\mathcal{R}T))}{1 - \exp(-\Theta_{v,i}/T)}.$$
(5.42)

Here Y is a dummy variable for dissociation energy.

Knab, Frühauf and Messerschmid [170] extended the model of Marrone and Treanor [168] to include exchange reactions. Thus, the model of Knab et al. treats dissociation and exchange reactions in a consistent manner in a single model. The general form for the nonequilibrium factor, Ψ , given by Knab et al. is:

$$\Psi(T, T_{v,i}) = \frac{Q_{v,i}^{D_i}(T)}{Q_{v,i}^{D_i}(T_{v,i})} \times \frac{\exp(-\alpha A/(\Re T))Q_{v,i}^{\alpha A}(\Gamma_i) + Q_{v,i}^{D_i}(T_i^0) - Q_{v,i}^{\alpha A}(T_i^0)}{\exp(-\alpha A/(\Re T))Q_{v,i}^{\alpha A}(-U_i) + Q_{v,i}^{D_i}(T_i^*) - Q_{v,i}^{\alpha A}(T_i^*)}$$
(5.43)

The additional pseudo-temperatures are defined as:

$$\frac{1}{T_i^0} = \frac{1}{T_{v,i}} - \frac{1}{U_i}$$
(5.44)

and

$$\frac{1}{T_i^*} = \frac{1}{T} - \frac{1}{U_i} \tag{5.45}$$

The expression for Ψ in Equation 5.43 is valid for both dissociation and exchange reactions; the value of *A* differs based on the type of reaction considered. Thus, for dissociation reactions, $A = D_i$; for exchange reactions, $A < D_i$; and for reverse reactions, $A \approx 0$. In Equation 5.43, α and U_i are parameters of the model: they are selected based on calibration against experimental data.

Section 5.4

5.4.2 Influence of chemical reactions on vibrational relaxation

The other aspect of modelling chemistry-vibration coupling is the calculation of the influence of chemical reactions on the average vibrational energy of the molecular species. This effect appears as term 10 in Equation 2.5. It is customary to write the rate of vibrational energy change as ([151,171]¹):

$$Q_{\text{Chem}-V_i} = \sum_{j=1}^{Nr} \left[-G_{va,ij} \frac{1}{f_i} \left(\frac{df_i}{dt} \right)_f + G_{app,ij} \frac{1}{f_i} \left(\frac{df_i}{dt} \right)_r \right]$$
(5.46)

Inspection of Equation 5.46 shows that its value is undefined when $f_i = 0$. In this work, a different form of expression has been used: one that allows us to make some comments about an appropriate treatment when f_i is very small (approaching zero). This expression may be derived by considering a collection of N_1 molecules all of the same type. Each molecule has a certain vibrational energy but on average the energy is e_1 , J/particle. First consider what happens to the average vibrational energy as some of the molecules "vanish" due to chemical reactions, that is, dissociate into atoms. An energy balance my be written for the average vibrational energy before and after some small time increment Δt :

$$N_1 e_1 = N_2 e_2 + (N_1 - N_2) e_{va}$$
(5.47)

In Equation 5.47, N_2 are the number of molecules remaining after the small time increment, e_2 is the average vibrational energy of the remaining molecules and e_{va} is the average vibrational energy of the molecules which vanished during the time increment. Note it is assumed that $N_2 < N_1$ because we are considering the case where molecules vanish. It is desirable to find an expression for $\Delta e = e_2 - e_1$; the working for this follows.

$$N_2 e_2 = N_1 e_1 - (N_1 - N_2) e_{va} (5.48)$$

$$= N_1 e_1 - (N_1 - N_2) e_{va} + N_2 e_1 - N_2 e_1$$
(5.49)

$$= (N_1 - N_2)e_1 - (N_1 - N_2)e_{va} + N_2e_1$$
(5.50)

$$N_2 e_2 - N_2 e_1 = (N_1 - N_2) e_1 - (N_1 - N_2) e_{va}$$
(5.51)

$$e_2 - e_1 = (e_1 - e_{va})(N_1 - N_2)/N_2$$
 (5.52)

By a similar derivation, an expression for the change in average vibrational energy over a small time increment, Δt , due to the molecules "appearing" is, assuming $N_2 > N_1$:

$$\Delta e = (e_2 - e_1) = (e_{app} - e_1)(N_2 - N_1)/N_2$$
(5.53)

By summing over all reactions which involve molecules of species *i*, the expression for change of vibrational energy for species *i* over a small time increment, Δt , is:

$$\Delta e_{i} = \frac{1}{N_{2}} \sum_{j=1}^{Nr} \left[(e_{va,j} - e_{i}) \Delta N_{ij,f} + (e_{app,j} - e_{i}) \Delta N_{ij,r} \right]$$
(5.54)

¹Treanor and Marrone [171] actually present this equation in terms of mole fraction instead of mass fraction as shown here. Thivet et al. [151] argue that Treanor and Marrone's use of mole fraction is incorrect; Thivet et al. show this in Appendix B of their paper [151].

In Equation 5.54, all of the energy terms are in J/particle. It remains for us to find expressions for $e_{va,j}$ and $e_{app,j}$. The evaluation of $\Delta N_{ij,f}$ and $\Delta N_{ij,r}$ come directly from solving the chemical kinetic ODE in mass-conserving form. This is discussed at the end of this section.

The values for $e_{va,j}$ and $e_{app,j}$ need to be modelled. The modelling basically addresses the following questions: (a) as molecules "vanish", what is the average vibrational energy of those vanishing molecules based on the present thermodynamic state — $e_{va,j}$; and (b) as molecules "appear", what is the average vibrational energy of those appearing molecules based on the present thermodynamic state — $e_{app,j}$. The coupling models for chemistry-vibration interactions also provide expressions for these energy terms. As we saw with the nonequilibrium factor Ψ in Section 5.4.1, the model of Knab et al. [170] is a more general extension of the work of Treanor and Marrone [171].

Knab et al. [170] give an expression for the average energy of a vanishing molecule, $G_{va,i}$, in J/mole (Equation (38) in [170]); the expression here is in J/kg:

$$G_{va,i} = \frac{\exp(-\alpha A/(k_B T))Q_{v,i}^{\alpha A}(\Gamma_i)L_i^{\alpha A}(\Gamma_i) + Q_{v,i}^{D_i}(T_i^0)L_i^{D_i}(T_i^0) - Q_{v,i}^{\alpha A}(T_i^0)L_i^{\alpha A}(T_i^0)}{\exp(-\alpha A/(k_B T))Q_{v,i}^{\alpha A}(\Gamma_i) + Q_{v,i}^{D_i}(T_i^0) - Q_{v,i}^{\alpha A}(T_i^0)}$$
(5.55)

where α and U_i are the same model parameters as those that appear in Equation 5.43. The energy value in J/kg may be converted to J/particle as $e_{va,i} = G_{va,i} \times \mathcal{M}/\mathcal{N}_A$, where \mathcal{N}_A is Avogadro's number. This equation is valid for both dissociation and exchange type reactions. The function *L* which appears in Equation 5.55 is:

$$L_{i}^{Y}(T) = \frac{R\Theta_{v,i}}{\exp(\Theta_{v,i}/T) - 1} - \frac{RY/k_{B}}{\exp(Y/(k_{B}T)) - 1}$$
(5.56)

This is the expression for the vibrational energy of a truncated harmonic oscillator.

The expression for the vibrational energy of an appearing molecule turns out to be the same for both dissociation and exchange reactions. It is function of translational temperature only and is found by evaluating Equation 5.55 with $T_{v,i} = T$, that is:

$$G_{app,i} = G_{va,i}^{EQ}(T) \tag{5.57}$$

We return now to discuss the calculation of $\Delta N_{ij,f}$ and $\Delta N_{ij,r}$. In the original form of Equation 5.46, the rate of change of vibrational energy of molecule *i* is dependent upon the rate of change of the molecule, in forward and reverse directions, for each reaction it participates in. There are two approaches to solve this equation based on how the coupling to the chemical kinetic problem is handled. The first approach involves an operator-splitting method: the chemical kinetic ODE is solved and then the rates at the end of the chemical kinetic ODE problem, $(df_i/dt)_f$ and $(df_i/dt)_r$, are used as input to solve the ODE for the change of the vibrational energy. The problem here is that the rates of molecule change are not updated during the solution for the change of vibrational energy. There is also a practical implementation issue to consider. When using a generic ODE solver, one does not usually have access to the derivatives: the return value is the final state. This means it is tedious (not impossible) and incurs

some computational expense to recalculate the rates of species change upon entry to solving the ODE for change of vibrational energy. The second approach is to couple the solution of vibrational energy change with the solution of the chemical kinetic problem. The advantage is that the coupling of the two physical processes is more accurate. This method has its difficulty also. Any advantage of treating the chemical kinetic problem with specialised ODE solvers which exploit the special structure of the equations, like Mott's alpha-QSS method [121] (see Section 4.2.3), is lost; the addition of the vibrational energy equations renders these methods inappropriate. These problems are what lead to the thinking of reformulating Equation 5.46 into Equation 5.54. Note that Equation 5.46 is the time rate of change of vibrational energy but Equation 5.54 gives the actual change with the time increment already included, that is, these equations are not exactly the same but they describe the same problem.

It was alluded to in Section 4.3 which discussed a mass-conserving formulation for the chemical kinetic ODE problem that this method is advantageous for chemistry-vibration coupling problem. We will see now why. In the mass-conserving formulation, we do not solve for the new species at the end of the timestep but rather the molar change per reaction in the forward and reverse directions. At the end of the ODE problem, we are left with a set of values which describe the molar change for each reaction in both directions. These may be used to directly calculate $\Delta N_{ij,f}$ and $\Delta N_{ij,r}$, that is,

$$\Delta N_{ij,f} = \nu_j \gamma_{f_j} \mathcal{N}_A \tag{5.58}$$

$$\Delta N_{ij,r} = -\nu_j \gamma_{r_j} \mathcal{N}_A \tag{5.59}$$

Refer to Section 4.3 (and specifically p. 60) for the definitions of γ_{f_j} and γ_{r_j} . The approach presented here and used in this thesis has its own advantages and disadvantages. While the mass-conserving ODE does not retain the special structure of the normal chemical kinetic formulation, it is still a less troublesome ODE than a hybrid rates of species change/rates of energy change ODE. This approach also fits into existing code frameworks easily because the outputs from the ODE solver are used directly and not the rates. A criticism of the approach is that the coupling of the physics is not as accurate as solving the hybrid problem.

Finally, we discuss the problem when the quantity of a molecular species approaches or is zero. To demonstrate the problem, Equation 5.54 is repeated here:

$$\Delta e_i = \frac{1}{N_2} \sum_{j=1}^{Nr} \left[(e_{va,j} - e_i) \Delta N_{ij,f} + (e_{app,j} - e_i) \Delta N_{ij,r} \right]$$

In practical implementation, errors associated with round-off and representation of accuracy lead to difficulties when N_2 becomes very small in Equation 5.54, and the value for Δe_i is undefined when N_2 is zero. However, at very small N_2 and the associated very small N_1 — we do not admit "large" differences between N_2 and N_1 because we solve over small time increments — the contribution of vibrational energy of this molecular species to the entire energy balance is, arguably, very small. In other words, it is appropriate to neglect this energy change for very small N_2 . Indeed, this is what I have chosen to do in the implementation: if the mass fraction

of a molecular species is less than 1.0×10^{-15} , then its vibrational energy content is neglected in the calculations.

5.5 Verification of the models for vibrational nonequilibrium effects

This section presents some test cases which demonstrate correct implementation of the models for vibrational nonequilibrium effects previously discussed. Each subsequent test case introduces more complexity to the problem. Thus, the first test case computes the simple vibrational relaxation (due to V-T processes only) of chemically inert nitrogen flowing over a cylinder at Mach 6.5. The second test case is also limited to vibrational relaxation only without the added complication of chemistry. However, this second test case has the added complexity of treating V-V processes as well as V-T processes; the case involves the relaxation of chemically inert air behind a shock. The third test case is the calculation of oxygen flow behind a normal shock. The post-shock flow is taken as being in general thermochemical nonequilibrium, that is, chemical and vibrational relaxation, and their coupling, are modelled. Each of these cases are compared to calculations by other researchers. They are idealised problems for the sake of testing the model equations and their implementations.

5.5.1 Flow of nitrogen over an infinite cylinder

In the modelling work for thermal nonequilibrium presented in this thesis, there is a fundamental assumption about the relaxation of thermal states through a series of Boltzmann distributions. Giordano et al. [155] investigated this assumption of vibrational relaxation through Boltzmann distributions by comparing to a detailed vibrational kinetics method. To assess the accuracy of the Boltzmann assumption, Giordano et al. computed the flow of chemically inert nitrogen over an infinite cylinder at Mach 6.5. The detailed kinetic approach involved solution to the master equation for the population distributions of the first 10 vibrational energy levels. The method based on the Boltzmann assumption ascribed to the flow two temperatures: a translational/rotational temperature and a vibrational temperature, with nitrogen treated as a harmonic oscillator. The relaxation rate between the vibrational and translational modes was modelled with the Landau-Teller expression (Equation 5.17), and the relaxation time was computed with Equation 5.20. Giordano et al. found that appropriate selection of the parameters for the relaxation time gave remarkable agreement to the vibrational kinetics method. The authors went on to caution about generalising these results on a blunt body which has a compressive flow field to expanding flows in nozzles.

The test case presented by Giordano et al. [155] is an excellent test case for my own implementation of vibrational nonequilibrium modelling: it has clear, well-defined input; the complexity of the problem is reduced to focus on one physical process, vibrational relaxation; and it provides a solution by a more detailed method which does not rely on curve fits to experimental data. In the work here, the calculations of Giordano et al. for the model of a harmonic oscillator are repeated using two different relaxation times: one based on Blackman's data [158] and the other, Millikan and White's data [154]. Additionally, a calculation is performed with the relaxation time computed using SSH theory [156]. These results from the harmonic oscillator model are compared to the detailed vibrational kinetics model, as was done by Giordano et al.

In this test case, the flow of inviscid, chemically inert nitrogen over an infinite cylinder is computed. The "infinite" nature of the cylinder means that a two-dimensional treatment is applicable. The cylinder has a radius of 1 m. The equilibrium free stream is at Mach 6.5 with $T_{\infty} = 300$ K. There are two cases corresponding to two different free stream pressures: (I) $p_{\infty} = 50$ Pa, and (II) $p_{\infty} = 500$ Pa. The first case, low pressure, gives rise to a large portion of nonequilibrium flow in the post-shock region. The second case, with higher pressure, more rapidly approaches thermal equilibrium. The grid was chosen to match that used by Giordano et al. [155] as closely as possible. There are 40 cells in the radial direction (body normal) and 120 cells tangential to the cylinder wall. The inflow boundary for the grid is based on the Billig correlation [113], but has been extended by 10% to ensure that the grid envelops the bow shock. A depiction of the grid is given in Figure 5.4.



Figure 5.4: Grid and geometry for simulation of an infinite cylinder. The grid has 40 cells in the body normal direction and 120 cells in the body tangential direction. For clarity, only every second grid line is shown.

The vibrational nonequilibrium effect is modelled by using the Landau-Teller equation (Equation 5.17) to account for the exchange of energy between the vibrational and translational/rotational modes of nitrogen, that is, N_2 - N_2 V-T transfers. This is the only energy exchange mechanism considered in this problem. At each of the two conditions (50 Pa and 500 Pa), three simulations were performed, each with a different calculation for the vibrational relaxation time. Two of the calculations replicated the work of Giordano et al. [155]: Equation 5.20 was used with constants based on data of Blackman [158], and of Millikan and White [154]. These constants were given earlier in Table 5.2. The third calculation of vibrational relaxation time, not part of the work by Giordano et al. [155], used SSH theory to estimate the relaxation time for N_2 - N_2 V-T transfers. To reiterate, all of the calculations in the present work use the assumption of a harmonic oscillator relaxing through a series of Boltzmann distributions; what differs is the manner in which the relaxation time is computed.

The results for these simulations are displayed in Figures 5.5 and 5.6 which graph the temperatures along the stagnation streamline. In Figure 5.5, the vibrational energy mode is slow to equilibriate with the translational/rotational energy modes; this is case (I) with the lower free stream pressure. The two modes do not reach equilibrium at the body surface (which is possible in this inviscid model). Case (II), $p_{\infty} = 500$ Pa, is shown in Figure 5.6. In this case, the approach to equilibrium is much more rapid as should be expected for the higher free stream pressure.

The results compare favourably to the detailed vibrational kinetic model used by Giordano et al. [155]. This provides confidence in the implementation of the model for Landau-Teller type relaxation and its coupling to the flow solver. There is some discrepancy in the relaxation of the vibrational model when comparing the detailed model to both the use of the Millikan and White constants [154] and SSH theory [156]. This is not a problem with the implementation but rather the inadequacy of these relaxation time models. This is analogous to the problems with poor reaction rates obscuring the validation of the finite-rate chemistry implementation as discussed in Section 4.5.1. The calculation of relaxation times is the analogue of computing reaction rate coefficients for chemical reactions. Giordano et al. also noted that the relaxation time based on Blackman's data [158] gave much better agreement with the detailed model compared to the fit based on Millikan and White's data. This result, that the fit to Blackman's data does a better job than either the Millikan and White fit or SSH theory, gives rise to a small puzzle. Referring back to Figure 5.1 which displays each of these relaxation time calculations, one could argue that relaxation times based on the Millikan and White fit or SSH theory are a better representation of the experimental measurements. Yet these models, which best fit the experimental data, do not give the best agreement to the detailed kinetic model. This puzzle leads to further questions, which I do not attempt to address here. How reliable are the experimental measurements for relaxation times in N2-N2 V-T exchanges? How well does the vibrational kinetic model validate against experiment?

5.5.2 Relaxation of chemically inert air behind a shock

This test case, like the one before it, ignores the complexity of chemical reactions and treats a problem with only vibrational energy exchange. However, unlike the first case, this case includes the effects of vibrational-vibrational exchanges. This verification problem is taken from Thivet et al. [151]; it involves the computation of the relaxing flow of chemically inert air behind a standing normal shock. The relaxation refers to the equilibriating among the energy modes, namely, the separate vibrational modes of oxygen and nitrogen with the mixture translation-al/rotational mode. In the work of Thivet et al., they repeated this test case three times, using different assumptions: first, assuming chemical relaxation alone (vibrational modes in equilibrium); second, vibrational relaxation with frozen chemistry; and third, general thermochemical relaxation (coupling of chemical and vibrational relaxation). This second case, vibrational relaxation with frozen chemistry, is computed in this section.

The standing shock problem was explained earlier in Section 4.4.2 where the problem of chemically relaxing air was considered. The free stream conditions, ahead of the shock, for this problem are:

$$M_{\infty} = 25.0, \quad T_{\infty} = 205.0 \,\mathrm{K}, \quad p_{\infty} = 2.5 \,\mathrm{Pa}$$



Figure 5.5: Nondimensional temperature profiles along the stagnation streamline for an infinite cylinder with r = 1 m; case (I): $M_{\infty} = 6.5$, $T_{\infty} = 300.0$ K and $p_{\infty} = 50$ Pa. The vibrational kinetic results are taken from Giordano et al. [155]. The other calculations are results from the present work: relaxation time calculated with a Landau-Teller type fit to Blackman's data [158] and Millikan and White's data [154], and application of SSH theory [156] to calculate the relaxation time. T_{tr} denotes the translational/rotational temperature while T_v denotes the vibrational temperature. These values are normalised by the free stream temperature, T_{∞} .

This corresponds to an altitude of 75 km. The composition of air is taken as 21 moles of O_2 and 79 moles of N_2 . Using the Rankine-Hugoniot relations across the shock, with chemistry and vibration frozen, the post-shock conditions are:

$$M_s = 0.38$$
, $T_s = 25001.5$ K, $p_s = 1859.1$ Pa

Thivet et al. [151] considered two cases for this problem: with and without V-V exchange transfers. These same cases are repeated as part of this exercise. In the first case, with V-T transfers only, there are four V-T exchange mechanisms to consider: N_2-N_2 , N_2-O_2 , O_2-N_2 and O_2-O_2 . Note that the N_2-O_2 and O_2-N_2 mechanisms are different; the former is the change of N_2 vibrational energy due to collisions with oxygen molecules while the latter is the change of O_2 vibrational energy due to collisions with nitrogen molecules. When the V-V exchange transfers are considered, along with all of the V-T mechanisms previously mentioned, two additional mechanisms are included: N_2-O_2 and O_2-N_2 . These mechanisms are really just one in the same but they are listed twice for consistency with the implementation. It is convenient, as part of the implementation, to list all of the mechanisms which alter the vibrational state of N_2 (V-T exchanges with N_2-N_2 and N_2-O_2 , and the V-V exchange N_2-O_2) and separately list all of the mechanisms which alter the vibrational state of O_2 (V-T exchanges with O_2-N_2 and O_2-O_2 , and the V-V exchange N_2-O_2) and S_2-N_2 . These mechanisms with O_2-N_2 and O_2-O_2 , and the V-V exchange N_2-O_2) and separately list all of the mechanisms which alter the vibrational state of N_2 (V-T exchanges with N_2-N_2 and N_2-O_2 , and the V-V exchange N_2-O_2) and S_2-N_2 . The sechanges with O_2-N_2 and O_2-O_2 , and the V-V exchange N_2-O_2) and separately list all of the mechanisms which alter the vibrational state of N_2 (N-T exchanges N_2-N_2). For all of the mechanisms, the SSH theory (Section 5.3.3) was used



Figure 5.6: Nondimensional temperature profiles along the stagnation streamline for an infinite cylinder with r = 1 m; case (II): $M_{\infty} = 6.5$, $T_{\infty} = 300.0$ K and $p_{\infty} = 500$ Pa. The vibrational kinetic results are taken from Giordano et al. [155]. The other calculations are results from the present work: relaxation time calculated with a Landau-Teller type fit to Blackman's data [158] and Millikan and White's data [154], and application of SSH theory [156] to calculate the relaxation time. T_{tr} denotes the translational/rotational temperature while T_v denotes the vibrational temperature. These values are normalised by the free stream temperature, T_{∞} .

to calculate the vibrational relaxation times. The input parameters used for the SSH theory calculations are the same as those given in Section 5.3.5 (in particular, see Table 5.1).

The relaxation of the temperatures behind the shock for the case without V-V coupling is shown in Figure 5.7. The vibrational temperatures are frozen through the shock, and thus begin their relaxation from the free stream temperature. The vibrational temperature of O_2 approaches equilibrium more rapidly than the vibrational temperature associated with N₂. The length scales for relaxation of T_{v,O_2} and T_{v,N_2} differ quite markedly; this lends weight to the argument that a multi-temperature model is required to correctly account for nonequilibrium effects in air as opposed to a two-temperature model which would lump the vibrational temperature of O₂ and N₂ into a single pool. Thivet et al. [151] also advance this same argument: "The different scales of evolution of the vibrational states of these two species show that a model with two vibrational temperatures is needed for nonequilibrium air." There are some discrepancies between the present calculations and those performed by Thivet et al., most noticeably in the comparison of vibrational temperature of O₂. A possible source for the discrepancy is the calculation of the relaxation times for V-T exchanges of N₂-O₂ and O₂-N₂. In the paper by Thivet et al., the relaxation times for V-T exchanges of O₂-O₂ and N₂-N₂ are plotted for a range of temperatures (Figures 1 and 2 respectively in that paper). The present calculations for these relaxation times were compared and found to agree identically. However, there are no plots for the relaxation times of V-T exchanges for N_2 - O_2 and O_2 - N_2 and so the present work could not be compared. That is not to say there is definitely disagreement on these relaxation times, rather, it is just not possible to compare. Thus, as stated earlier, this is a possible source of discrepancy between the two calculations of the post shock relaxation process. On the whole, the agreement is good and provides confidence that the present implementation correctly treats the multi-temperature model (in contrast, the previous test case, the infinite cylinder, had only one vibrational temperature).



Figure 5.7: Relaxation of temperatures behind a normal shock in air ($X_{O_2} = 0.21$, $X_{N_2} = 0.79$): $M_{\infty} = 25.0$, $T_{\infty} = 205.0$ K, $p_{\infty} = 2.5$ Pa. In this calculation the chemistry is frozen and only V-T exchanges are considered (no V-V coupling). Also shown are calculations by Thivet et al. [151] (see Figure 5 of their paper).

In Figure 5.8, the same shock relaxation calculation is shown but this time with the V-V exchanges betwen N_2 and O_2 included. The results are, once again, compared to those of Thivet et al. [151]. As in the previous calculation, Figure 5.7, there is generally good agreement between the two calculations. The differences are probably best accounted for by discrepancies in the calculations of the relaxation times. It is difficult to find fault with the present calculations for vibrational relaxation times; the present results compare well to experiment where available. For example, the calculation of transition probability for O_2 - N_2 V-V transitions compared to experiment, shown earlier in Figure 5.2, gives confidence that the relaxation times for V-V exchanges are being correctly computed; the transition probability is used as input to the relaxation time calculation (see Equation 5.25).



Figure 5.8: Relaxation of temperatures behind a normal shock in air ($X_{O_2} = 0.21$, $X_{N_2} = 0.79$): $M_{\infty} = 25.0$, $T_{\infty} = 205.0$ K, $p_{\infty} = 2.5$ Pa. In this calculation the chemistry is frozen but vibrational relaxation is allowed, including V-V coupling between N₂ and O₂. Also shown are calculations by Thivet et al. [151] (see Figure 5 of their paper).

The effect of V-V coupling, that is, the inclusion of V-V exchange transfers, is shown in Figure 5.9; the results of the two preceding calculations are shown on the one graph. The same conclusion is drawn as that made by Thivet et al [151]: the effect of the V-V coupling is to enhance the rate at which the two vibrational states come to equilibrium.

Overall, the calculations of this test case compare well to those by Thivet et al. [151]. These calculations allow for the testing of the vibrational energy exchange mechanisms without the added complexity of chemistry effects. This additional complexity is the subject of the next section.

5.5.3 Relaxation of oxygen behind a shock

The final test case treats the relaxation of oxygen behind a shock. During the relaxation, the oxygen is in a state of general thermochemical nonequilibrium: the gas is simultaneously reacting and vibrationally relaxing. Thus the coupled effects of chemistry and vibrational nonequilibrium need to be considered. This test case exercises the implementation of the model for chemistry-vibration coupling presented previously in Section 5.4.

This test case was first presented by Treanor and Marrone [171] as a demonstration of their model for dissociation-vibration coupling. Thivet et al. [151] use this test case also in their



Figure 5.9: Relaxation of temperatures behind a normal shock in air ($X_{O_2} = 0.21$, $X_{N_2} = 0.79$): $M_{\infty} = 25.0$, $T_{\infty} = 205.0$ K, $p_{\infty} = 2.5$ Pa. The results from Figure 5.7, V-T transfer only, and Figure 5.8, including V-V coupling, are plotted on the one graph for ease of comparison.

paper on a unified model for nonequilibrium hypersonic flows. As in the previous test case, this problem consists of a standing normal shock with relaxing flow in the post-shock region. The free stream flow is 100% diatomic oxygen, O₂. The other species considered in the problem is monatomic oxygen, O, which appears as the oxygen molecules dissociate in the post-shock region. The conditions in the free stream, ahead of the shock, are:

$$u_{\infty} = 7.0 \times 10^3 \,\mathrm{m/s}, \quad p_{\infty} = 22.595 \,\mathrm{Pa}, \quad T_{\infty} = 249.0 \,\mathrm{K}$$

Assuming frozen conditions (for chemistry and vibration) across the shock, the immediate post-shock conditions are:

$$u_s = 1177.45 \text{ m/s}, \quad p_s = 14257.0 \text{ Pa}, \quad T_s = 26427.7 \text{ K}.$$

Due to the vibrational mode being frozen across the shock, the vibrational temperature of O_2 is 249.0 K at the beginning of the relaxation problem.

Thivet et al. [151] used the same kinetic mechanisms as used by Treanor and Marrone [171] so that any observed differences would be due to the modelling and not the rate parameters. That same philosophy is adopted here. The vibrational relaxation time for O_2 is calculated using numerical fits to Blackman's data [158]. Thus Treanor and Marrone give the following

expression:

$$\tau_{v,O_2} p = 1.6 \times 10^{-9} \exp\left(\frac{101.44}{T^{1/3}}\right)$$
atm.s (5.60)

As indicated by the units, the pressure, *p*, used in the expression is given in atmospheres. A single dissociation reaction is considered:

$$O_2 + M \rightleftharpoons 2O + M$$

Treanor and Marrone cite Matthews for the forward dissociation rate constant:

$$k_f = 1.1 \times 10^{25} T^{-2.5} \exp\left(-\frac{59380}{T}\right) \frac{\text{cm}^3}{\text{mole.s}}$$
 (5.61)

It is assumed in the present work that the reverse rate may be computed from the equilibrium constant. Treanor and Marrone make no statement about the reverse rate for this oxygen dissociation reaction.

The relaxation of temperatures behind the shock is shown in Figure 5.10. Note that the vibrational temperature for O_2 does not overshoot the translational/rotational temperature; preventing an overshoot was part of the motivation for Treanor and Marrone's attempt to improve the coupling models for vibration-dissociation interactions [171]. The agreement with the calculations by Thivet et al. [151] is excellent. These results confirm that the implementation of the models for chemistry-vibration coupling by Knab et al. [170], as presented in Section 5.4, is correct. Also shown in Figure 5.10 is the relaxation of temperature for the equivalent single-temperature calculation, that is, dissociating oxygen in thermal equilibrium. This demonstrates that the effect of the vibrational nonequilibrium is to prolong the approach to equilibrium.

As a further check for consistency, a plot of the mole fractions for O_2 and O behind the shock is given in Figure 5.11. The dissociation process is clearly evident: the mole fraction of molecular oxygen, O_2 , decreases, and there is a corresponding increase of monatomic oxygen, O. Also note that the corresponding mole fractions for the single-temperature model are shown. Consistent with the more rapid approach to equilibrium demonstrated by the temperature in Figure 5.10, the dissociation is more rapid for the single-temperature model. In other words, the vibrational nonequilibrium influences the dissociation rate of the oxygen such that its approach to equilibrium is delayed.

5.6 Summary

The correct accounting for the thermal state of the gas feeds directly into calculations of radiating flow fields, that is, the accuracy of radiative transfer calculations is affected by how well the thermal state is quantified. The work in this chapter on the modelling of vibrational nonequilibrium effects provides the groundwork for attempting radiating flow field calculations. The work presented covers the theory of the modelling and verification of the implementation; the validation of this model is hindered by the availablity of reliable experimental data, and is left as future work.

The thermodynamic relations for a mixture of perfect gases with nonequilibrium thermal states was presented in Section 5.1. It is assumed that the energy modes of the components



Figure 5.10: Relaxation of temperatures behind a normal shock with oxygen in general thermochemical nonequilibrium: $u_{\infty} = 7.0 \times 10^3 \text{ m/s}$, $p_{\infty} = 22.595 \text{ Pa}$, $T_{\infty} = 249.0 \text{ K}$. Also shown are calculations by Thivet et al. [151] (see Figure 10 of their paper).



Figure 5.11: Change of mole fractions due to dissociation behind a normal shock with oxygen in general thermochemical nonequilibrium: $u_{\infty} = 7.0 \times 10^3 \text{ m/s}$, $p_{\infty} = 22.595 \text{ Pa}$, $T_{\infty} = 249.0 \text{ K}$.

are separable, and that the various modes have independent Boltzmann distributions, that is, they are described by separate temperature values. Thus, the multi-temperature model presented here has one translational/rotational temperature and one vibrational temperature for each vibrating molecule type in the mixture. The modelling assumes that the various energy modes will relax towards equilibrium through a series of Boltzmann distributions. Two energy exchange mechanisms are considered: vibrational-translational energy exchange (of the Landau-Teller type); and vibrational-vibrational energy exchange (according to the expression of Schwartz, Slawsky and Herzfeld). These were presented in Section 5.2. Each of these exchange mechanisms requires the calculation of an appropriate relaxation time; Section 5.3 presents various methods for the calculation of vibrational relaxation times and discusses where each of these methods are appropriate. The final part of the theory for the modelling treats the coupling between chemistry and vibrational nonequilibrium. There are two aspects to this coupling: the influence that a vibrational nonequilibrium state has on the reaction rate; and how the chemical reactions alter the vibrational energy state. The modelling for this part of the problem is based on the work of Knab et al. [170].

The final section of this chapter showed how the implementation has been verified. Three test cases have been attempted with each test case introducing an extra piece of complexity to the problem. The first test case, the flow of chemically inert nitrogen over an infinite cylinder, only considers one exchange mechanism: the vibrational-translational energy exchange. This test case was first performed by Giordano et al. [155]. The present work agrees very well with detailed calculations made by Giordano et al; the detailed calculations can be considered as a reference solution. The discrepancies were attributed to the model for relaxation times rather than any problems with the implementation. The next test case, Section 5.5.2, added one additional complexity to the simulation, and that was, the inclusion of vibrational-vibrational energy exchange. This test case considered the vibrational relaxation of chemically inert air behind a shock. The present work was compared to calculations made by Thivet et al. [151]. On the whole the agreement is good. It is suspected that the observed discrepancies are due to differences in the calculation of relaxation times. The final test case, relaxation of dissociating oxygen behind a shock, treated the problem of general thermochemical nonequilibrium. In this case, the agreement with the calculations of Thivet et al. [151] is excellent. These verification test cases provide confidence that the modelling has been correctly implemented. The future work in this area will focus on validation of the model by comparing to appropriate experiments.

Applications

In Chapters 4 and 5 the development work on models for thermochemical nonequilibrium was presented; this chapter discusses the applications of that development work, that is, the range of calculations which make use of the models for thermochemical nonequilibrium. At the very beginning of the discussion (Section 1.4), it was stated that there were two direct benefits of this thesis work: a longer term benefit, providing a foundation for modelling of radiating flow fields; and an immediate benefit, the simulation of flows in impulse facilities. That immediate benefit is the subject of this chapter: two "demonstration" calculations of expansion tube flows are presented as examples of application of this work.

The work on modelling chemical nonequilibrium — the finite-rate chemistry model — has had considerable use during the course of this project. At the beginning of this work, general codes for computing the influence of chemistry in compressible flows were not widely available or easily obtainable.¹ There were implementations of specific models, such as models for dissociating nitrogen or reacting air, but not generalised implementations to treat an arbitrary mixture of gases. Yet over the years, the interest in reacting gases in the hypersonic regime has continued to grow, now including mixtures containing carbon dioxide (the atmospheres of Mars and Venus); hydrogen and helium (the Jovian atmosphere); and methane and nitrogen (the Titan atmosphere). Thus a general chemistry code with easy user input was a desirable addition to the local modelling capabilities. The implementation of a finite-rate chemistry module as part of this work has been used in a number of calculations over the course of this project: one-dimensional simulations of expansion tube flows (Stewart [172] and Chiu [173]); two-dimensional (axisymmetric) simulations of expansion tube flows (Chiu [173], Jacobs et al. [174], Scott [175], Brandis et al. [176] and Gollan et al. [177]); in the analysis of results for radiation measurements on blunt bodies (Capra [178]); and as part of studies on modelling turbulent boundary layers with heat release (Denman [179]).

More recently, the general thermochemical nonequilibrium model (finite-rate chemistry with vibrational nonequilibrium) has been used in calculations of carbon dioxide flows in an expansion tube facility (Potter et al. (2007) [180] and Potter et al. (2008) [181]). These are the first CFD calculations to quantitatively assess the extent of vibrational nonequilibrium in the test gas of an expansion tube flow.

¹This statement is still true at the time of writing.

In this chapter, I will focus on just two of these applications: the calculations in the paper by Brandis et al. [176] and those presented in the paper by Gollan et al. [177]. The content presented here draws heavily from the aforementioned papers, but it only uses content which was the original contribution of myself. Any exceptions to this, that is works that are not directly my own, are noted in the subsequent text. The first simulation (Section 6.2) is of the operation of the X2 facility in expansion tunnel mode in order to estimate the free stream conditions for an experiment with a gas representing a Titan-like atmosphere. The second simulation (Section 6.3) is of the operation of the X2 facility in nonreflected shock tube mode, again with a Titan-like gas, in order to assess the suitability of the flow for optical measurements of flow field radiation. Thus, the two simulations share a common theme: both simulate a reacting mixture of nitrogen and methane in order to replicate the Titan atmosphere. The two simulations also exhibit contrast: the first simulates experiments on subscale models, and the second simulates experiments with flows at true flight densities. The differences between these two types of experiment and the associated changes to operation of the X2 facility are the subject of the next section.

6.1 Description of expansion tube facilities and experiments

Extreme flow speeds, in excess of 10 km/s, are required for the testing of atmospheric-entry vehicles in wind tunnels. The operation of a continuous wind tunnel producing the requisite flow speeds is problematic for pragmatic reasons. First, it is difficult to design a facility that would bear the sustained heating rates to the tube walls from "long-lived" hypersonic bound-ary layers. Second, the energy requirements for continuous operation are fiscally prohibitive. Thus, impulse facilities are attractive for testing at hypersonic speeds.

There are two types of impulse facilities used for hypersonic testing: shock tunnels and expansion tubes/tunnels.² Of these, the expansion tube has the capability to produce flows at the speeds required for testing of atmospheric-entry vehicles. In essence, a shock tunnel relies on a reflected shock to stagnate some test gas. This test gas is allowed to expand, that is, accelerate through a hypersonic nozzle to produce a test flow. After the nozzle has started, the nozzle flow is effectively steady (in normal operation). The expansion tube, in contrast to the shock tunnel, does not stagnate the flow. The acceleration of test gas is achieved by an unsteady expansion into a low density region as the shock propagates down the tube. Ideally, the gas is never stagnated in the expansion tube process, and that is the essential difference between the two types of facility. Because the gas is never stagnated, the expansion tube can realise higher dynamic pressures; at no point is the total pressure of the test gas physically contained in the facility. Also, because the gas is never stagnated, the gas does not lose energy to radiation; the radiation of the stagnated gas in a shock tube limits the achievable speeds. In both facility types, shock tunnels and expansion tunnels, there must be some means to produce the initial

²Strictly speaking the expansion tube is a straight-through tube arrangement, while the expansion tunnel has a nozzle at the end of the acceleration tube. I will use the terms interchangably when talking about the facilities in a general sense. I will, however, adhere to the strict definition when referring to specific experiments in the X2 facility.

shock which drives the process. At the University of Queensland, the free piston driver is the favoured technique for shock production.

There are three expansion tube facilities at the University of Queensland. In order of their commissioning, and physical size, they are: X1, X2 and X3. The following discussion will focus on the specifics of the X2 facility, though the principles of operation are the same in all three facilities. In the present experiments performed on radiating flow in X2, the facility is operated in one of two modes: expansion tube/tunnel and nonreflected shock tube mode.

In expansion tube/tunnel mode, experiments are performed on subscale models of aeroshell configurations. Because the models in the experiment are scaled, the flow conditions also require appropriate scaling to maintain similarity between the experiment and the true flight conditions. If the velocities of the two flows (flight and experiment) are matched, then one tries to keep the binary scaling parameter, ρL , constant to ensure flow similarity. The use of the binary scaling parameter is valid for flows with chemistry effects, in which the dominant chemical reactions are binary interactions — this is the case for hypersonic blunt body flows of interest. There is an upper limit to the efficacy of the binary scaling parameter for ensuring flow similarity: for shock layer flows that emit (and absorb) appreciable amounts of radiation, the binary scaling argument fails. The details of scaling arguments for hypersonic blunt body flows with radiation and the influence on experimental testing are given by Capra and Morgan [182]. The essence of those arguments is as follows. On a true flight vehicle, the heat transfer to the vehicle surface comprises two components: convective heating and radiative heating. For the sake of argument, assume that convective heating contributes 30% to the overall heating and the radiative heating accounts for the remaining 70%. Now consider a subscale model for testing in an expansion tube and consider these statements about heat transfer scaling for a flow that retains ρL similarity: (1) the scaling of convective heating with nose radius goes as $R^{-1/2}$; and (2) the amount of radiative heating (not the proportion) remains constant. This leads to the important conclusion that the heat transfer to the subscale model will be in different proportions compared to the true flight vehicle; the convective heating component increases, while the radiative heating component remains constant. For example, the convective heating component may now account for 95% of the surface heating and the radiative heating only 5%. Because the proportions of the heat transfer modes are changed, there is a direct effect on the flow field: it is no longer similar to flow about the true flight vehicle. This argument is related to the Goulard number or what Anderson Jr. [7] calls the radiation loss parameter, $\Gamma = E_s \delta / \frac{1}{2} \rho_\infty V_\infty^3$, where E_s the radiative energy emitted immediately behind the shock in all directions per second per unit volume and δ is the shock detachment distance. It is not possible to retain similarity with the Goulard number when using the binary scaling parameter, ρL . This is not to say that subscale experiments for flows with radiation are of no value; merely, we must be mindful of how the scaling will affect the experimental design and the limits of what can be measured.

When it is necessary to study a radiating flow field at exact flight conditions, the expansion tube may be operated in nonreflected shock tube mode. When using nonreflected shock tube mode, there is no subscale model placed in the test flow. Instead, the object of observation is the relaxing flow immediately behind the shock as it propagates into the test gas. It is helpful to think of this type of experiment as observing the bow shock that is driven by the aeroshell. (There is no actual aeroshell driving the shock, rather just high pressure gas generated in the shock tube.) The two types of experiment, subscale testing in expansion tube mode and direct observation in nonreflected shock tube mode, are shown in Figure 6.1.



Figure 6.1: Schematic representation of types of experiments performed in X2 for the study of radiating blunt body flows. *This figure is provided courtesy of Dr Peter Jacobs.*

Figure 6.2 shows a schematic of the X2 facility and a wave diagram of the flow process. The representation in Figure 6.2 corresponds to use of the facility in expansion tunnel mode. The test gas which eventually passes over the model (or in this diagram, the Pitot rake), initially resides in the shock tube. The gas initially at rest in the acceleration tube is called the accelerator gas. In the diagram, t = 0 corresponds to the rupture of the primary diaphragm; at this point the 35 kg piston is nearing the end of its stroke. The primary diaphragm is made of mild steel. Its thickness is varied according to the desired rupture pressure. The rupture of the diaphragm produces a shock, labelled the primary shock. This shock travels through the shock tube compressing and accelerating the test gas. The secondary diaphragm is only very light and so ruptures when the primary shock arrives. The secondary shock propagates into the acceleration tubes, with its faster speed a consequence of the lower density medium. The compressed test gas now expands, in an unsteady manner, into the acceleration tube. This expansion process drives the low pressure accelerator gas before it. This interface between test gas and accelerator gas is marked as the contact surface. The amount of test gas expansion is controlled by the presence of the accelerator gas, that is, a lower pressure accelerator gas gives rise to larger amounts of expansion. The steady test time, as indicated in Figure 6.2, is limited by the arrival of a u + a wave from the centred expansion. For further details about the principles of expansion tubes see the works of Neely and Morgan [183] and Morgan [184].



Figure 6.2: A schematic of the X2 facility configured for expansion tunnel operation. A wave diagram (x - t diagram) shows the flow process. *Source: Figure 2 from Potter et al.* (2008) [181]

The X2 facility is operated as a conventional shock tube when used in nonreflected shock tube mode. Figure 6.3 shows a schematic of the facility and a wave diagram for the flow process. Prior to t = 0, the piston compresses the driver gas which is often a mixture of helium and argon. The rupture of the diaphragm corresponds to t = 0 in Figure 6.3. After diaphragm rupture, the shock then propagates into the shock tube which contains the test gas. The experiment involves making optical measurements of the radiating flow as the shock emerges from the shock tube and into the test section. The section of the flow labelled test time in Figure 6.3 distinguishes this mode of operation from the expansion tunnel mode: for the nonreflected shock tube mode, the gas immediately behind the primary shock is of interest whereas for the expansion tunnel mode, the test gas has been previously "gathered up" in the shock tube and allowed to expand in the accelerator tube. The designation of test gas between the two modes of operation. In the experiments using nonreflected shock tube mode only a small portion of the test gas is of interest, namely, the nonequilibrium radiating gas immediately behind

the shock.



Figure 6.3: A schematic of the X2 facility configured for nonreflected shock tube operation. A wave diagram (x - t diagram) shows the flow process. *This figure is provided courtesy of Carolyn Jacobs*.

Numerical simulations aid the expansion tube testing by estimating a full set of flow properties that are not directly measurable. For example, numerical simulations help to establish the set of flow conditions in the test gas when operated in expansion tunnel mode. This is important because these are the flow conditions which form the free stream flow for the subscale model; subsequent analysis of the experiment depends on reliable estimates of the free stream flow conditions. An example simulation for a condition in the X2 facility, operated in expansion tunnel mode, is given in Section 6.2. The simulations of nonreflected shock tube operation are used to estimate the spatial variation of flow properties along the optical path used for radiation measurements; this type of simulation is the subject of Section 6.3.

6.1.1 Motivation for experiments associated with Titan entry

In the introduction to this thesis (in particular, Section 1.2), the problems of obtaining reliable estimates for heat transfer to aeroshells were discussed. The quote by Giordano made as recently as 2007 [9] shows that state-of-the-art estimates of thermal loads on entry vehicles are still far from ideal (see page 5 of this work). One specific problem for the aerothermal research community is the estimation of heating in the nonequilibrium shock layer typical of entries into the Titan atmosphere.

For a proposed mission to Titan as part of NASA's In-Space program, current best knowledge CFD simulations indicate that the radiative mode will dominate the heat transfer [88]. The calculations performed to date [88, 90] suggest that this dominating radiation heat transfer is due to the presence of the cyanogen molecule, CN, formed during the dissociation of nitrogen and methane behind the shock. The exact composition of Titan's atmosphere is still the subject of study but results from the recent Huygens entry probe measured a methane composition of 1.41% mole fraction at altitudes above 150 km [185]. Previous estimates of vehicle heat transfer used an engineering model of the Titan atmosphere that assumed a mole fraction for methane of 5% [186]. This upper value for methane composition provided a conservative estimate of radiative heating load for heatshield design purposes, and, in the case of the Huygens probe, a successful entry was executed based on this value [1].

Despite the uncertainties in exact methane composition, cyanogen is such a strong radiator that the nonequilibrium kinetics of its formation are still worthy of study. To accurately quantify the radiative heating requires a theoretical model which can: a) calculate the chemical kinetics of CN formation and describe the population of excited states; and b) couple the effect of radiative absorption/emission with the kinetics of populating/de-populating excited states. Therefore it is desirable to have accurate experimental data of the shock-heated radiative emission as a means of validating and assessing the theoretical treatment of the problem.

This provision of data on nonequilibrium radiation is the underlying motivation for both types of experiments which are discussed in Sections 6.2 and 6.3.

6.2 Simulation of X2 operated in expansion tunnel mode

In this section, the numerical simulations of the X2 facility used in expansion tunnel mode are presented. The motivation for the experimental work was previously discussed in Section 6.1.1.

The work presented in the paper by Brandis et al. [176] is on the establishment of operating conditions suitable for studying Titan aeroshell flows. Note that the work is preliminary, leading to the final goal of experimental measurements of the Titan aeroshell flow field. This preliminary work, reported in the paper [176], is solely concerned with demonstrating an appropriate operating condition which can achieve test flows of relevance to Titan entry problems. Previous experiments at the University of Queensland in the X3 expansion tube investigated the feasibility of using expansion tubes to measure radiative heating (Capra [178]). At the conditions of these experiments, the free stream flow was sufficiently hot such that all of the methane was dissociated. The primary focus of the paper by Brandis et al. is to report

Reservoir fill pressure	1.65 MPa gauge	
Driver tube fill pressure	480 mbar	
Driver gas	33.5% Ar, 66.5% He (by volume)	
Primary diaphragm	1.6 mm cold rolled steel	
Shock tube fill pressure	29 kPa	
Test gas (initially in shock tube)	95% N ₂ , 5% CH ₄ (by volume)	
Acceleration tube fill pressure	15 Pa	
Acceleration gas	air	

Table 6.1: Operating conditions in X2 for an experiment with the Titan-like atmosphere gas in expansion tunnel mode (Shot 99)

on the development of a 'colder' Titan gas condition with the aim of minimising the amount of dissociated methane in the free stream and thus, better simulate the true flight conditions. Part of the work involved numerical simulations of the operating conditions. The CFD analysis aids the experimenters by providing estimates for the flow properties of the test gas that are not directly measurable. This section reports on those numerical simulations; they serve as a demonstration of the finite-rate chemistry work applied to a large-scale CFD simulation. These calculations using the finite-rate chemistry module are able to assess the state of chemical nonequilibrium of the test gas, that is, the question about levels of free stream methane dissociation can be directly addressed.

6.2.1 Target test condition and operating condition

Takashima et al. [187] have analysed a proposed trajectory for a Titan aerocapture vehicle and identified certain cases of interest. For example, case 3 is the point of maximum heating on the trajectory and case 4 is the point of maximum dynamic pressure. The work of Brandis et al. [176] has attempted to develop conditions in the X2 facility that approximate cases 3 and 4. We focus here on what Brandis et al. identify as condition 1. This condition produces a test gas with a free stream velocity of approximately 6000 m/s. This is close to the target velocity of 5760 m/s for case 3. The other conditions for case 3 (of Takashim et al.) are as follows: $M_{\infty} = 22.7$, $\rho_{\infty} = 1.49 \times 10^{-4} \text{ kg/m}^3$, and $p_{\infty} = 6.91 \text{ Pa}$.

Based on some preliminary simulation work with L1d [93], a set of operating conditions were devised. These operating conditions are shown in Table 6.1. The values in Table 6.1 are used as the initial inputs for the numerical simulations which will be discussed in the next section. We will use the numerical simulations to make an assessment about the relevance of these conditions; this follows in Section 6.2.3.

6.2.2 Numerical simulation procedure

The calculations reported here apply to the X2 facility when operated in expansion tunnel mode. This corresponds to the arrangement indicated in Figure 6.2 and the experiments on subscale models shown in Figure 6.1. The numerical simulation of the expansion tunnel is an

important part of characterising the free stream flow which is applied to the subscale model. This free stream flow is estimated from a mix of direct measurements and calculations. Parameters that can be directly measured are the initial fill pressures and temperatures, the shock speeds, Pitot pressures at the end of the nozzle and the static pressures at a number of locations in both the shock tube and acceleration tube. The shock speeds and static pressures in the acceleration tube are used to check the numerical simulation.

In this work, the X2 facility has been simulated by the same method used by Jacobs et al. [174] for their work on the X3 facility. The simulation is performed in two parts: (1) a one-dimensional simulation computes the flow in the driver tube and shock tube, and (2) an axisymmetric calculation is used to compute the flow in the acceleration tube, through the nozzle and into the dump tank. Referring to Figure 6.2, the first part of the method simulates the piston motion, the rupture of the primary diaphragm and the propagation of the primary shock in the shock tube until the point of secondary diaphragm rupture. For this one-dimensional part of the simulation the L1d code [93] is used. This part of the calculation assumes equilibrium chemistry using a look-up table for the thermodynamic properties generated with the CEA code [38]. The one-dimensional part of the calculation is continued beyond the point of secondary diaphragm rupture so as to provide transient input for the second part of the calculation. The history of the flow just upstream of the secondary diaphragm location is used as a transient inflow condition for the second part of the simulation. Thus, the second part of the method simulates the propagation of the secondary shock down the length of the acceleration tube and through the nozzle (refer again to Figure 6.2). For this second part, a viscous axisymmetric calculation is performed of the unsteady expansion process down the acceleration tube and through the nozzle using mbcns [91,92]. Due to significant boundary layer growth in this part of the flow, the one-dimensional assumption used in the shock tube is no longer valid. We are interested in estimating the free stream conditions, including the level of recombined methane. For this reason, a single temperature, finite-rate chemistry gas model is considered as presented in Chapter 4. The flow dynamics and chemistry source terms are loosely coupled using the timestep-splitting approach. The chemistry source terms are integrated with the quasi-steadystate method by Mott [121]. The chemical kinetic scheme used is the reduced scheme recommended by Gökçen [188]; this scheme is listed in Appendix C.3.1. We have ignored argon as this is not used in the test gas presently. We have also ignored all of the ionisation reactions. We did not include ionisation, which may be significant in this flow, because the transport properties for ionised gases are poorly understood. The error for not including ionisation was no worse than the uncertainties introduced by its inclusion. Thus 13 species are considered in the flow: N_2 , CH_4 , CH_3 , CH_2 , CH, C_2 , H_2 , CN, NH, HCN, N, C, and H.

The thermodynamic properties for each of the species have been taken from the curve fits recommended by McBride and Gordon [38]. These curve fits assume that internal energy modes are fully excited at a single temperature and thus model a thermally perfect gas. Individual component viscosities are calculated using the curve fits provided by McBride and Gordon also. The mixture viscosity is calculated as per the formulae in Section 4.1.2, but those

species with mole fractions which are less than 1.0×10^{-3} have been neglected in the mixture. This was done to circumvent the lack of viscosity data in the CEA database for CH3, CH2, CH, CN, and NH. We expect this assumption to have little influence on the mixture viscosity as it will be dominated by molecular nitrogen.

The results of the numerical simulation are presented in the next section where they are compared to the directly measured quantities.

6.2.3 Simulation results

First we examine the one-dimensional simulations.³ The results of the one-dimensional simulation of the shock tube compare favourably with the results based on recorded shock speed. This is indicated in Figure 6.4 which shows a comparison of static pressure at three locations down the shock tube (those locations are indicated in Figure 6.2). There is a discrepancy in the pressure rise for the first pressure measurement. When scaled to 80% of its value, the scaled value and trend agrees well with the numerical simulation. Given that the trend (and not the actual value) agrees so well, there could be some experimental calibration issue for this pressure transducer.



Figure 6.4: A comparison of measured and simulated pressure histories in the shock tube.

The calculations for the second part of the method, viscous axisymmetric calculations, were performed on three grids: a coarse, medium, and fine grid. For the coarse grid, 4000 cells were used axially and 40 cells radially; for the medium grid, 6000 cells axially and 60 cells radially; and for the fine grid, 9000 cells axially and 90 cells radially. In all cases, the discretisation of

³These one-dimensional simulations are not the work of the author. This work was done by Aaron Brandis, as was stated at the beginning of the thesis under the heading of "Contributions of Work by Others".
Form of estimate	shock speed (m/s)
experiment	5806
axisymmetric modelling: mbcns	
coarse grid	5710
medium grid	5715
fine grid	5624

Table 6.2: Shock speed estimates at the end of the acceleration tube based on pressure transducers located at at4 and at5.

the cells in the radial direction is clustered towards the wall of the tube. The computational domain includes all of the acceleration tube and nozzle. A small portion (0.1 m) of the down stream end of shock tube is included also; this is the point where the history of flow from the one-dimensional simulation is applied as an inflow boundary condition.

Figure 6.5 shows a comparison between the simulation and the experimental measurement of static pressure at three locations in the tunnel: at3, at5 and the end of the nozzle. The simulation results shown are those performed on the finest grid. The values agree closely for each of the traces. The time of shock arrival has been adjusted so that the shock is coincident at station at3. Examination of at5 and the nozzle exit shows that the simulation computes a greater extent of shock speed attenuation than what is observed in the experiment. The largest discrepancy in shock speed throughout the enitre expansion process is about 5%. A demonstration of the grid convergence is shown in Figure 6.6 which compares the numerical results for pressure histories for the three grids. An estimate of the shock speed at the end of acceleration tube can be made by use of the static pressure data recorded at at4 and at5 (see Figure 6.2); Table 6.2 displays these estimates based on the experimental measurement and the numerical simulations. The estimate of shock speed from the coarser simulations (coarse and medium) give better agreement with the experimental data than the fine resolution calculation; this is considered spurious. The relative error of shock speed estimate at the end of the acceleration tube between the fine grid calculation and the experiment is approximately 3%; this is considered good enough to provide confidence in the numerical simulations. We can use these simulations, therefore, to estimate the flow conditions, that is, the test gas free stream properties at the end of the nozzle.

Figure 6.7 shows the history of various flow properties at the exit plane of the nozzle. This is the gas that forms the free stream for the subscale aeroshell models. The properties of the test gas are estimated by averaging over 50 μ s of quasi-steady flow, from t = 1.2-1.25 ms. The following conditions are estimated, based on the fine resolution calculations and taking the data near the nozzle centreline: $M_{av} = 18.8$, $p_{av} = 96.6$ Pa, $T_{av} = 211$ K, and $u_{av} = 5763$ m/s. The average composition is given in Table 6.3. The history for some selected species is shown in Figure 6.7(f). Note that the free stream composition is far from the desired equilibrium: the methane (CH₄) fraction is quite small and a comparatively larger fraction of HCN has formed.



Figure 6.5: A comparison of measured and simulated pressure histories in the acceleration tube and nozzle. The zero-offset for the experimental measurements and the numerical simulations differ because the numerical simulation was started at the time of secondary diaphragm rupture. Thus, the time for the simulated results has been adjusted so that the shock arrival at at3 coincides with the experimental trace at that location.



Figure 6.6: A comparison of simulated pressure histories based on grids of three different resolutions.

Table 6.3: Estimate of free stream composition (species mass fractions) for Titan-like atmosphere test gas in expansion tube experiments

N ₂	CH ₄	CH ₃	CH ₂	СН	C ₂	H ₂
0.9452	$3.14 imes 10^{-5}$	$1.58 imes 10^{-7}$	$3.20 imes 10^{-8}$	$6.29 imes 10^{-10}$	$2.53 imes10^{-8}$	$5.47 imes 10^{-3}$
CN	NH	HCN	Ν	С	Н	
$4.16 imes10^{-7}$	$1.23 imes 10^{-13}$	$4.92 imes 10^{-2}$	$3.24 imes 10^{-14}$	$1.00 imes 10^{-11}$	$4.07 imes 10^{-5}$	



Figure 6.7: Simulated history of flow properties at the nozzle exit. These results are from the calculations on the fine grid. To give an indication of the flow uniformity in the radial direction, the flow history at three radial locations is plotted.

6.2.4 Discussion of results

The numerical simulations have provided an estimate of the free stream conditions. This discussion considers those free stream conditions and what they mean for experiments on subscale aeroshells. Two items are discussed: the required subscale model size based on the free stream estimates; and how the extent of free stream nonequilibrium affects the usefulness of this condition.

The free stream estimates for velocity and density can be used to determine the size for the subscale model by basing that determination on the binary scaling parameter. (This ignores the difficulties of scaling for flow fields with appreciable radiation as described in Section 6.1, but as a first attempt, binary scaling is a reasonable start.) The target flight condition is case 3 as identified by Takashima et al. [187]: $M_{\infty} = 22.7$, $\rho_{\infty} = 1.491 \times 10^{-4} \text{ kg/m}^3$, $p_{\infty} = 6.91 \text{ Pa}$, and $u_{\infty} = 5.76 \text{ km/s}$. Fortunately, the estimate of free stream velocity for the test gas, 5.76 km/s, matches that of the nominal flight condition, so no adjustment for velocity is required. The binary scaling parameter, ρL , is $5.218 \times 10^{-4} \text{ kg/m}^2$; this is based on a flight vehicle with a diameter of 3.5 m and a free stream density of $1.491 \times 10^{-4} \text{ kg/m}^3$. Using the estimated free stream density for the test flow, $1.43 \times 10^{-3} \text{ kg/m}^3$, the appropriate length for the subscale model is 0.365 m. This presents a significant problem for experimental testing of subscale models at this condition: the usable core flow of test gas has a diameter of only approximately 0.1 m. It may be possible to scale the fill pressures in the tunnel such that the shock speed remains constant but the density of the test gas is increased. This would allow for smaller subscale models, ones that fit within the usable test flow core.

Next we discuss how the effect of free stream nonequilibrium affects the usefulness of this test condition. The original motivation for investigating a 'colder' Titan condition (as compared to previous work in X3 [178]) was the hope that more of the dissociated methane could be recovered at colder temperatures, however, it was uncertain if there would be enough time for recombination to occur during the unsteady expansion process. In Figure 6.7(f) it appears that HCN is completely frozen and very little methane has been able to recombine. As the majority of carbon is frozen in the HCN, there is little chance for any methane to reform. This result is somewhat unfortunate in that complete chemical similarity of the expansion tube flow with the flight condition, at chemical equilibrium, does not seem possible.

Despite the fact that chemical similarity is not identical, we believe that there is still value in subscale model testing in expansion tube flows. As mentioned earlier, the main problem for CFD analyses of the Titan hypersonic flows is the modelling of the strong CN radiator and its coupling to the gas dynamics of the shock layer flow. We argue that the nonequilibrium free stream flow produced in the expansion tube gives rise to a radiating flow which is CN dominated in the blunt body shock layer similar to that which would be produced by an equilibrium free stream. In other words, for the purposes of producing a blunt body shock layer with CN present as a strong radiator, it does not seem to matter if the free stream is in equilibrium or nonequilibrium. ⁴

⁴The nature of the 'nonequilibrium' in that statement requires some qualification. Specifically, we refer to a

To demonstrate the argument in the previous paragraph, consider the following thought experiment. Take the predicted free stream conditions at a certain velocity, temperature and pressure. For example, we use the estimates of free stream properties based on the coarse grid calculations: $u_{\infty} = 5717 \text{ m/s}$, $T_{\infty} = 210 \text{ K}$, and $p_{\infty} = 113 \text{ Pa}$. With these conditions, the chemically reacting flow behind a steady normal shock is computed using the same technique as described in Section 4.4.2 but the free stream composition is varied. In the first case, we use the desired situation of chemical equilibrium at the given pressure and temperature, and in the second case, we take the nonequilibrium composition predicted by the simulations. The inviscid nonequilibrium flow behind a steady normal shock is equivalent to the flow along the stagnation streamline of a blunt body in the immediate post-shock region, before there is appreciable deceleration of the stagnation streamline flow as it approaches the body. Thus the normal shock flow is representative of the gas dynamic environment in the vicinity of the subscale model during testing. In what follows, we use the terms equilibrium and nonequilibrium to refer to the nature of the free stream flow and not the post-shock flow, which will surely be in thermochemical nonequilibrium. The results of this thought experiment, that is, the two calculations with differing free stream compositions, are shown in Figures 6.8 and 6.9 which show the spatial variation of various flow properties behind the shock.



Figure 6.8: Post-shock CN density and length integated value of CN for two different free stream conditions: one in equilibrium and the other in a nonequilibrium state as calculated in the simulations.

Figure 6.8 compares the density of CN and the integrated value with respect to length for the two cases: equilibrium composition and nonequilibrium composition. The length relates to

chemical nonequilibrium caused by shocking and subsequently unsteadily expanding a test gas that initially had the correct equilibrium composition.



Figure 6.9: Post-shock temperature and velocity for two different free stream conditions: one in equilibrium and the other in a nonequilibrium state as calculated in the simulations.

the distance behind the normal shock. The result for CN density is particularly encouraging; this shows that almost equivalent amounts of CN are produced in both bow shock flows even though they have followed different reaction paths to get to the equivalent density level. The equilibrium case involves a number of steps that requires the breaking down of the methane molecule whereas the nonequilibrium case involves a single step to break HCN and form CN. Less than 1 mm behind the shock, the density of CN is roughly equal, regardless of the pre-shock composition.

Figure 6.9 shows the comparison of post-shock temperature and velocity for the two cases. These results further support the argument that there is much in common in the post-shock region of the two flows, despite starting with different free stream compositions.

The nonequilibrium flow should also be expected to replicate the same physics in terms of excitation of CN as the flow with an equilibrium free stream would. The excitation of CN is directly proportional to the number of particle collisions. Given that the total density and temperature are similar, there will be similar numbers of collisions with the CN molecule giving rise to equivalent excited state populations.

Finally, we argue that the emitted radiant energy in the flow will be similar for the two cases, and this is of most interest from the perspective of using expansion tube testing for the study of radiating flows. The similarity of the emitted radiation follows from the density of CN being similar in both flows. Emitted radiation for the Titan aerocapture flows is proportional to the product $\rho_{CN}L$ (if we consider CN the dominant radiator) where *L* can be taken as the shock layer thickness. Figure 6.8 shows that the integral under the density curve for CN, that is, the

value of $\rho_{CN}L$ (right axis), agrees well for both cases.

6.2.5 Concluding remarks

Although the investigation of a 'colder' Titan condition did not yield a test gas free stream with a composition in chemical equilibrium, we believe there is still value in testing with these conditions, but corrected to increase the free stream density. This is because the free stream flow, once processed by the bow shock, exhibits almost identical properties less than 1 mm behind the shock, including the same levels of CN density regardless of the free stream composition. The increased free stream density is required so that appropriately sized subscale test models can be used in the X2 facility. The ultimate aim still remains to take measurements of heat transfer on the model surface, and, thereby, provide data against which to validate the models of the flow physics.

The contribution of the work in this thesis has allowed these large-scale simulations of the expansion tube with the inclusion of finite-rate chemistry effects to be attempted for the first time. This has directly addressed the question of free stream composition which was previously not possible. Additionally, the analysis of the chemically relaxing normal shock flow, also a contribution of this thesis, has allowed us to assess how detrimental (or otherwise) a nonequilibrium free stream is for subscale model testing of radiating flows. The answer: the nonequilibrium free stream is not detrimental to producing the flow features of interest.

6.3 Simulation of X2 operated in nonreflected shock tube mode

As a different approach to studying the same problem of nonequilibrium radiating flow (associated with entry into Titan), the X2 facility has also been use in nonreflected shock tube mode. In this mode, the facility emulates the same post-shock conditions that the true flight vehicle would generate behind the normal part of the bow shock, that is, the same velocity and density.

Bose et al. [189] provide a review of key shock tube studies of radiative emission specifically for the CN molecule. They identify work related to the Huygens mission and also Mars entry missions. The main difficulty with the use of the data for validation from these earlier studies is that the experiments were conducted at somewhat higher pressures (above 200 Pa) than the condition of interest for the proposed Titan mission, which has a peak heating point on the trajectory where the free stream has a pressure of approximately 15 Pa and a velocity of 5.1 km/s [189]. At higher pressures, the approach to an equilibrium state is much more rapid and so the data is not particularly useful for validating models for nonequilibrium excited state population kinetics.

We restrict our attention therefore to more recent experiments that have been performed at lower pressures. In the same paper, Bose et al. [189] describe a series of experiments in the Electric Arc Shock Tube (EAST) at the NASA Ames Research Centre. The experiments were performed with a gas mix of $N_2/CH_4/Ar$ and the shock was driven into pressures ranging from 13.3–133.3 Pa at speeds from 5–9 km/s. Spectrograph imaging allowed the recording of spectrally and spatially resolved intensities for these tests.

At the University of Provence, Marseille, a series of experiments have been performed in

the TCM2 shock tube facility by Rond et al. [190]. This study was conducted at a shock speed of 5.5 km/s and at pressures of 50, 200, and 1100 Pa. The measurement technique allowed for the determination of time-resolved absolute intensities of radiative flux in the post-shock region of gas.

At the University of Queensland, in the X2 facility, a series of experiments has been initiated to study a low pressure Titan-like atmosphere condition. In particular, a condition suggested at the Radiation of High-temperature Gases in Atmospheric Entry Workshop [191] is being investigated — TC2-T1. This condition is being investigated at other facilities also. Our motivation is to provide a complementary and independent set of data for this condition.

The focus of this section is to describe a numerical simulation technique that is used to analyse the flows produced in our experimental facilities. We use this technique to simulate the current campaign of experiments at the TC2-T1 condition. Numerical simulations aid the wind tunnel testing by estimating a full set of flow properties that are not directly measurable. We aim to simulate the propagation of the shock into the test section in order to estimate the spatial variation of flow properties along the optical path used for the radiation measurements.

The preliminary part of the gas flow including, the piston dynamics, is treated by a quasione-dimensional model. The results of a one-dimensional simulation are used as input to a viscous axisymmetric simulation of the shock propagation through the shock tube and into the test section. This technique was first demonstrated by Jacobs et al. [174] in a simulation of an air condition at approximately 8 km/s in the X3 expansion tube facility. This technique was also used extensively in the thesis by Scott [175] in his study of air and Titan-like atmosphere gas conditions in the X2 facility. In this previous work, the simulation technique was applied to "normal" expansion tube operation. In the current work, the technique is applied to a nonreflected shock tube mode and finite-rate chemical effects for a Titan-like atmosphere gas are simulated in the axisymmetric part of the calculations. Thus the calculations here serve as a second demonstration of the modelling work contributed by this thesis.

6.3.1 Description of experiment

The X2 facility is nominally a free-piston driven expansion tube. In the experiments described here the facility is operated as a "classical" shock tube in a nonreflected mode of operation. A 35 kg piston travels through the driver tube of 4.5 m length with a bore of 0.257 m. The shock tube is 3.71 m and the acceleration tube is 5.70 m long. The bore for both the shock and acceleration tubes is 85 mm. In the shock tube arrangement (see Figure 6.10(a)), there is no barrier for the flow between the shock tube and acceleration tube — these tubes are connected giving an effective shock tube length of 9.41 m.

The experiment aims to produce a shock speed of 7 km/s into low pressure gas at 80 Pa. The experimental shots for this condition are labelled as *x2s197* and *x2s198*. The operating conditions for these shots are shown in Table 6.4.

The instrumentation for these shots included wall pressure sensors along the length of the tube as indicated in Figure 6.10(a). A Pitot pressure sensor was located in the test section at approximately 4 cm downstream of the shock tube exit accounting for tunnel recoil and at

Reservoir fill pressure	1.15 MPa gauge
Compression tube fill pressure	300 mbar (30000 Pa)
Test gas pressure	80 Pa
Primary diaphragm burst pressure	15.5 MPa
Reservoir gas	air
Driver gas	5.5% Ar, 94.5% He (by volume)
Test gas	95% N ₂ , 5% CH ₄ (by volume)

Table 6.4: Fill conditions in X2 for an experiment with the Titan-like atmosphere gas in nonreflected shock tube mode

a radial height of 28 mm above the centreline of the flow. Additionally radiation data were gathered with a photodiode and a photomultiplier which focused on a region of the flow at the same axial location as the Pitot probe but 28 mm below the centreline. The experimental setup is shown in Figure 6.10(b).

6.3.2 One-dimensional simulation

The one-dimensional simulation presented here are not the work of the author but rather of Carolyn Jacobs. They are included in this discussion to help complete the picture of the simulation technique; the output from these one-dimensional simulations form the input for the axisymmetric simulations.

Quasi-one-dimensional simulations were completed using the L1d code [93]. The code provides viscous simulations of the gas flow in a variable-area duct and models the piston dynamics. A number of gas slugs, pistons and diaphragms can be modelled in L1d using a Lagrangian formulation for the gas slugs, with second order accuracy in both space and time. Flow in one dimension only is calculated and changes in duct area are assumed to be gradual. Boundary layers are approximated by the addition of wall shear stress to the momentum equation and heat transfer to the energy equation.

The L1d computational results are used as both an aid in developing the experimental operating conditions and as input to the axisymmetric simulations. In the hybrid technique for complete simulation of the facility, the results of the one-dimensional simulation are used at the point in time of primary diaphragm rupture. The hot driver gas between the piston face and primary diaphragm is used as input initial conditions for the axisymmetric simulation.

For the one-dimensional simulations, four slugs of gas are used, as shown in Figure 6.10(a). These slugs model the reservoir gas, the driver gas and the test gas (two slugs). The test gas is split into two slugs; the gas initially in the shock tube and the acceleration tube respectively, both at the same conditions. In the model, the piston is initially stationary in the firing position. A diaphragm is positioned at 4.81 m and given a hold time of 5 μ s once the burst pressure is reached. A gas interface is placed between the slugs of test gas in the shock and acceleration tubes. At the reservoir end, the initial boundary is set to a stationary wall, and at the end of the acceleration tube the boundary is set to a free end. Two loss regions with a head loss coefficient



Figure 6.10: (a) X2 geometry for L1d simulations; (b) Pictorial view of the test-section in X2 *Figure* (*b*) *provided courtesy of Dr David Buttsworth*

of 0.35 are added at the changes in area. The initial temperature of all gas slugs is 296 K.

6.3.3 Axisymmetric simulation: method and results

In order to include the effects of boundary layer development and nonequilibrium chemistry, viscous axisymmetric simulations were performed with the code mbcns [91]. The Titan test gas is treated as a mixture of thermally perfect gases of which 13 component species are considered: N₂, CH₄, CH₃, CH₂, CH, C₂, H₂, CN, NH, HCN, N, C, and H. An additional two species, Ar and He, are present in the simulation to represent the driver gas. Note that the argon is part of the driver gas only whereas the test gas is the mixture of 95% N₂/5% CH₄ reported in Table 6.4. The details of thermodynamic and transport properties calculations were presented earlier in Chapter 4. The CH₄, CH₃, CH₂, CH and NH species are all present in mole fractions less than 1.0×10^{-3} and thus were ignored when computing mixture properties for viscosity and thermal conductivity. The flow solver is coupled to the finite-rate chemistry module by using the operator-splitting approach. The reduced chemical kinetic scheme recommended by Gökçen [188] has been used but the ionisation reactions have been ignored. This scheme is listed in Appendix C.3.1. The ionisation reactions have little influence on the blunt body shock layer flow [88] and this should hold for the direct simulation of the propagating shock in the experimental flow.

The computational domain is shown in Figure 6.11. The blocks shown in the tube and dump tank region were further subdivided giving a total of 130 blocks. The calculation is performed in parallel on up to 65 processors. The centreline is treated as a symmetry condition. The remainder of the boundaries are specified as fixed temperature walls at 296 K with the exception of the right-hand end of the domain. Since only part of the dump tank is modelled, an outflow boundary condition is used there. In the simulations presented here, that boundary will have no influence as the simulation is terminated before any flow reaches the right end. Blocks 0, 1 and 2 are initially filled with high pressure, high temperature driver gas. The conditions for this gas are taken from the one-dimensional simulations computed using L1d. The initial con-



Figure 6.11: Computational domain for axisymmetric calculations

dition for the remaining blocks is the Titan-like atmosphere test gas at a pressure of 80 Pa and assumed temperature of 296 K. The discretisation of the domain consists of 3000 cells axially and 30 cells radially in the shock tube for the low resolution calculations. The discretisation of the remainder of the domain was chosen to give cells of approximately equal dimension to those in the shock tube. At this coarse discretisation level, a total of approximately 11 605 CPU hours were required to simulate 1.4 ms of flow. Because the calculation was performed in parallel (using 65 processors), the wall clock time was about 178 hours (a little over a week).

Table 6.5 gives a comparison between the experimentally recorded shock speed and the numerical estimates. The comparison of shock speeds between experiment and simulation is one indicator of how well the simulations are approximating the experimental flow. The errors for the simulations given in Table 6.5 are quite high. Unfortunately the accuracy is limited by grid resolution and the modelling assumptions inherent in the L1d calculation. In terms of grid resolution, the width of a finite-volume cell for the low resolution calculations is approximately 3 mm and thus the transducer can only be located to within \pm 3 mm for the axisymmetric simulations. The L1d calculations consistently estimate a higher driver gas temperature due to the model of heat transfer being essentially convective. The effect of a higher driver gas temperature, finite-rate calculations estimate a shock speed of 7.20 \pm 0.3 km/s which is within the uncertainty for the experimental values.

This calculation also shows good agreement with the pressure values recorded at the wall of the shock tube just before the exit into the test section. This is shown in Figure 6.12. The noise present in the simulation would appear to be a numerical artifact. This noise is substantially diminished in the high resolution calculation (twice the number of cells axially) for the equilibrium gas when compared to the low resolution calculation. An interesting result is the poor performance of the equilibrium gas calculations in terms of shock speed estimate. This result suggests that the equilibrium gas assumption is inappropriate for these conditions and that a finite-rate chemistry gas model should be used to simulate these flows. Due to the size of the calculation, a high resolution calculation for the finite-rate gas has not been completed at the time of writing.⁵ However, the good agreement for the low resolution calculation means

⁵Doubling the grid resolution in each dimension of the two dimensions increases the number of cells by four. At the same time, the allowable time step approximately halves for this explicit scheme. The cumulative effect is

Form of estimate	shock speed (km/s)		
experiment			
x2s197	6.95 ± 0.1		
x2s198	7.04 ± 0.1		
one-dimensional modelling: L1d2	7.35 ± 0.4		
axisymmetric modelling: mbcns2			
finite-rate: low res.	7.20 ± 0.3		
equilibrium: low res.	8.18 ± 0.3		
equilibrium: high res.	8.00 ± 0.3		

Table 6.5: Comparison of shock speed estimates. The error bounds are based on spatial and temporal sampling resolution.

that we can apply these results to analyse the flow in test section.

One of the issues the numerical simulations aimed to address was the question of flow uniformity behind the shock as it enters the test section. As the shock emerges from the tube (where the flow is contained by the tube walls), it undergoes a sudden expansion. The effect of that sudden expansion takes a finite amount of time to influence the core of the flow, and that finite time for information propagation is a function of the sound speed. The question the experimenters would like the answer to is how far the planar shock front persists as the shock emerges from the tube. This knowledge influences where the optics should be focused during the experiment. Figure 6.13 depicts the flow field (numerically computed) at a short time after the shock has emerged. Some flow features are identified in Figure 6.13 that are pertinent to the following discussion: the planar shock front; the reverse shock formed as expanding flow around the corner decelerates into the slower moving curved shock front; the Mach cone which divides the flow into a region which is "aware" of the sudden expansion and a region which is not; the contact surface (1) between the test gas and driver gas; the contact surface (2) between the test gas which was initially in the tube and the gas which was initially in the test section; the developing boundary layer; and the nonequilibrium radiating region which is of most interest for the experiments.

The development of the flow as the shock emerges from the tube is shown by means of contour plots in Figure 6.14: contours of pressure, Mach number, temperature, and density of CN. These plots are from the simulations using the finite-rate chemistry model and only show a small fraction of the full computational domain. At t = 1.365 ms the shock has just emerged from the tube.⁶ Five microseconds later, t = 1.370 ms, there is still a large portion of planar shock flow, though the influence of the centred sudden expansion is evident. The Mach

an 8-fold increase in compute time; so one week's compute time on a coarse grid would become eight weeks on a grid of double resolution. Even at 1.5 times the resolution of the coarse grid, the compute time becomes more than 3 weeks.

⁶These times are based on the results from the numerical simulation. In the axisymmetric part of the numerical simulations, t = 0 corresponds to the bursting of the primary diaphragm.



Figure 6.12: Comparison of experimental and simulated pressure history at transducer locations at4 (x = 12.675m) and at5 (x = 12.855m). The experimental data is taken from shot *x2s197* and the simulation results are for the finite-rate chemistry simulation.



Figure 6.13: Contour plots of various flow properties with flow features marked at t = 1.380 ms. In the top image, contact surface 1 refers to the diffuse interface between the driver gas and test gas. Contact surface 2 refers to the interface between the test gas which was initially in the tube and the gas which was initially in the test section (dump tank).

cone which bounds the disturbance propagation can be seen in the contours of Mach number and temperature. (The propagating "disturbance", in this sense, is the termination of the tube wall.) Later at t = 1.375 ms the planar portion of the shock has diminished to an appreciable extent, and by t = 1.380 ms the shock front is completely curved. Based on these simulations, the recommendations for the experimenters are to focus on the emergent flow within 1 tube diameter length from the end of the tube; after this distance the planar shock front is disturbed too much by the sudden expansion. Presently, the experiments are in the preliminary stages of development and the details of what and how much of the flow is "seen" by the optics are still being quantified. The results here give a guide as to how much of the radiating flow emerging from the shock is usable for the purposes of experimental measurements.

A further demonstration of the radial flow uniformity, that is, how planar the shock is, is given in Figure 6.15. The profiles in Figure 6.15 show the axial variation of temperature and the density of CN at various radial locations. These profiles are taken at t = 1.370 ms. Also shown is a comparison with a space-marching calculation (using a code called poshax which is the name given to the code which solves the problem discussed in Section 4.4.2). Again this result is encouraging for the experimentalists as it identifies a region (radially) in the core flow with largely uniform conditions. The calculation from the space-marching method is better able to capture the detailed post-shock relaxation as it does not suffer from the diffusion to due operator-splitting present in the mbcns calculations. For future simulations of the nonreflected shock tube mode, it would appear that a combination of one-dimensional modelling (L1d) and steady flow space-marching analysis (poshax) is more useful than the large-scale axisymmetric simulations. However, the present axisymmetric simulations are still useful in terms of assessing the uniformity of the core flow.

6.3.4 Concluding remarks

In this work we have demonstrated a numerical simulation technique that models the nonreflected shock tube mode of the X2 facility. This technique uses a one-dimensional model to simulate the flow from the piston launch through to the rupture of the primary diaphragm. The hot driver gas, computed by the one-dimensional simulation, is used as input for a viscous axisymmetric calculation. We showed that the results are influenced by the type of gas model and that a chemical nonequilibrium gas model is most appropriate. This calculation is the first to simulate the flow of a reacting Titan-like atmosphere gas in a large-scale simulation of a shock tube facility.

There are a few issues related to the numerical modelling we hope to address in future work. These include a high resolution calculation using the finite-rate model and calibration of the one-dimensional model in terms of its convective heat transfer model.

6.4 Summary

Each of the "demonstration" calculations presented in this chapter have their own concluding remarks. So rather than belabour those points, it should suffice to remind the reader briefly about the purpose of this chapter. The work reported in this chapter shows some applications



Figure 6.14: Development of the flow as the shock emerges from the tube. The left column shows contours of pressure (logarithmic scale), and the right column, contours of temperature.



Figure 6.14: (continued) Development of the flow as the shock emerges from the tube. The left column shows contours of Mach number, and the right column, contours of CN density (logarithmic scale).



Figure 6.15: Profiles through the emerging shock at various radial locations at t = 1.37 ms.

of the model development work which was presented in earlier parts of the thesis. To that end, two particular simulations were discussed both pertaining to the X2 expansion tube: a simulation of the facility operated in expansion tunnel mode; and a simulation of the facility when used as nonreflected shock tube. In both cases a Titan-like atmosphere test gas was used, and thus the finite-rate chemistry model was used to correctly account for the extent of chemical nonequilibrium in the flows.

Conclusion

In the introduction to this thesis, the general blunt body problem was presented. It was stated that one important aspect of this problem is providing accurate estimates of surface heat transfer. One approach to the problem is through the use of numerical simulation: one attempts to solve for the shock layer flow which surrounds the blunt body, and thereby extract estimates for heat transfer at the surface. The computation of the surrounding shock layer flow is a challenging problem in itself. This flow field is complex due to the interplay of a number of physical phenomena such as chemical and vibrational nonequilibrium, radiative heat transfer and surface catalycity effects. The work in this thesis has concentrated on just two of these phenomena: the modelling of chemical nonequilibrium, and the modelling of vibrational nonequilibrium. This work is a contributing step towards the complete numerical solution of aeroshell-type flow fields.

The specific aims of the thesis were listed in the Introduction and are repeated here:

- 1. to implement a model for the treatment of gas flows in chemical nonequilibrium,
- 2. to implement a model for the treatment of gas flows in thermal nonequilibrium,
- 3. to implement a model that treats the coupling between chemical and thermal nonequilibrium and
- 4. to use the models of high-temperature gas dynamics to simulate expansion tube operation.

With these aims in mind, we may now summarise how the presented work addressed these aims.

Chapter 2 provided a general background to the hypersonic blunt body flow problem. The governing equations for a multi-temperature flow were given and discussed. The remainder of this chapter focussed on how these governing equations can be solved numerically. The research progress of the aerospace community on the blunt body problem was discussed from its historical beginnings through to the state-of-the-art: beginning with inverse problems; then a paradigm shift with the move to time-dependent solutions; the evolution of finite-volume methods from finite-difference methods, initially as a means for better solution efficiency; and as the flow solving technology matured, the inclusion of high-temperature effects such as

chemical and thermal nonequilibirum, and radiative transfer. It was noted that despite the quite substantial progress, there are still large uncertainties in the base flow field calculations and the derived results like surface heat transfer, particularly when radiative transfer is included. Thus, the review suggested that there is scope for improvement in the area of aeroshell modelling. It also placed the current work on thermochemical nonequilbrium modelling in the context of the work that has come before it; the current work seeks to use the most "physically consistent" engineering models of high-temperature nonequilibrium gas effects.

The compressible flow solver, mbcns, was provided "as is" for this project; this thesis work sought to extend the program by including models for chemical and vibrational nonequilibrium. Chapter 3 introduced the flow solver and reported on the underlying algorithms and methods which it employs. As part this project work, the flow solver was verified with modern techniques: the Method of Manufactured Solutions verified the spatial order of accuracy in a shock-free flow; and the Method of Exact Solutions verified the solver for treatment of flows with multiple species and embedded shocks (that is, the shock-capturing reconstructors). The flow solver was validated by calculation of shock detachment distances on spheres fired into noble gases and comparing these to experiment. This was an important demonstration because later work in the thesis relies on the code's ability to accurately capture the shock detachment distance; this measure is used later to validate the high-temperature modelling.

The first aim listed above, the implementation of a model for chemical nonequilibrium, was addressed in Chapter 4. The background theory was presented along with verification and validation exercises. The verification work involved two cases: a simple H₂-HI-I₂ batch reactor with an analytical solution for the evolution of species concentration; and the chemically relaxing flow of air behind a strong shock. The second of these two cases exposed one of the difficulties in using "older" reaction rate data from the literature: the reaction rate data is closely coupled to the thermodynamic data. In other words, one should ensure that the reaction rate data which is being used is consistent with the thermodynamic data in use. The validation cases were the calculation of ignition delay times in hydrogen-air systems and the calculation of shock detachment distances for spheres fired into air. The former showed how the choice of reaction data influences the assessment of validity, while the latter showed why one experimental measurement taken in isolation does not necessarily imply a valid model. In the case of Lobb's measurements for shock detachment distance, it is possible to choose a single condition that may fortuitously agree with numerical simulation. However, comparison over the whole range of conditions provides a stronger argument for validity of the model. Finally, this chapter presented the initial work on the inclusion of multicomponent species diffusion. The species diffusion problem goes hand-in-hand with chemical nonequilibrium, in that both of these phenomena become important for the same flow regimes.

The second and third aims of this thesis were addressed in Chapter 5. This chapter discussed the modelling related to vibrational nonequilibrium effects. The modelling itself was pressented as three subproblems: (1) how to calculate the rates of energy exchange between various thermal modes; (2) how to calculate the vibrational relaxation times which influence energy exchange rates; and (3) how to couple the effects of chemistry and vibrational relaxation. A series of test cases with increasing complexity was used to verify the implementation. The first case looked at the vibrationally relaxing flow of chemically inert nitrogen over an infinite cylinder. This case was the simplest of the three in that only vibrationaltranslational energy exchanges were considered. For an appropriate selection of vibrational relaxation time model, very good agreement was obtained when compared to a vibrationally specific kinetic model. It was observed that certain models for vibrational relaxation time gave only fair agreement; this is akin to the problem of selecting reaction rate data for a finite-rate chemistry problem. The second test case computed the relaxing flow of chemically inert air behind a shock, the air being composed of O_2 and N_2 . Both O_2 and N_2 had separate vibrational temperatures, and thus the multi-temperature (as opposed to two-temperature) formulation was tested. The additional complexity introduced in this second test case was the inclusion of vibrational-vibrational energy exchange mechanisms. The successful completion of these two cases satisfied the second aim of this thesis. The third aim, modelling the coupling between chemistry and vibrational nonequilibrium, was addressed in the third test case. This test case considered the general thermochemical relaxation of oxygen behind a shock. The oxygen was dissociating, and at the same time, the vibrational temperature of the oxygen was allowed to equilibriate with the translational/rotational temperature. The vibration/chemistry coupling model of Knab et al. [170] was used to compute a solution which agreed very well with the calculations of Thivet et al. [151].

In Chapter 6, two demonstration calculations which made use of the earlier thesis work were presented. These calculations fulfill the final aim of the thesis: to use the models of hightemperature gas dynamics to simulate expansion tube operation. The first calculation simulated the operation of the University of Queensland's X2 facility when operated in expansion tunnel mode. The finite-rate chemistry simulations of the facility helped to quantify the extent of nonequilibrium in the test gas free stream. It was found that an equilibrium composition had not been recovered by the end of the nozzle flow despite the hopes of the experimenters. Nevertheless, at a minimum, the simulation was able to provide an answer to that question. The second demonstration calculation was again of the X2 facility, but this time, when it was operated in nonreflected shock tunnel mode. There was no question of whether or not the flow was in equilibrium; the particular condition was chosen to study the nonequilibrium radiation from a Titan-like atmosphere gas. Instead, the simulations aided the experimenters in answering a different question: how much of the nonequilibrium flow behind the shock as it emerges from the shock tube is useful in terms of making optical measurements. The calculations showed a portion of the flow where the shock was still relatively planar after tube exit, and suggested that the measurements should be made within one tube diameter of the tube exit. Beyond that distance, the expansion fan has begun to appreciably degrade the planarity of the emerging shock.

7.1 Contributions made by this thesis

The contributions made by this body of work is a subjective matter, but the following discussion reflects my views on the value of this work.

In this thesis, an attempt has been made to collect the best available engineering models for nonequilibrium effects into one body of work. By "best", I mean those models which are still defensible today on physical grounds. Also, this work presents a set of verification and validation cases that may be used to "provably" demonstrate the correct implementation of these models. The collection of test cases is by no means extensive, that is, we are not at the end of the road for high-temperature gas dynamics modelling, but the collection makes a contribution in that direction.

The other major contribution is a step towards characterising the free stream flow for impulse type facilities. Park's [25] quote is repeated to show the importance of this contribution:

..., because of uncertainties about the thermochemical state of the flows produced, the data obtained in those tunnels cannot be used presently for the purpose of CFD validation without certain amount of caveats. Characterization of the flows in those tunnels must be carried out to a much greater extent than has been before the data can be considered sufficiently reliable for CFD validation.

While the work in this thesis does not address every tunnel configuration, it has certainly contributed to a better characterisation of the free stream flow in our local expansion tube facilities. For the first time, we have been able to quantify the extent of nonequilibrium in the free stream flow and this leads to better anlysis of the experimental data. I view this a positive step towards allaying Park's (and other members of the community's) concerns about the use of data from high-enthalpy wind tunnels.

Finally, this work contributes a legacy of verified and validated code which is in daily use at the University of Queensland and collaborating organisations.

7.2 Recommendations for future work

The recommendations for future work are discussed in two parts: the specific extensions to this work; and the general recommendations pertaining to the research area.

The local code now has the capability to compute flows with finite-rate chemistry effects, multicomponent diffusion and vibrational nonequilibrium effects. The following list gives specific extensions to this work which can be made based on the infrastructure provided by the present implementation:

- the modelling of surface catalycity effects by the inclusion of appropriate wall boundary conditions;
- the extension of the vibrational nonequilibrium modelling to include polyatomic molecules;
- the modelling of transport properties for the multi-temperature gas; and

• the coupling of the flow solver with its ability to characterise the thermochemical state to a radiative transport solver, and in that way, tackle the radiating blunt body problem.

There is also a pressing need to validate the multi-temperature modelling, but a dearth of reliable experimental data has made this difficult; this leads to the more general recommendations for the research community.

The larger question for the research community is about the appropriateness of various engineering type models to the blunt body heating problem. This problem has been discussed at length by Giordano [9] (and a part of that argument appears on page 5 of this document). My general recommendation is that there should be a concerted effort by the community to address the range of validity for these various engineering models for the high-temperature nonequilibrium effects. It is clear for the immediate future that our modelling will rely on various engineering models; the computational expense of detailed vibrational specific models prohibits their use as a deisgn analysis tool. Given that we rely on these engineering models, it would be desirable to have some cohesive assessment of their validity for various flow conditions. This also presents opportunties for modellers to work closely with experimenters to design specific experiments which may be used to differentiate the efficacy of various engineering models.

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Appendix A

Input files for Chapter 3

A.1 Input file for Method of Manufactured Solutions verification case

```
gdata.title = "Method of Manufactured Solutions: Euler test case."
gdata.viscous_flag = 0
gdata.stringent_cfl = 1
# perfect air
create_perf_gas(R=287.0, gamma=1.4)
gdata.set_gas_model()
p0 = 1.0e5
u0 = 800.0
v0 = 800.0
T0 = p0 / 287.0
initial = FlowCondition(p=p0, u=u0,
                                       v=v0, T=T0, mf=[1.0,])
a = Node(0.0, 0.0, label="a")
b = Node(1.0, 0.0, label="b")
c = Node(0.0, 1.0, label="c")
d = Node(1.0, 1.0, label="d")
ab = Line(a, b)
ac = Line(a, c)
cd = Line(c, d)
bd = Line(b, d)
nx = 64
ny = 64
blk_0 = Block2D(make_patch(cd, bd, ab, ac),
                nni=nx, nnj=ny,
                fill_conditions=initial, label="blk-0",
                bc_list=[ExtrapolateOutBC(), ExtrapolateOutBC(),
                         EulerManufacturedBC(), EulerManufacturedBC()])
gdata.flux_calc = AUSM
gdata.max_time = 500.0e-3
gdata.max_step = 1000
gdata.dt = 1.0e-6
gdata.cfl = 0.5
```

gdata.dt_plot = 100.0e-3

A.2 Input file for the oblique detonation wave verification case

In this input file the wall spline is created based on the analytical solution for the oblique detonation wave. The code for the method create_wall_spline which appears in this input file is given in the program for the analytical soluation in Appendix B.3.

```
gdata.title = "The oblique detonation wave verification case."
#
# Gas model setup
#
create_ideal_gas( 287.0, 1.2, filename="reactant.dat");
create_ideal_gas( 287.0, 1.2, q=300000.0, filename="product.dat");
create_ideal_gas_mix(["reactant.dat", "product.dat"], "ideal_gas_mix.dat")
gdata.set_gas_model("ideal_gas_mix", "ideal_gas_mix.dat")
#
# Reaction scheme details
gdata.reacting_flag = 1
gdata.reaction_scheme_name = "Single-step, irreversible reaction"
gdata.reaction_scheme_file = "artificial-single-step.rsi"
#
# Flow conditions
#
inflow = FlowCondition(p=86.1e3, u=964.302, v=0.0, T=300.0, mf=[1.0, 0.0])
initial = FlowCondition(p=28.7e3, u=0.0, v=0.0, T=300.0, mf=[1.0, 0.0])
#
# Geometry
#
xmin = -0.25
xmax = 1.75
ymin = 0.0
ymax = 2.0
nnx = 64
nny = 64
from oblique_detonation import *
from math import pi
od = ObliqueDetonation( pi/4.0, 300.0, 3.0, 1.0)
wall = od.create_wall_spline(0.0, xmax, 1.0e-5)
a = Node( xmin, 0.0, label="a")
b = Node( 0.0, 0.0, label="b")
c = Node( wall.eval(1.0).x, wall.eval(1.0).y, label="c" )
d = Node( xmin, ymax, label="d")
e = Node( 0.0, ymax, label="e")
f = Node( xmax, ymax, label="f")
south0 = Line(a, b)
west0 = Line(a, d)
```

```
south1 = wall
eastOwest1 = Line(b, e)
east1 = Line(c, f)
north0 = Line(d, e)
north1 = Line(e, f)
nnx0 = int( 0.125 * nnx )
nnx1 = nnx - int(0.125 * nnx)
blk_0 = SuperBlock2D(
    psurf=make_patch(north0, east0west1, south0, west0),
    nni=nnx0, nnj=nny, nbi=1, nbj=4,
    bc_list=[ExtrapolateOutBC(), AdjacentBC(), SlipWallBC(), SupInBC(inflow)],
    fill_conditions=[inflow,],
    label="blk_0"
    )
blk_1 = SuperBlock2D(
    psurf=make_patch(north1, east1, south1, east0west1),
    nni=nnx1, nnj=nny, nbi=4, nbj=4,
    bc_list=[ExtrapolateOutBC(), ExtrapolateOutBC(), SlipWallBC(), AdjacentBC()],
    fill_conditions=[inflow,],
    label="blk_1"
    )
identify_block_connections()
# Do a little more setting of global data.
gdata.flux_calc = AUSMDV
gdata.max_time = 1.0e-2 # seconds
gdata.max_step = 30000
gdata.dt = 1.0e-6
gdata.dt_plot = gdata.max_time/20.0
gdata.dt_history = 10.0e-5
```

A.3 Input file for spheres fired into noble gases

This input makes use of the Billig correlation [113], for a shock shape in a perfect gas with $\gamma = 1.4$, in order to specify the inflow boundary. The coding for this correlation is not shown here but is a straight-forward implementation of Equations 5.36, 5.37 and 5.38 from the text by Anderson Jr. [7].

```
# sphere.py
# Rowan J Gollan
# 26-June-2005
#
# This file can be used to simulate the experiments reported by:
# Schwartz and Eckerman (1956)
# Shock Location in Front of a Sphere as a Measure of Real Gas Effects
# Journal of Applied Physics 27:2 pp 169--174
#
# Description:
# A ball bearing 5/16 inch diameter is fired into a ballistic
# test range.
#
# Updated: 17-March-2007
Db = 5.0 / 16.0 * 0.0254 # Diameter of ball bearing
```

```
Rc = Db / 2.0
from math import sqrt, atan2, cos
from billig import x_from_y, delta_over_R, y_from_x
from cases import *
case_no = int(os.environ['SGE_TASK_ID'])
p = 100.0 \# mm Hg
M_inf = 8.0
p_inf = p * 133.32239 # convert mm Hg to Pa
T_{inf} = 300.0
MW_Kr = 83.80000e-3 # from CEA database
gas_model = "perf_gas"
create_perf_gas(R=PC_R_u/MW_Kr, gamma=5.0/3.0, filename="perf_krypton.dat")
gas_file = "perf_krypton.dat"
set_type_of_gas(gas_model, gas_file)
Q = gas_data()
set_array_sizes_in_gas_data(Q, get_number_of_species(), get_number_of_vibrational_species())
Q.p = p_inf
Q.T = T_{inf}
set_massf(Q, 0, 1.0)
EOS_pT(Q, False)
a_inf = Q.a
u_inf = M_inf * a_inf
job_title = "Ball bearing in krypton gas (M= %.1f, p= %.f mm Hg)" % (M_inf, p_inf / 133.32239)
flow_lengths = 30
# grid discretization
nn = 135
BFL = Db / u_inf
# Setup simulation
gdata.title = job_title
# Gas model and flow properties
gdata.reacting_flag = 0
gdata.set_gas_model(gas_model, gas_file)
inflow = FlowCondition(p=p_inf, u=u_inf, v=0.0, T=T_inf, mf=[1.0,])
initial = FlowCondition(p=p_inf/3.0, u=0.0, v=0.0, T=T_inf, mf=[1.0,])
# Build the geometry from the bottom-up, starting with nodes...
# Scale it with the cylinder radius.
delta = delta_over_R(M_inf, 1) * Rc
delta_offset = 50.0/100.0*delta
y_{inc} = 20.0/100.0
x_shift = delta_offset
# In preparation for defining nodes, generate a few sample points
# along the expected shock position
# (which is estimated via Billig's correlation).
xys = []
y_top = y_from_x(0.0, M_inf, theta=0.0, axi=1, R_nose=Rc)
```

 $dy = y_{top}/5.0$

```
for y in [ i*dy for i in range(6) ]:
    x = x_from_y(y, M_inf, theta=0.0, axi=1, R_nose=Rc)
    xys.append((x,y)) # a new coordinate pair
    print "x=", x, "y=", y
a = Node(-Rc, 0.0, label="a")
b = Node( 0.0, Rc, label="b")
c = Node( 0.0, 0.0, label="c")
d = [] # will use a list to keep the nodes for the shock boundary
# point on x-axis
x, y = xys[0]
xd = x + x_shift
d.append(Node(-1.0*xd, y, label="d"))
for x, y in xys[1:-1]:
    # the outer boundary should be a little further than the shock itself
    xd = x + x_shift
    yd = y * (1.0 + y_{inc})
    d.append(Node(-1.0*xd, yd, label="d"))
x, y = xys[-1]
yd = y * (1.0 + y_{inc})
d.append(Node(-1.0*x, yd, label="d"))
# ... then lines, arcs, etc, that will make up the block boundaries.
axis = Line(d[0], a) # first-point of shock to nose of sphere
body = Arc(a, b, c)
shock = Spline(d)
top = Line(d[-1], b) # top-point of shock to top of sphere
# Specify the boundary discretization
nnx = nn
nny = nn
# ... and finally, assemble the block from its boundary faces.
block_0 = Block2D(make_patch(top, body, axis, shock),
                  bc_list=[ExtrapolateOutBC(), SlipWallBC(), SlipWallBC(), SupInBC(inflow)],
                  nni=nnx, nnj=nny,
                  fill_conditions=initial,
                  hcell_list=[(nnx, 1)])
# simulation control
gdata.flux_calc = ADAPTIVE
gdata.max_time = flow_lengths * BFL # should be large enough to allow steady flow
gdata.max_step = 600000
gdata.axisymmetric_flag = 1
gdata.cfl = 0.25
gdata.dt = 1.0e-10
gdata.dt_history = 1.0e-5
gdata.dt_plot = 1.0e-3
```

Analytical solution for an oblique detonation wave

This section presents the solution for the oblique detonation wave as given by Powers and Aslam [108], based on the work of Powers and Stewart [106]. It is the case of a straight shock supported by a curved wedge. No derivation of the solution is given — the reader is referred to the articles by Powers and Aslam (2006) and Powers and Stewart (1992).

A schematic of the oblique detonation flow field is shown in Figure B.1. The shock angle β is specified and the resulting curved wedge and flow field may be calculated. The solutions for flow field variables are all given in terms of the reaction progress variable, λ . The reaction progress variable is related to the mass fractions of the reactants and products such that, $f_p = 1 - \lambda$ and $f_r = \lambda$. The independent variables in this problem are as follows: R is the gas constant in J/kg.K⁻¹; α is the reaction rate in s⁻¹; β is the shock angle in radians; γ is the ratio of specific heats; T_1 is the free stream temperature in K; M_1 is the free stream Mach number; ρ_1 is the free stream density in kg/m³; and q is the heat release during the chemical conversion of reactants to products in J/kg. Based on this, two dependent parameters are u_1 , the free stream velocity in m/s, and p_1 , the free stream pressure in Pa. Also a coordinate transform is applied that is more amenable to the solution procedure. This is also shown in Figure B.1. The transformation equations for the coordinates are:

$$X = x \sin \beta - y \cos \beta \tag{B.1}$$

$$Y = x\cos\beta + y\sin\beta \tag{B.2}$$

and the corresponding velocity component transformations are:

$$U = u \sin \beta - v \cos \beta \tag{B.3}$$

$$V = u\cos\beta + v\sin\beta \tag{B.4}$$

Based on this, the reverse mapping for coordinates and velocity components is:

$$x = X\sin\beta + Y\cos\beta \tag{B.5}$$

$$y = -X\cos\beta + Y\sin\beta \tag{B.6}$$

$$u = U\sin\beta + V\cos\beta \tag{B.7}$$

$$v = -U\cos\beta + V\sin\beta \tag{B.8}$$



Figure B.1: Schematic of flow field and coordinate system for an oblique detonation wave. *Source: Powers and Aslam* (2006) [108]

The solutions for the various flow field parameters based on the shock angle, β , and as a function of the reaction progress variable, λ , may now be listed. The solution for the *X*-ordinate as a function of the reaction progress is

$$X(\lambda) = u_1 \left(2a_3(\sqrt{1 - a_4\lambda} - 1) + \ln\left(\left(\frac{1}{1 - \lambda}\right)^{a_2} \times \left\{ \frac{\left[1 - \sqrt{(1 - a_4\lambda)/(1 - a_4)}\right] \left[1 + \sqrt{1/(1 - a_4)}\right]}{\left[1 + \sqrt{(1 - a_4\lambda)/(1 - a_4)}\right] \left[1 - \sqrt{1/(1 - a_4)}\right]} \right\}^{a_3\sqrt{1 - a_4}} \right) \right)$$
(B.9)

where the parameters a_1, \ldots, a_4 are

$$a_1 = \frac{1}{(\gamma+1)M_1 \sin\beta} \frac{\sqrt{\gamma R T_1}}{\alpha}$$
(B.10)

$$a_2 = 1 + \gamma M_1^2 \sin^2 \beta \tag{B.11}$$

$$a_3 = M_1^2 \sin^2 \beta - 1 \tag{B.12}$$

$$a_4 = 2 \frac{M_1^2 \sin^2 \beta}{\left(M_1^2 \sin^2 \beta - 1\right)^2} \frac{\gamma^2 - 1}{\gamma} \frac{q}{RT_1}$$
(B.13)

The *Y*-ordinate at the wall is given as

$$Y_w(\lambda) = (u_1 \cos \beta / \alpha) \ln \left[1 / (1 - \lambda) \right]. \tag{B.14}$$

The remaining flow field parameters are:

$$\rho(\lambda) = \frac{\rho_1(\gamma + 1)M_1^2 \sin^2 \beta}{1 + \gamma M_i^2 \sin^2 \beta - \sqrt{\left(1 + \gamma M_i^2 \sin^2 \beta\right)^2 - (\gamma + 1)M_1^2 \sin^2 \beta \left\{2 + \left[(\gamma - 1)/(\gamma)(2\lambda q/RT_1) + (\gamma + 1)M_1^2 \sin^2 \beta\right\}}}$$
(B.15)

$$U(\lambda) = \frac{\rho_1 u_1 \sin \beta}{\rho(\lambda)}$$
(B.16)

$$p(\lambda) = p_1 + \rho_1^2 u_1^2 \sin^2 \beta \left[\frac{1}{\rho_1} - \frac{1}{\rho(\lambda)} \right]$$
 (B.17)

$$T(\lambda) = \frac{p_1}{\rho(\lambda)R} + \frac{\rho_1^2 u_1^2 \sin^2 \beta}{\rho(\lambda)R} \left[\frac{1}{\rho_1} - \frac{1}{\rho(\lambda)} \right]$$
(B.18)

The value for *V* is constant behind the shock and is derived from the Rankine-Hugoniot relations as

$$V = u_1 \cos \beta. \tag{B.19}$$

B.1 Procedure to determine curved wedge

When setting up the numerical simulation, one requires the geometry of the curved wedge as input. The procedure for determining the x, y coordinates of the curved wedge is as follows:

- 1. Find *X*, *Y* coordinates of wegde by solving *X*(λ), *Y*_w(λ) for a range of λ : $0 \le \lambda < 1$.
- 2. Transform from the *X*, *Y* values to *x*, *y* coordinates.

B.2 Procedure to compute the analytical flow field

The steps for calculating the flow properties at a point *x*, *y* in the flow field are as follows:

- 1. Find the corresponding *X*-ordinate based on the given *x*, *y* coordinates.
- 2. Using Equation B.9, find λ based on *X*. As λ is an implicit function of *X* a zero-finding method (like the secant method) is used.
- 3. Based on λ , compute the remaining flow field variables ρ , p, T and U. Apply transformations to get u and v.

B.3 A program to compute the analytical solution for an oblique detonation wave

Included here is a Python program which computes the flow field properties at a given coordinate pair *x*, *y* based on the analytical solution presented in Section B. The solution is encapsulated by a class, ObliqueDetonation. The initialisation of an object of type ObliqueDetonation requires the problem parameters as input. Various methods of the initialised object may then be called to access aspects of the analytical solution. For example, the flow field variables at a point *x*, *y* in the field are computed and returned by calling the solution method. An example is included at the end of the program script. This script is not completely self-standing. It relies on a standard implementation of the secant method provided in the module zero_solvers and the geometric entity Spline which is part of the libgeom2 module.

```
#!/usr/bin/env python
# oblique_detonation.py
#
# This Python script contains a class
# which encapsulates the analytical
# solution for an oblique detonation wave.
#
# The analytical solution was originally published
# by Powers and Stewart (1992) and then re-presented
# as a verfication test case by Powers and Aslam (2006).
# The form of the solution is easier to interpret
# in the 2006 paper.
#
# References:
£
# 1. Powers, J.M. and Stewart, D.S. (1992)
    Approximate solutions for oblique detonations
#
    in the hypersonic limit.
#
    AIAA Journal, 30:3 pp. 726--736
#
#
# 2. Powers, J.M and Aslam, T.D. (2006)
     Exact solution for multidimensional compressible
#
#
    reactive flow for verifying numerical algorithms
    AIAA Journal, 44:2 pp. 337--344
#
#
# This Python script was created by...
# Rowan J Gollan
# 23-Jul-2006
#
from math import cos, sin, sqrt, pow, log, fabs
from zero_solvers import secant
from libgeom2 import *
class ObliqueDetonation:
    def __init__(self, beta, T1, M1, rho1,
                R=287.0, alpha=1000.0, gamma=6.0/5.0,
                 q=300000.0):
        self.beta = beta
        self.T1 = T1
        self.M1 = M1
        self.rho1 = rho1
        self.R = R
        self.alpha = 1000.0
        self.gamma = gamma
        self.q = q
        self.p1 = rho1*R*T1
        self.a1 = sqrt(gamma * R * T1)
        self.u1 = self.M1 * self.a1
        self.v1 = 0.0
        self.V = self.u1 * cos(self.beta)
```

```
def get_V(self):
    return self.V
def calculate_X(self, lmbda ):
    MsinBeta2 = (self.M1 * sin(self.beta))**2
    a1 = (1.0/ ((self.gamma + 1.0) * self.M1 * sin(self.beta))) * (self.a1 / self.alpha)
    a2 = 1.0 + self.gamma * MsinBeta2
    a3 = MsinBeta2 - 1.0
    a4 = ((2.0 * MsinBeta2) / (MsinBeta2 - 1)**2) * ((self.gamma**2 - 1.0) / self.gamma) * \
    ( self.q / (self.R*self.T1))
    OneMinusA4L = 1.0 - a4*lmbda
    OneMinusA4 = 1.0 - a4
    t1 = 2.0*a3*(sqrt(OneMinusA4L) - 1.0)
    t2 = pow((1.0/(1.0 - lmbda)), a2)
    t3 = 1.0 - sqrt((OneMinusA4L)/(OneMinusA4))
    t4 = 1.0 + \text{sqrt}(1.0 / \text{OneMinusA4})
    t5 = 1.0 + sqrt((OneMinusA4L)/(OneMinusA4))
    t6 = 1.0 - \text{sqrt}(1.0 / \text{OneMinusA4})
    X = a1 * ( t1 + log( t2 * pow( (t3*t4) / (t5*t6) , a3*sqrt(OneMinusA4) ) ) )
    return X
def calculate_rho(self, lmbda ):
    MsinBeta2 = (self.M1 * sin(self.beta))**2
    t1 = self.rho1 * (self.gamma + 1.0 ) * MsinBeta2
   t2 = 1.0 + self.gamma * MsinBeta2
   t3 = t2 * t2
    t4 = (self.gamma + 1.0)*MsinBeta2
    t5 = ((self.gamma - 1.0)/self.gamma) * (2.0*lmbda*self.q / (self.R*self.T1))
    t6 = (self.gamma - 1.0)*MsinBeta2
    rho = t1 / ( t2 - sqrt( t3 - t4 * (2.0 + t5 + t6) ) )
    return rho
def calculate_U(self, lmbda, rho ):
    U = self.rho1 * self.u1 * sin(self.beta) / rho
    return U
def calculate_T(self, lmbda, rho ):
    t1 = self.p1 / (rho*self.R)
    t2 = (self.rho1*self.u1*sin(self.beta))**2 / (rho*self.R)
    t3 = 1.0/self.rho1 - 1.0/rho
   T = t1 + t2 * t3
   return T
def calculate_p(self, lmbda, rho ):
   t2 = (self.rho1*self.u1*sin(self.beta))**2
   t3 = 1.0/self.rho1 - 1.0/rho
   p = self.p1 + t2 * t3
   return p
def calculate_Yw(self, lmbda ):
    Yw = ( self.u1*cos(self.beta) / self.alpha ) * log( 1.0 / (1.0 - lmbda) )
    return Yw
def transform_xy_2_XY(self, x, y):
    X = x * sin(self.beta) - y * cos(self.beta)
```

```
Y = x * cos(self.beta) + y * sin(self.beta)
    return (X, Y)
def transform_XY_2_xy(self, X, Y):
   x = X * sin(self.beta) + Y * cos(self.beta)
    y = Y * sin(self.beta) - X * cos(self.beta)
    return (x, y)
def transform_UV_2_uv(self, U, V):
    u = U * sin(self.beta) + V * cos(self.beta)
    v = V * sin(self.beta) - U * cos(self.beta)
    return (u, v)
def find_XYw_from_x(self, x):
    def f( lmbda ):
        X = self.calculate_X(lmbda)
        Yw = self.calculate_Yw(lmbda)
       (xg, yg) = self.transform_XY_2_xy(X, Yw)
        return (x - xg)
    lmbda = secant(f, 0.0, 0.999, limits=[0.0, 0.999])
    X = self.calculate_X(lmbda)
    Yw = self.calculate_Yw(lmbda)
   return (X, Yw)
def create_test_spline(self, xmin, xmax, no_points):
    dx = (xmax - xmin) / (no_points - 1.0)
    (X, Yw) = self.find_XYw_from_x( xmin )
    (x, y) = self.transform_XY_2_xy(X, Yw)
    points = [ Node(x, y) ]
    for i in range(no_points-2):
       x = xmin + dx*(i+1)
        (X, Yw) = self.find_XYw_from_x( x )
        (x, y) = self.transform_XY_2_xy(X, Yw)
        points.append( Node(x, y) )
    (X, Yw) = self.find_XYw_from_x( xmax )
    (x, y) = self.transform_XY_2_xy(X, Yw)
    points.append( Node(x, y) )
   return Spline(points)
def test_wall_spline(self, wall_spline):
   no_div = 2000
    dt = 1.0 / (no_div - 1.0)
    sp_point = wall_spline.eval( 0.0 )
    xs = sp_point.x
    ys = sp_point.y
   X, Yw = self.find_XYw_from_x(xs)
    xa, ya = self.transform_XY_2_xy(X, Yw)
```

```
max_error = fabs(ya - ys)
       for i in range(1, no_div):
           t = dt * i
           sp_point = wall_spline.eval( t )
           xs = sp_point.x
           ys = sp_point.y
           X, Yw = self.find_XYw_from_x(xs)
            xa, ya = self.transform_XY_2_xy(X, Yw)
            error = fabs(ya - ys)
           if error > max_error:
               max_error = error
       return max error
   def create_wall_spline(self, xmin, xmax, error_tol):
       no_points = 70
       error = 1.0
       while( error > error_tol ):
           spline = self.create_test_spline( xmin, xmax, no_points )
           error = self.test_wall_spline( spline )
           no_points += 1
       return spline
   def solution( self, x, y):
       (X, Y) = self.transform_xy_2_XY(x, y)
       if( X < 0.0):
           rho = self.rho1
           p = self.p1
           T = self.T1
           f = [1.0, 0.0]
           u = self.u1
           v = self.v1
       else:
           def f( lmbda ):
               X = self.calculate_X(lmbda)
                (xg, yg) = self.transform_XY_2_xy(X, Y)
               return (x - xg)
           lmbda = secant(f, 0.0, 0.999, limits=[0.0, 0.999])
           rho = self.calculate_rho( lmbda )
           p = self.calculate_p( lmbda, rho )
           T = self.calculate_T(lmbda, rho)
           U = self.calculate_U( lmbda, rho )
           V = self.V
           (u, v) = self.transform_UV_2_uv( U, V)
           f = [1.0 - lmbda, lmbda]
       return (x, y, rho, p, T, f, u, v, X, Y)
if __name__ == '__main__':
   from math import pi
   obl = ObliqueDetonation( pi/4.0, 300.0, 3.0, 1.0)
```

```
X = obl.calculate_X(0.1)
Y = obl.calculate_Yw(0.1)
(x, y) = obl.transform_XY_2_xy(X, Y)
rho = obl.calculate_rho(0.1)
p = obl.calculate_p(0.1, rho)
T = obl.calculate_T(0.1, rho)
U = obl.calculate_U(0.1, rho)
print "X(lmbda=0.1)= ", X
print "Yw(lmbda=0.1)= ", Y
print "x(lmbda=0.1)= ", x
print "y(lmbda=0.1)= ", y
print "rho(lmbda=0.1)= ", rho
print "p(lmbda=0.1)= ", p
print "T(lmbda=0.1)= ", T
print "U(lmbda=0.1)= ", U
(X, Yw) = obl.find_XYw_from_x(x)
print "X from x: ", X
print "Yw from x: ", Yw
print "Solution at x=0.066116, y=0.035483..."
print obl.solution( 0.066116, 0.035483 )
print "Done."
```

Reaction schemes

All reaction rate coefficients are given in cgs units. The values in the tables below correspond to the following equation for the generalised Arrhenius form:

$$k_f = AT^n \exp\left(\frac{-C}{T}\right)$$

Note this differs in form from Equation 4.25, that is, $C = E_a/k$. The first column of values is for variable *A*, the second, variable *n* and the third, variable *C*.

C.1 Air reaction schemes

C.1.1 Marrone [32]

Reaction	Reaction rate coefficients			
1. 02 + 0 <=> 0 + 0 + 0	k_f	2.100e+18	-0.50	59380.0
2. 02 + 02 <=> 0 + 0 + 02	k _f	3.600e+21	-1.50	59380.0
3. 02 + M <=> 0 + 0 + M	k _f	1.190e+21	-1.50	59380.0
4. N2 + N <=> N + N + N	k _b	7.500e+20	-1.50	0.0
5. $N2 + N2 \iff N + N + N2$	k _b	1.500e+20	-1.50	0.0
6. N2 + M <=> N + N + M	k _b	5.000e+19	-1.50	0.0
7. NO + M $\leq N$ + O + M	k_f	5.180e+21	-1.50	75490.0
8. N + O2 <=> NO + O	k _f	1.000e+12	0.50	3120.0
9. 0 + N2 <=> N0 + N	k_f	5.000e+13	0.00	38016.0
10. N + O <=> NO+ + e-	k _b	1.800e+21	-1.50	0.0

-

Reaction		Reaction rate coefficients				
1. 02 + 0 <=> 0 + 0 + 0	k_f	3.610e+18	-1.00	59400.0		
2. 02 + 02 <=> 0 + 0 + 02	k_f	3.610e+18	-1.00	59400.0		
3. 02 + M <=> 0 + 0 + M	k_f	3.610e+18	-1.00	59400.0		
4. N2 + N <=> N + N + N	k_f	4.150e+22	-1.50	113100.0		
5. $N2 + N2 \iff N + N + N2$	k_f	1.920e+17	-0.50	113100.0		
6. N2 + M <=> N + N + M	k_f	1.920e+17	-0.50	113100.0		
7. NO + M $\leq N$ + O + M	k_f	3.970e+20	-1.50	75600.0		
8. N + O2 <=> NO + O	k_f	9.630e+11	0.50	3600.0		
9. 0 + N2 <=> NO + N	k_f	6.750e+13	0.00	37500.0		
10. N + O <=> NO+ + e-	k_f	9.030e+09	0.50	32400.0		
	k_b	1.800e+21	-1.50	0.0		

C.1.2 Marrone reaction scheme with reaction rates from Gupta et al. [118]

Reaction		Reaction rate coefficients			
1. 02 + M <=> 0 + 0 + M	k_f	3.610e+18	-1.00	59400.0	
	k_b	3.010e+15	-0.50	0.0	
2. N2 + M <=> N + N + M	k_f	1.920e+17	-0.50	113100.0	
	k_b	1.090e+16	-0.50	0.0	
3. N2 + N <=> N + N + N	k_f	4.150e+22	-1.50	113100.0	
	k_b	2.320e+21	-1.50	0.0	
4. NO + M <=> N + O + M	k_f	3.970e+20	-1.50	75600.0	
	k_b	1.010e+20	-1.50	0.0	
5. NO + O <=> O2 + N	k_f	3.180e+09	1.00	19700.0	
	k_b	9.630e+11	0.50	3600.0	
6. N2 + 0 <=> NO + N	k_f	6.750e+13	0.00	37500.0	
	k_b	1.500e+13	0.00	0.0	

C.1.3 Gupta et al. [118] scheme for neutral air reactions

C.2 Hydrogen/Air combustion schemes

C.2.1 Rogers and Schexnayder [127]

Reaction	Reaction rate coefficients			
1. M + O2 <=> O + O + M	k _f	7.200e+18	-1.00	59340.0
2. M + H2 <=> H + H + M	k _f	5.500e+18	-1.00	51987.0
3. M + H2O <=> H + OH + M	k _f	5.200e+21	-1.50	59386.0
4. H + O2 + M <=> HO2 + M	k _f	2.300e+15	0.00	-403.0
5. M + NO2 <=> NO + O + M	k _f	1.100e+16	0.00	32710.0
6. M + NO <=> N + O + M	k _f	4.100e+18	-1.00	75330.0
7. M + H + NO <=> HNO + M	k _f	5.400e+15	0.00	-300.0
8. M + H2O2 <=> OH + OH + M	k _f	1.200e+17	0.00	22899.0
9. M + OH + NO <=> HNO2 + M	k _f	8.000e+15	0.00	-1000.0
10. M + OH + NO2 <=> HNO3 + M	k _f	1.300e+16	0.00	-1107.0
11. M + 03 <=> 02 + 0 + M	k _f	1.300e+21	-2.00	12800.0
12. M + O + H <=> OH + M	k _f	7.100e+18	-1.00	0.0
13. H2O + O <=> OH + OH	k _f	5.800e+13	0.00	9059.0
14. H2 + OH <=> H2O + H	k _f	2.000e+13	0.00	2600.0
15. 02 + H <=> 0H + 0	k _f	2.200e+14	0.00	8455.0
16. H2 + 0 <=> OH + H	k _f	7.500e+13	0.00	5586.0
17. H2 + O2 <=> OH + OH	k _f	1.000e+13	0.00	21641.0
18. H + HO2 <=> H2 + O2	k _f	2.400e+13	0.00	350.0
19. H2 + O2 <=> H2O + O	k _f	4.100e+13	0.00	25400.0

Reaction	Reaction rate coefficients			cients	
20. H + HO2 <=> OH + OH	k _f	k _f 2.400e+14 0.00 95			
21. H20 + 0 <=> H + H02	k _f	5.800e+11	0.50	28686.0	
22. 0 + HO2 <=> OH + O2	k _f	5.000e+13	0.00	503.0	
23. OH + HO2 <=> O2 + H2O	k _f	3.000e+13	0.00	0.0	
24. H2 + H02 <=> H20 + OH	k _f	2.000e+13	0.00	12582.0	
25. H02 + H2 <=> H + H2O2	k_f	7.300e+11	0.00	9400.0	
26. H202 + H <=> OH + H20	k _f	3.200e+14	0.00	4504.0	
27. H02 + OH <=> 0 + H202	k _f	5.200e+10	0.50	10600.0	
28. H02 + H20 <=> 0H + H202	k _f	2.800e+13	0.00	16500.0	
29. H02 + H02 <=> H202 + 02	k _f	2.000e+12	0.00	0.0	
30. 0 + 03 <=> 02 + 02	k _f	1.000e+13	0.00	2411.0	
31. 03 + NO <=> NO2 + O2	k _f	5.400e+11	0.00	1200.0	
32. 03 + H <=> 0H + 02	k _f	7.000e+13	0.00	560.0	
33. 03 + 0H <=> 02 + H02	k _f	9.000e+11	0.00	1000.0	
34. 0 + N2 <=> N0 + N	k _f	5.000e+13	0.00	37940.0	
35. H + NO <=> OH + N	k _f	1.700e+14	0.00	24500.0	
36. 0 + NO <=> O2 + N	k _f	1.500e+09	1.00	19500.0	
37. NO2 + H <=> NO + OH	k _f	3.500e+14	0.00	740.0	
38. NO2 + 0 <=> NO + O2	k _f	1.000e+13	0.00	302.0	
39. NO2 + H2 <=> HNO2 + H	k _f	2.400e+13	0.00	14595.0	
40. HO2 + NO <=> NO2 + OH	k _f	3.000e+12	0.50	1208.0	
41. NO2 + H2O <=> HNO2 + OH	k _f	3.200e+12	0.00	22000.0	
42. NO2 + OH <=> HNO2 + O	k _f	2.100e+12	0.00	12580.0	
43. HNO + H <=> H2 + NO	k _f	4.800e+12	0.00	0.0	
44. HNO + OH <=> H2O + NO	k _f	3.600e+13	0.00	0.0	
45. NO + HO2 <=> HNO + O2	k _f	7.200e+12	0.50	5500.0	
46. HNO + O <=> NO + OH	k _f	5.000e+11	0.50	0.0	
47. HNO3 + 0 <=> HO2 + NO2	k_f	1.000e+11	0.00	0.0	
48. HO2 + NO2 <=> HNO2 + O2	k_f	2.000e+11	0.00	0.0	
49. 03 + HO2 <=> 2 02 + OH	k_f	1.000e+11	0.00	1409.0	

All third body efficiencies are 1.0 except for the following:

 $\begin{array}{rll} r1: & O_2-4.0, & O-10.0, & H_2O-2.0\\ r2: & H-5.0, & H_2-2.0, & H_2O-8.0\\ r3: & H_2O-6.0\\ r4: & H_2-2.0, & H_2O-13.0\\ r8: & H_2O-3.0\\ r9: & H_2O-6.0 \end{array}$

C.2.2 Evans and Schexnayder [129]

Reaction		Reaction rat	e coeffi	cients
1. HNO2 + M <=> NO + OH + M	k_f	5.000e+17	-1.00	25000.0
	k_b	8.000e+15	0.00	-1000.0
2. NO2 + M <=> NO + O + M	k_f	1.100e+16	0.00	32712.0
	k_b	1.100e+15	0.00	-941.0
*3. H2 + M <=> H + H + M	k_f	5.500e+18	-1.00	51987.0
	k_b	1.800e+18	-1.00	0.0
*4. O2 + M <=> O + O + M	k_f	7.200e+18	-1.00	59340.0
	k_b	4.000e+17	-1.00	0.0
*5. H2O + M <=> OH + H + M	k_f	5.200e+21	-1.50	59386.0
	k_b	4.400e+20	-1.50	0.0
*6. OH + M <=> O + H + M	k_f	8.500e+18	-1.00	50830.0
	k_b	7.100e+18	-1.00	0.0
7. HO2 + M <=> H + O2 + M	k_f	1.700e+16	0.00	23100.0
	k_b	1.100e+16	0.00	-440.0
*8. H2O + O <=> OH + OH	k_f	5.800e+13	0.00	9059.0
	k_b	5.300e+12	0.00	503.0
*9. H2O + H <=> OH + H2	k_f	8.400e+13	0.00	10116.0
	k_b	2.000e+13	0.00	2600.0
*10. 02 + H <=> 0H + 0	k_f	2.200e+14	0.00	8455.0
	k_b	1.500e+13	0.00	0.0
*11. H2 + 0 <=> OH + H	k_f	7.500e+13	0.00	5586.0
	k_b	3.000e+13	0.00	4429.0
12. H2 + O2 <=> OH + OH	k_f	1.700e+13	0.00	24232.0
	k_b	5.700e+11	0.00	14922.0
13. H2 + O2 <=> H + HO2	k_f	1.900e+13	0.00	24100.0
	k_b	1.300e+13	0.00	0.0
14. OH + OH <=> H + HO2	k_f	1.700e+11	0.50	21137.0
	k_b	6.000e+13	0.00	0.0
15. H20 + 0 <=> H + H02	k _f	5.800e+11	0.50	28686.0
	k_b	3.000e+13	0.00	0.0
16. OH + O2 <=> O + HO2	k _f	3.700e+11	0.64	27840.0
	k_b	1.000e+13	0.00	0.0
17. H20 + 02 <=> 0H + H02	k_f	2.000e+11	0.50	36296.0
	k_b	1.200e+13	0.00	0.0
18. H20 + OH <=> H2 + H02	k _f	1.200e+12	0.21	39815.0

Reaction	Reaction rate coefficients			
	k _b	1.700e+13	0.00	12582.0
19. 0 + N2 <=> N + N0	k _f	5.000e+13	0.00	37940.0
	k_b	1.100e+13	0.00	0.0
20. H + NO <=> N + OH	k _f	1.700e+14	0.00	24500.0
	k_b	4.500e+13	0.00	0.0
21. 0 + NO <=> N + O2	k _f	2.400e+11	0.50	19200.0
	k_b	1.000e+12	0.50	3120.0
22. NO + OH <=> H + NO2	k _f	2.000e+11	0.50	15500.0
	k_b	3.500e+14	0.00	740.0
23. NO + O2 <=> O + NO2	k_f	1.000e+12	0.00	22800.0
	k_b	1.000e+13	0.00	302.0
24. NO2 + H2 <=> H + HNO2	k_f	2.400e+13	0.00	14500.0
	k_b	5.000e+11	0.50	1500.0
25. NO2 + OH <=> NO + HO2	k_f	1.000e+11	0.50	6000.0
	k _b	3.000e+12	0.50	1200.0

The reduced scheme uses the 8 starred reactions only.

Reaction	Reaction rate coefficients			
1. H + O2 <=> OH + O	k _f	1.590e+17	-0.93	8491.2
2. 0 + H2 <=> OH + H	k _f	3.870e+04	2.70	3151.1
3. OH + H2 <=> H2O + H	k _f	2.160e+08	1.51	1731.9
4. OH + OH <=> 0 + H20	k _f	2.100e+08	1.40	-192.4
5. 0 + 0 + M <=> 02 + M	k_f	1.000e+17	-1.00	0.0
6. H + H + M <=> H2 + M	k_f	6.400e+17	-1.00	0.0
7. H + OH + M <=> H2O + M	k_f	8.400e+21	-2.00	0.0
8. H + O2 + M <=> HO2 + M	k _f	7.000e+17	-0.80	0.0
9. HO2 + H <=> OH + OH	k _f	1.500e+14	0.00	505.1
10. HO2 + H <=> H2 + O2	k _f	2.500e+13	0.00	348.8
11. H02 + H <=> H20 + 0	k _f	5.000e+12	0.00	709.6
12. HO2 + 0 <=> 02 + 0H	k _f	2.000e+13	0.00	0.0
13. HO2 + OH <=> H2O + O2	k _f	6.020e+13	0.00	0.0
14. H02 + H02 <=> H202 + 02	k _f	1.060e+11	0.00	-853.9
15. H2O2 + M <=> OH + OH + M	k _f	1.000e+17	0.00	22851.7
16. H202 + H <=> H02 + H2	k _f	1.700e+12	0.00	1888.3
17. H2O2 + H <=> H2O + OH	k_f	1.000e+13	0.00	1804.1
18. H2O2 + 0 <=> HO2 + OH	k _f	2.800e+13	0.00	3223.3
19. H2O2 + OH <=> H2O + HO2	k_f	7.000e+12	0.00	721.6

C.2.3 Frenklach, Wang and Rabinowitz [130]

Reaction		Reaction rat	e coeffi	cients
1. H + O2 <=> OH + O	k _f	1.590e+17	-0.93	8491.2
	k_b	5.500e+14	-0.56	-166.0
2. 0 + H2 <=> OH + H	k _f	3.870e+04	2.70	3151.1
	k_b	2.040e+04	2.69	2175.0
3. OH + H2 <=> H2O + H	k _f	2.160e+08	1.51	1731.9
	k_b	6.620e+08	1.57	9370.0
4. OH + OH <=> 0 + H20	k _f	2.100e+08	1.40	-192.4
	k_b	1.280e+09	1.47	8414.0
5. 0 + 0 + M <=> 02 + M	k _f	1.000e+17	-1.00	0.0
	k_b	3.700e+18	-1.05	59760.0
6. H + H + M <=> H2 + M	k _f	6.400e+17	-1.00	0.0
	k _b	1.930e+18	-0.69	52080.0
7. H + H + H2 <=> H2 + H2	k_f	9.190e+16	-0.60	0.0
	k _b	2.750e+16	-0.29	52080.0
8. H + H + H2O <=> H2 + H2O	k_f	5.990e+19	-1.25	0.0
	k _b	1.760e+19	0.93	52080.0
9. H + OH + M <=> H2O + M	k_f	8.400e+21	-2.00	0.0
	k _b	9.500e+21	-1.66	59740.0
10. H + O2 + M <=> HO2 + M	k_f	7.000e+17	-0.80	0.0
	k _b	3.090e+17	-0.67	24460.0
11. H + O2 + H2 <=> HO2 + H2	k_f	2.800e+18	-0.86	0.0
	k _b	1.220e+18	-0.72	24460.0
12. H + O2 + O2 <=> HO2 + O2	k_f	3.000e+20	-1.72	0.0
	k _b	1.320e+20	-1.59	24460.0
13. H + O2 + N2 <=> HO2 + N2	k_f	3.750e+20	-1.72	0.0
	k _b	1.650e+20	-1.59	24460.0
14. H + O2 + H2O <=> HO2 + H2O	k_f	9.390e+18	-0.76	0.0
	k_b	4.040e+18	-0.62	24460.0
15. HO2 + H <=> OH + OH	k_f	1.500e+14	0.00	505.1
	k_b	2.210e+11	0.56	18690.0
16. HO2 + H <=> H2 + O2	k_f	2.500e+13	0.00	348.8
	k_b	1.280e+13	0.22	27950.0
17. HO2 + H <=> H2O + O	k_f	5.000e+12	0.00	709.6
	$ k_b $	4.110e+10	0.59	27330.0

C.2.4	Mott's rates	[121]	with	the	mechanism	by	Frenklach,	Wang	and	Rabi-
	nowitz [130]									

Reaction	Reaction rate coefficients			
18. HO2 + 0 <=> 02 + 0H	k _f	2.000e+13	0.00	0.0
	k_b	5.010e+12	0.21	26630.0
19. HO2 + OH <=> H2O + O2	k_f	6.020e+13	0.00	0.0
	k_b	3.950e+13	0.24	35260.0
20. H02 + H02 <=> H202 + 02	k_f	1.060e+11	0.00	-853.9
	k_b	1.770e+13	-0.40	18650.0
21. H2O2 + M <=> OH + OH + M	k_f	1.000e+17	0.00	22851.7
	k_b	1.080e+12	0.85	-2617.0
22. H2O2 + H <=> HO2 + H2	k_f	1.700e+12	0.00	1888.3
	k_b	4.300e+09	0.65	9980.0
23. H2O2 + H <=> H2O + OH	k_f	1.000e+13	0.00	1804.1
	k_b	1.290e+08	1.19	35550.0
24. H2O2 + O <=> HO2 + OH	k_f	2.800e+13	0.00	3223.3
	k_b	3.470e+10	0.64	10330.0
25. H202 + OH <=> H20 + H02	k_f	7.000e+12	0.00	721.6
	k_b	6.620e+10	0.68	16460.0

Reaction	Reaction rate coefficients			
1. H2 + O2 <=> H + HO2	k _f	28183.2		
2. H + O2 <=> OH + O	k_f	2.600e+14	0.00	8455.0
3. 0 + H2 <=> OH + H	k _f	1.800e+10	1.00	4479.1
4. OH + H2 <=> H2O + H	k_f	2.200e+13	0.00	2591.8
5. OH + OH <=> H2O + O	k _f	6.300e+12	0.00	548.6
6. H + OH + M <=> H2O + M	k _f	2.200e+22	-2.00	0.0
7. H + H + M <=> H2 + M	k _f	6.400e+17	-1.00	0.0
8. H + O + M <=> OH + M	k _f	6.000e+16	-0.60	0.0
9. H + O2 + M <=> HO2 + M	k _f	2.100e+15	0.00	-503.3
10. HO2 + H <=> OH + OH	k _f	1.400e+14	0.00	543.5
11. HO2 + H <=> H2O + O	k _f	1.000e+13	0.00	543.5
12. H02 + 0 <=> 02 + 0H	k _f	1.500e+13	0.00	478.1
13. H02 + OH <=> H20 + O2	k _f	8.000e+12	0.00	0.0
14. H02 + H02 <=> H202 + 02	k _f	2.000e+12	0.00	0.0
15. H + H2O2 <=> H2 + HO2	k _f	1.400e+12	0.00	1811.8
16. 0 + H202 <=> OH + H02	k _f	1.400e+13	0.00	3220.9
17. OH + H2O2 <=> H2O + HO2	k _f	6.100e+12	0.00	719.7
18. M + H2O2 <=> OH + OH + M	k _f	1.200e+17	0.00	22898.8
19. 0 + 0 + M <=> 02 + M	k _f	6.000e+17	0.00	-905.9
20. N + N + M <=> N2 + M	k_f	2.800e+17	-0.75	0.0
21. N + O2 <=> NO + O	k_f	6.400e+09	1.00	3170.6
22. N + NO <=> N2 + O	k _f	1.600e+13	0.00	0.0
23. N + OH <=> NO + H	k _f	6.300e+11	0.50	0.0
24. H + NO + M <=> HNO + M	k _f	5.400e+15	0.00	-302.0
25. H + HNO <=> NO + H2	k _f	4.800e+12	0.00	0.0
26. 0 + HNO <=> NO + OH	k _f	5.000e+11	0.50	0.0
27. OH + HNO <=> NO + H2O	k _f	3.600e+13	0.00	0.0
28. H02 + HN0 <=> N0 + H202	k_f	2.000e+12	0.00	0.0
29. HO2 + NO <=> NO2 + OH	k_f	3.400e+12	0.00	-130.9
30. H + NO2 <=> NO + OH	k_f	3.500e+14	0.00	754.9
31. 0 + NO2 <=> NO + O2	k_f	1.000e+13	0.00	302.0
32. M + NO2 <=> NO + O + M	k_f	1.160e+16	0.00	33215.9

C.2.5 Jachimowski [131] with the modifications of Oldenborg et al. [132]

All third body efficiencies are 1.0 except for the following:

 $\begin{array}{lll} r6: & H_2O-6.0 \\ r7: & H_2-2.0, & H_2O-6.0 \\ r8: & H_2O-5.0 \\ r9: & H_2-2.0, & H_2O-16.0 \\ r19: & H_2O-15.0 \end{array}$

Reaction	Reaction rate coefficients			
1. 02 + H <=> 0H + 0	k _f	2.000e+14	0.00	8455.1
2. H2 + 0 <=> OH + H	k _f	5.060e+04	2.67	3163.2
3. H2 + OH <=> H2O + H	k _f	1.000e+08	1.60	1659.8
4. OH + OH <=> H2O + O	k _f	1.500e+09	1.14	50.5
5. H + H + M <=> H2 + M	k_f	1.800e+18	-1.00	0.0
6. H + OH + M <=> H2O + M	k_f	2.200e+22	-2.00	0.0
7. 0 + 0 + M <=> 02 + M	k _f	2.900e+17	-1.00	0.0
8. H + O2 + M <=> HO2 + M	k _f	2.300e+18	-0.80	0.0
9. HO2 + H <=> OH + OH	k _f	1.500e+14	0.00	505.1
10. HO2 + H <=> H2 + O2	k _f	2.500e+13	0.00	348.8
11. HO2 + H <=> H2O + O	k _f	3.000e+13	0.00	866.0
12. HO2 + 0 <=> OH + O2	k _f	1.800e+13	0.00	-204.5
13. HO2 + OH <=> H2O + O2	k _f	6.000e+13	0.00	0.0
14. H02 + H02 <=> H202 + 02	k _f	2.500e+11	0.00	-625.4
15. OH + OH + M <=> H2O2 + M	k _f	3.250e+22	-2.00	0.0
16. H2O2 + H <=> H2 + HO2	k _f	1.700e+12	0.00	1888.3
17. H2O2 + H <=> H2O + OH	k _f	1.000e+13	0.00	1804.1
18. H202 + 0 <=> 0H + H02	k _f	2.800e+13	0.00	3223.3
19. H2O2 + OH <=> H2O + HO2	k_f	5.400e+12	0.00	505.1

C.3 Titan atmosphere chemistry

C.3.1 Gökçen [188] reduced scheme

Reaction	Reaction rate coefficients				
1. N2 + M <=> N + N + M	k _f	7.000e+21	-1.60	113200.0	
2. CH4 + M <=> CH3 + H + M	k _f	4.700e+47	-8.20	59200.0	
3. CH3 + M <=> CH2 + H + M	k _f	1.020e+16	0.00	45600.0	
4. CH3 + M <=> CH + H2 + M	k_f	5.000e+15	0.00	42800.0	
5. CH2 + M <=> CH + H + M	k_f	4.000e+15	0.00	41800.0	
6. CH2 + M <=> C + H2 + M	k _f	1.300e+14	0.00	29700.0	
7. CH + M <=> C + H + M	k _f	1.900e+14	0.00	33700.0	
8. C2 + M <=> C + C + M	k _f	1.500e+16	0.00	716000.0	
9. H2 + M <=> H + H + M	k_f	2.230e+14	0.00	48350.0	
10. CN + M <=> C + N + M	k_f	2.530e+14	0.00	71000.0	
11. NH + M <=> N + H + M	k_f	1.800e+14	0.00	37600.0	
12. HCN + M <=> CN + H + M	k_f	3.570e+26	-2.60	62845.0	
13. CH3 + N <=> HCN + H + H	k_f	7.000e+13	0.00	0.0	
14. CH3 + H <=> CH2 + H2	k_f	6.030e+13	0.00	7600.0	
15. CH2 + N2 <=> HCN + NH	k_f	4.820e+12	0.00	18000.0	
16. CH2 + N <=> HCN + H	k_f	5.000e+13	0.00	0.0	
17. CH2 + H <=> CH + H2	k_f	6.030e+12	0.00	-900.0	
18. CH + N2 <=> HCN + N	k_f	4.400e+12	0.00	11060.0	
19. CH + C <=> C2 + H	k_f	2.000e+14	0.00	0.0	
20. C2 + N2 <=> CN + CN	k_f	1.500e+13	0.00	21000.0	
21. CN + H2 <=> HCN + H	k_f	2.950e+05	0.00	1130.0	
22. CN + C <=> C2 + N	k_f	5.000e+13	0.00	13000.0	
23. N + H2 <=> NH + H	k_f	1.600e+14	0.00	12650.0	
24. C + N2 <=> CN + N	k_f	5.240e+13	0.00	22600.0	
25. C + H2 <=> CH + H	k_f	4.000e+14	0.00	11700.0	
26. H + N2 <=> NH + N	k_f	3.000e+12	0.50	71400.0	
27. H + CH4 <=> CH3 + H2	k_f	1.320e+04	3.00	4045.0	

Input files for Chapter 4

D.1 Input file for the simulation of the Lobb sphere experiments

```
# sphere.py
# Rowan J Gollan
# 26-June-2005
   Lobb, R.K. (1964)
#
   Experimental measurement of shock detachment distance on spheres
#
#
   fired in air at hypervelocities.
#
   pp 519--527 in
#
   The High Temperature Aspects of Hypersonic Flow
   edited by Nelson, W.C.
#
#
   Pergamon Press, Oxford, 1964
#
# Description:
   A nylon sphere 0.5-inch diameter fired into a ballistic
#
#
   test range.
# Updated: 08-April-2007
Db = 1.0/2.0 * 0.0254 \# Diameter of ball bearing
Rc = Db / 2.0
from math import sqrt, atan2, cos
from cfpylib.gasdyn.billig import x_from_y, delta_over_R, y_from_x
#-----
# parameter setup
# based on rho.R and u_inf
#
rR = 1.0e-4
u_inf = 4000.0
rho_inf = rR/Rc
T_{inf} = 293.0
f_{inf} = [0.78, 0.22, 0.0, 0.0, 0.0]
from libgas2 import *
reaction_scheme_name = "Neutral air reactions"
reaction_scheme_file = "air-5sp-6r.rsi"
gas_model = "perf_gas_mix"
gas_file = "air-5sp.pgm"
set_type_of_gas(gas_model, gas_file)
```

```
Q = gas_data()
set_array_sizes_in_gas_data(Q, get_number_of_species(), get_number_of_vibrational_species())
Q.rho = rho_inf
Q.T = T_{inf}
set_massf(Q, 0, 0.78) # mf[N2]
set_massf(Q, 1, 0.22) # mf[02]
EOS_rhoT(Q, False)
p_inf = Q.p
M_inf = u_inf / Q.a
job_title = "Sphere fired into air: p=%f, u=%f" % (p_inf, u_inf)
flow_lengths = 30
# grid discretization
nn = 135
# body flow lengths
BFL = Db / u_inf
#
\# end parameter setup
#-----
# Setup simulation
gdata.title = job_title
# Gas model and flow properties
gdata.reacting_flag = 1
gdata.reaction_scheme_name = reaction_scheme_name
gdata.reaction_scheme_file = reaction_scheme_file
gdata.set_gas_model(gas_model, gas_file)
gdata.energy_exchange_flag = 0
inflow = FlowCondition(p=p_inf, u=u_inf, v=0.0, T=T_inf, mf=f_inf)
initial = FlowCondition(p=p_inf/3.0, u=0.0, v=0.0, T=T_inf, mf=f_inf)
# Build the geometry from the bottom-up, starting with nodes...
# Scale it with the sphere radius.
delta = delta_over_R(M_inf, 1) * Rc
delta_offset = 5.0/100.0*delta
y_{inc} = 5.0/100.0
x_shift = delta_offset
# In preparation for defining nodes, generate a few sample points
# along the expected shock position
# (which is estimated via Billig's correlation).
xys = []
y_top = y_from_x(0.0, M_inf, theta=0.0, axi=1, R_nose=Rc)
dy = y_{top}/5.0
for y in [ i*dy for i in range(6) ]:
    x = x_from_y(y, M_inf, theta=0.0, axi=1, R_nose=Rc)
   xys.append((x,y)) # a new coordinate pair
    print "x=", x, "y=", y
a = Node(-Rc, 0.0, label="a")
b = Node( 0.0, Rc, label="b")
c = Node( 0.0, 0.0, label="c")
d = [] # will use a list to keep the nodes for the shock boundary
```

```
# point on x-axis
x, y = xys[0]
xd = x + x_shift
d.append(Node(-1.0*xd, y, label="d"))
for x, y in xys[1:-1]:
    # the outer boundary should be a little further than the shock itself
        theta = atan2(y, x)
    #
    #
        Rx = Rc*cos(theta)
    xd = x + x_shift
    yd = y * (1.0 + y_inc)
    d.append(Node(-1.0*xd, yd, label="d"))
x, y = xys[-1]
yd = y * (1.0 + y_inc)
d.append(Node(-1.0*x, yd, label="d"))
\# ... then lines, arcs, etc, that will make up the block boundaries.
axis = Line(d[0], a) # first-point of shock to nose of sphere
body = Arc(a, b, c)
shock = Spline(d)
top = Line(d[-1], b) # top-point of shock to top of sphere
# Specify the boundary discretization
nnx = nn
nny = nn
# ... and finally, assemble the block from its boundary faces.
block_0 = Block2D(make_patch(top, body, axis, shock),
                  bc_list=[ExtrapolateOutBC(), SlipWallBC(), SlipWallBC(), SupInBC(inflow)],
                  nni=nnx, nnj=nny,
                  fill_conditions=initial,
                  hcell_list=[(nnx, 1)])
# simulation control
gdata.flux_calc = ADAPTIVE
gdata.max_time = flow_lengths * BFL # should be large enough to allow steady flow
gdata.max_step = 600000
gdata.axisymmetric_flag = 1
gdata.cfl = 0.4
gdata.dt = 1.0e-10
gdata.dt_history = 1.0e-5
gdata.dt_plot = 1.0e-3
```