Transport and equilibrium in molecular plasmas: the sulfur lamp

PROEFSCHRIFT

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CHAPTER 1

General Introduction

Any technological advance is ultimately the result of the manipulation of matter. The initial progress of the human race is even characterized by its mastery over materials; from the stone through to the iron age. Over the last century or so, advances have been distinguished by the manipulation of matter on the microscopic scale. One of the more important developments has been our ability to artificially maintain the plasma state. The exploitation of plasmas, facilitated by their ability to preserve local neutrality while free electrons are heated by an external source, is based on the access to the internal states of atoms and molecules which they provide. The energy transfer to the surrounding environment via the excited states of various particles is the key to their usefulness. The tremendous freedom afforded by the plasma state makes it ideal for many applications such as spectrochemical analysis [1], material deposition [2], welding and cutting [3]. However, the most important use of artificial plasmas is in the generation of visible light [4].

This thesis deals with a new medium for this purpose; a high pressure sulfur plasma. The discharge has the appealing property of producing a pleasant spectrum and doing so efficiently. Moreover, sulfur is more environmentally friendly than mercury, which is biologically hazardous and environmentally persistent, and found in most contemporary gas discharge lamps. First discovered as such in 1980 by Michael Ury and Chuck Wood the use of sulfur in lighting applications was the sole preserve of Fusion Lighting Systems which produced a system under the name Solar 1000 for several years from 1995 [5] to 1999. The bulb used is simply a hollow quartz ball filled with several milligrams of sulfur powder and argon gas (an example of which is shown on the cover of this thesis).

The human eye is sensitive to radiation in the 400-700 nm range and is most receptive around 555 nm and less so at other wavelengths. First established as a standard in 1924 by the international illumination society, the Commission Internationale de l’Eclairage, this sensitivity is quantified by the so-called eye sensitivity curve, which is shown in figure 1.1. It is important that a lamp not only produce much light efficiently, but to do so at many wavelengths, i.e. be polychromatic. Furthermore, the distribution of power in the spectrum should be centered as close to 555 nm as is possible rather than at another
Chapter 1: General Introduction

Figure 1.1: *Eye sensitivity curve together with the spectrum of a high pressure sulfur discharge*

wavelength where the efficacy of the source is prejudiced by the inherent insensitivity of the eye. A typical spectrum of a high pressure sulfur discharge is also shown in figure 1.1. The emission is broad, starting at 380 nm and tails off beyond 900 nm with the maximum in emission at 536 nm. The advantages of sulfur become more apparent when one considers current plasma lamps. Two of the more common examples of these are mercury and sodium lamps. The former employs a mercury plasma where upwards of 70% of input electrical power can be radiated in the 253.7 nm line, generated by the decay of the $6^3P_2$ state to the $6^1S_0$ ground state in the atom. This line is invisible, and indeed dangerous to the naked eye, and is converted to visible wavelengths by a fluorescent powder on the inside of the lamp. Sodium discharges on the other hand rely on atomic lines emitted around 589 nm. The spectrum is more or less a monochromatic yellow.

These are good examples of the limitations present in current light sources. Either efficiency is high or the spectrum is not sufficiently polychromatic. There are of course many lamps in which these issues have been addressed by the addition of various trace species or where fill pressures are varied. However, not only does a sulfur based system provide an environmental alternative, the spectrum is also entirely molecular in origin. The chief advantage of using the radiative decay of a molecular electronic state for light production is that rather than emitting in a narrow wavelength range as atoms tend to do, the small increments in excitation energy at which they lie above the zeroth level means that by populating vibrational levels in the excited state a broader spectrum about a central wavelength can be produced. However, where this lies in a vibronic transition is subject to the balance between population distribution over vibrational states and self absorption.

While a sulfur based light source would appear to be an excellent prospect there are several important factors that restrict its use. Firstly, sulfur is highly electronegative
and in the plasma state destroys electrodes made from conventional materials. Secondly, pressures above three bar are required to produce visible light which in turn require high power densities. Finally, in order to optimize light production the bulb has to be of a certain size such that it has been rotated in order that the effects of convection are overcome and the necessary vapour pressure achieved. The most cost effective option for generating the required powers is to use a magnetron, very much like those in microwave ovens and indeed the Solar 1000 was so constructed. The bulb was rotated in a resonant cavity placed on top of a magnetron. In this thesis the arrangement of a magnetron, waveguide, resonant cavity and rotating bulb is referred to as the sulfur lamp. Despite much initial fanfare and publicity the Solar 1000 is at this time no longer on the market. Nevertheless, what remains interesting is the basis of the lamp, the molecular spectrum produced by \( S_2 \).

The most important step in studying a new lamp is to understand its energy balance. To achieve this a combined modelling/experimental approach is taken. The integrated environment for the construction and execution of plasma models PLASIMO \([6, 7]\) is used for that aspect of the sulfur lamp that is of chief interest, i.e. the spectrum, the effect of rotation is ignored and the plasma-electric field interaction is treated in the most straightforward means possible. As is suitable for the first investigations into a new and previously unstudied system, the plasma will be modelled as if it were in local thermal equilibrium (LTE). Several atomic lines found in the spectrum were used for validation of the model and the technique of power interruption was employed to expose any inconsistencies in the LTE approach.

An issue that quickly arose in the course of the work was that of a lack of fundamental data. Not only is little known about sulfur in the plasma state but also the elementary interactions between species, that permit studies into more established plasmas for which can one rely upon several decades of literature, are also unavailable. This is not a problem restricted to the current subject. In fact “the dearth of basic data for the simulation of plasma generation and transport” \([8]\) means that “the lack of fundamental data for the most important chemical species is the largest factor limiting the successful application of models of industrial interest” \([9]\). A secondary goal of this work is to address this lack of data as it applies to the production of radiation from diatomic molecules and the transport properties of plasma mixtures. This is done in a general way which can be applied to arbitrary systems and is not sulfur specific.

**Thesis outline**

In chapter 2 the first LTE model of the lamp is developed. Here, radiation generation is treated semi-classically and a single radiating transition in \( S_2 \) is chosen. The efficiency of the lamp due to that single transition is confirmed and the response of the spectrum to operational changes in pressure and power agree with experiment. In chapter 3 the absolute measurement of several sulfur atomic lines found in the spectrum is used to determine an effective central temperature. Again an LTE approach was used and the average value found of 4100 K agrees very well with the results of the models. In chapter 4 the model of the energy balance is developed further and radiation generation is treated quantum mechanically. The most important addition to the model is the inclusion of \( S_3 \), UV absorption in which is shown to be responsible for the short wavelength behaviour of
the spectrum. In both models the simulated spectrum was deficient at longer wavelengths which even the inclusion of several extra radiating states in $S_2$ could not remedy.

The response of the atomic and molecular spectra to an interruption of the supplied power are examined in chapter 5, experimentally, via global considerations and with simulations. For the latter the model from chapter 4 was modified. The large inelastic losses associated with the production of the molecular states are shown to prevent a substantial difference between electron and heavy particle temperatures from developing. Furthermore, the simulated decay of the spectrum with the LTE model not only predicts the timescale on which the spectrum decays but also the response as a function of wavelength. The observed decay of the molecular spectrum at longer wavelengths is found to be too fast if the system were to be ruled by a single temperature. This indicates that the excitation temperature over the vibrational states in the $B$ state decreases with increasing vibrational quantum number.

Chapters 6 and 7 present two scaling laws. The former shows how the electronic transition dipole moment for a molecular absorption, which is crucial for studying molecular radiation, can be found from that in a similar species while the latter reports a power law in which the high order polarizabilities of atoms and molecules can be found from the dipole values. Chapter 8 shows that in conjunction with the results of chapter 7 a polarizability approach for molecular collisions leads to extremely accurate data for van der Waals potentials for a large class of interacting species. Chapter 9 prescribes an fixed set of model potentials that can be used to find the transport properties of LTE plasma mixtures. Several test case plasmas are treated with the approach. Given only information needed for the composition calculation and species data, which can be determined for any atom or molecule, the accuracy of the approach is shown to be high.

The thesis ends with general conclusions in chapter 10.

References


A self consistent LTE model of a microwave driven, high-pressure sulfur lamp

A one dimensional LTE model of a microwave driven sulfur lamp is presented to aid our understanding of the discharge. The energy balance of the lamp is determined by Ohmic input on one hand and transport due to conductive heat transfer and molecular radiation on the other. We discuss the origin of, and operational trends in the spectrum, present the model and discuss how the material properties of the plasma are determined. Not only are temperature profiles and electric field strengths simulated but also the spectrum of the lamp from 300 nm to 900 nm under various conditions of input power and lamp filling pressure. We show that simulated spectra demonstrate observed trends and that radiated power increases linearly with input power as is also found from experiment.

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2.1 Introduction

There are essentially three criteria that a lighting application should fulfill: good colouring, high efficiency and longevity. However, the first two of these are often mutually exclusive. A familiar example is the low pressure mercury lamp in which more than 70% of input power is converted into UV photons. The overall efficiency of the lamp is reduced by the need to convert these quanta into visible photons via the fluorescent coating. The issue of lamp lifespan has been addressed in recent years by the use of electrode-less configurations such as Osram’s Endura and Philips’ QL lamp. However, the light emitting particle remains mercury, which brings us to a fourth criterion, of ever increasing importance, that lamp fillings should have little environmental impact. Mercury, present in most plasma lamps, is a notorious pollutant.

Alongside the well known lamp fillings and power in-coupling techniques, Fusion Lighting Systems produced the Solar 1000 in 1995, a microwave driven high pressure lamp with sulfur as the radiating medium. This lamp displays all of the properties listed above. Firstly it has excellent colouring; the spectrum of the lamp appears continuous and overlaps the eye-sensitivity curve very well. Little of the spectrum lies in the UV and no more than a few percent of total spectral power is found in the infrared. Secondly its radiative efficiency is very high; up to 70% of power coupled into the plasma can be emitted as (visible) light. Thirdly, since there are no electrodes in the bulb and the wall is unaffected by the plasma, the bulb is expected to have a long lifetime. Finally, sulfur is much less environmentally damaging than mercury.

Nevertheless, there are some disadvantages. Hot re-ignition is a problem due to the high vapour pressure during operation. Also the lifetime and efficiency of the magnetron power supply are low which reduces the overall system efficacy and lifespan; in fact the magnetron would have to be replaced more often than the bulb. Another factor is that the lamp contains moving parts: the bulb itself needs to be rotated.

However, despite its striking difference to conventional lamps, its high plasma efficiency and good colouring are indisputable. Thus such a new lamp, with a radiating medium previously unknown as such, presents the challenge of identifying the phenomena that result in its unique properties. Insight gained in studying the sulfur lamp could subsequently lead to the better understanding of other molecular lamps.

In the first instance an experimental approach to understanding the lamp is hampered by several factors. A consequence of the lamps large spectral power density and the fact that the bulb rotates is that standard laser diagnostics would be rather involved. Also identification of molecular vibrational/rotational structure in the spectrum is very difficult due to the high operating pressure where there are ca. $10^6$ overlapping lines. Therefore, in light of the many advantages associated with sulfur discharges, the lack of detailed information on its internal processes and the inherent difficulty of applying standard diagnostics, we attempt to explain the discharge by constructing a numerical model for the system. To facilitate the construction of the model we use the plasma simulation toolkit PLASIMO [1, 2], which provides the framework for the plasma properties, such as thermal and electrical conductivity, used in the transport and energy balances which are solved subject to user definable boundary conditions.

This paper is structured as follows: firstly, we examine the origin of the spectrum and operational trends. After reviewing the state of the art, we concentrate on the model itself
Figure 2.1: \textit{Left: potential curves for the ground and excited states [4]. The B excited state is pre-dissociated at } v = 9 \textit{ by the } \Pi, \textit{ an unbound state. Right: potential curves completed using an enhanced Morse potential to the available data.}

and discuss the electromagnetic and radiation generation/transport approaches. Then we choose which species to include in the model and demonstrate how we calculate the electrical and thermal conductivity of the plasma. Finally we present the results of simulations, examining the behaviour of various field variables as functions of power and pressure, and finish with our conclusions.

\section{2.2 Origin and operational trends in the spectrum}

An apparatus used to ignite, maintain and measure the lamps spectrum has already been described elsewhere [3]. Despite some differences with the Solar 1000 the two systems are essentially the same: a magnetron introduces EM radiation at 2.45 GHz into a waveguide to which a resonator is attached. The main difference between the two is the resonator used. In our case it is a hemi-ellipse which supports a TM$^{101}$ mode, while the Fusion lamp employs a cylindrical cavity that resonates in the TE$^{111}$ mode.

\subsection{2.2.1 Origin of the spectrum}

Radiation produced by the sulfur lamp has been identified as primarily arising from transitions between the molecular excited state, $B^3\Sigma_u^+$, and the ground state, $X^3\Sigma_g^{-}$ [4]. There may also be a contribution to the spectrum from transitions between the $^1\Pi_u$ and the ground state. However this is an unbound-bound transition which is excluded from the model.

Only part of the Potential Energy Curve (PEC) for the molecular ground state is known. Given the dissociation energy and the energy spacing of the lowest vibrational levels, there ought to be 60 vibrational states. However, only 30 have been measured.
The $B$ state is pre-dissociated by the $\Pi$ state at the ninth vibrational level. An enhanced Morse potential [5], was used to complete the PECs up to their dissociation energy - see figure 2.1.

Transitions between states that lie at radial separations greater than 2.5 Å produce radiation at wavelengths longer than 620 nm. Above this, transitions from the unbound state may contribute to the lamp’s spectrum. The exclusion of the unbound state could mean that there will be less red in simulated spectra compared to the measured spectra.

### 2.2.2 Bulb characterization

The bulbs are quartz spheres fixed at the end of a quartz rod to allow it to be rotated from outside the cavity. A typical bulb filling is 30 mg sulfur powder and 100 mbar argon (at room temperature). Argon is used as the ignition gas which forms a precursor plasma to bring the sulfur powder into the gas phase. Krypton or xenon may also be used but breakdown is difficult to achieve. The total pressure in the lamp is taken to be the sum of pressure of an ideal sulfur gas, consisting only of $S_2$, and the argon gas pressure. Both are evaluated at 2500 K which is taken to be the typical plasma temperature, $T_P$. The sulfur gas pressure, $P_{S_2}$, and the argon gas pressure, $P_{Ar}$, are given by

$$P_{S_2} = \frac{mRT_P}{VM} \quad \text{(2.1)}$$

$$P_{Ar} = \frac{T_P P_{Ar}^{Fill}}{T_{Fill}} \quad \text{(2.2)}$$

where $V$ is the bulb volume in m$^3$, $R$ is the gas constant in J mol$^{-1}$K$^{-1}$, $M$ the molar mass of $S_2$ in kg mol$^{-1}$, while $m$ is the amount of the sulfur powder in the bulb. $P_{Ar}^{Fill}$ and $T_{Fill}$ are the pressure and temperature of the argon buffer gas when added to the bulb.
2.3 State of the art

(at room temperature). The typical operating pressure is 6 bar, 5 bar due to sulfur and 1 bar due to argon. However, from now on when we refer to a lamp we do this by the sulfur pressure alone at $T_P$. In our simulations the operating buffer gas pressure, $P_{Ar}$, is always 1 bar and the lamp diameter 36 mm.

2.2.3 Spectral trends

In figures 2.2 and 2.3 spectra are shown as a function of input power and pressure. The following trends can be observed:

- Power: at a fixed filling pressure, an increase in power causes a linear increase in the spectral radiant power (see figure 2.2) - there is almost no shift in the wavelength of the spectral maximum.

- Pressure: the spectrum shifts to the red with increasing sulfur pressure as can be seen in figure 2.3. The radiated power also decreases above 4 bars.

2.3 State of the art

Most of what is reported concerning microwave powered high pressure sulfur lamps can be found in patent literature and is appropriate to that medium. As far as we are aware the only quantitative information published, has been by van Dongen [3]. Here we summarize the principal conclusions from these experiments.

The temperature on the bulb’s outer wall was measured with an infrared camera and was found to be between 1000 K and 1200 K for most situations. An estimate of the central temperature was made by examining the spectrum at 676 nm, the wavelength at which atomic sulfur has a non self-absorbing line. Since this line could not be detected above the molecular background, the maximum temperature at the centre of the lamp was estimated to be 5500 K. The electric field at the cavity wall was measured by placing a metal probe just inside it and the field strength at the lamps position could then be determined. Under most operating conditions the electric field strength was found to be 400 V/cm [3]. With this knowledge of the electric field, power losses in the cavity were estimated and the power balance for the whole system was completed. The main result was that about 70% of power generated by the magnetron was coupled into the plasma.

2.4 The Model

2.4.1 Simplifications

In order to reduce the complexity and dimensionality of the model, we present here the assumptions and simplifications made in the description of the system. Firstly, we assume LTE, which is a standard assertion applied to high pressure lamps. This may seem a drastic assumption given the huge radiation losses. However, the equilibrium restoring processes are extremely fast due the high pressure - the electron $S_2$ collision frequency is
Chapter 2: A self consistent LTE model

ca. 10 GHz. In the first instance we assume that this is sufficient to allow us to proceed as if the lamp were in LTE.

Secondly we discount convective transport as generated by rotation and gravity. Thus the system is a closed one for which a Navier-Stokes approach is not needed. The assumption of LTE precludes the solution of particle balances and leaves us with a 1-D energy equation, which we discuss now.

2.4.2 The energy balance

The energy balance which describes the competition between Ohmic dissipation and the energy transport due to conduction and radiation can be written as:

\[
\frac{1}{2} \sigma(r)E(r)^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r} T(r)) + \int_0^\infty 4\pi \left[ j_{\nu}(r) - \frac{1}{4\pi} \int_0^\infty \kappa_{\nu}(r) I_{\nu} d\Omega \right] d\nu
\]  
(2.3)

The thermal conductivity, \(\lambda\), and the electrical conductivity, \(\sigma\), will be discussed in sections 2.5.3 and 2.5.4. We will begin by detailing how we calculate the electric field strength, then discuss radiation generation and transport and finally illustrate the various steps in the iterative process.

2.4.3 Electromagnetic module

A complete description of the microwave field is beyond the scope of this study, instead we require a representative model to describe the plasma-electric field interaction. We use a skin depth model for which the electric field everywhere in the lamp is principally determined by the field strength at the outer wall, \(E_{\text{wall}}\):

\[
E(r) = E_{\text{wall}} e^{-\frac{\delta_0}{\delta(x)}}, \tag{2.4}
\]

where \(R\) is the lamp radius and \(\delta(x)\) is the skin depth ( \(\delta(x) = \sqrt{\frac{2}{\mu_0 \sigma(x) \omega}}\) ). The value of the electric field strength at the wall is determined by \(P_{\text{Ohm}}\), the total dissipated power, which is an input model parameter. This is done by equating the integral of the local power density \(\frac{1}{2} \sigma(r)E(r)^2\) over the lamp volume to the total power

\[
P_{\text{Ohm}} = 2\pi \int_0^R \sigma(r)E(r)^2 r^2 dr \tag{2.5}
\]

Inserting (2.4) into (2.5) we get that

\[
E_{\text{wall}} = \left( \frac{P_{\text{Ohm}}}{2\pi} \left[ \int_0^R \sigma(r) e^{-2 \int_0^R \frac{dr}{\pi r^2}} \right]^{-1} \right)^{1/2} \tag{2.6}
\]

\(E_{\text{wall}}\) is determined at each iteration using \(P_{\text{Ohm}}\) and the electrical conductivity profile. The new electric field value is then used to determine the Ohmic dissipation throughout the lamp and a new temperature profile is found by solving equation (2.3). The new electrical conductivity profile is used to find the new \(E_{\text{wall}}\) and so on.
2.4 The Model

2.4.4 Generation and transport of radiation

Since we are dealing with a plasma for which a considerable part of the input power is converted into radiation (it is a lamp after all) it is extremely important to describe the generation and transport of radiation as well as possible. However, a full quantum mechanical description of the origin of the spectrum is out of question. We have already mentioned that the spectrum is the result of the overlap of many thousands of lines that result from rovibrational transitions in the S\textsubscript{2} molecule. This is an extremely complex task since the equation of radiative transport must be solved for the entire lamp, for about 500,000 frequency intervals during each iteration of the energy balance.

Radiation generation

Our approach in overcoming the problem sketched above is to employ an approximate technique for the generation of molecular radiation. It is based on the Classical Franck-Condon Principle (CFCP), and is a means to determine \( j_\nu \) and \( \kappa_\nu \) as smooth functions of frequency. We present only an overview of the approach here, see [6] for a detailed discussion.

The generation of molecular radiation can be seen in analogy with that of atomic line radiation for which the emission coefficient is given by

\[
 j_\nu = n(Q) \frac{h\nu}{4\pi} A(Q, P)\phi_\nu(\nu)
\]  

(2.7)

Here \( n(Q) \) is the density of the radiating upper state, \( A(Q, P) \) the transition probability and \( \phi_\nu(\nu) \) is the line profile.

Classically, molecular radiation can be seen as a high pressure limit of atomic radiation, where the species density is sufficient for internuclear potentials to become relevant and the line-profile is subsequently connected to the distribution of molecular states. Transitions between these states are dictated by the CFCP, in which there is no loss of atomic kinetic energy and bound atoms are stationary during a transition. Thus, the energy of an emitted photon is determined solely by the change in potential energy where the transition takes place at a fixed internuclear distance. Thus, the energy of a photon can be written in terms of internuclear distance \( r \);

\[
h\nu(r) = V_Q(r) - V_P(r).
\]

Here \( V_Q \) and \( V_P \) are the potential energies of the upper and lower states. The line profile of radiation emitted in the range \( r \ldots r + \Delta r \) is therefore

\[
\phi(\nu) = \frac{1}{d\nu} = \left( \frac{d\nu(r)}{dr} \right)^{-1}
\]  

(2.8)

Using equation (2.11) for the density of the molecular state in terms of its constituent atoms we get the molecular analog to equation (2.7)

\[
j_\nu(r) = \eta_A \eta_B \left( \frac{h}{\sqrt{2\pi \mu k_B T}} \right)^{1/3} \exp \left( \frac{V_Q(r)}{k_B T} \right) \frac{h\nu A_{QP}(\nu(r))}{4\pi} \frac{4\pi r^2}{|d\nu(r)/dr|} 
\]  

(2.9)
Figure 2.4: Spectral absorption coefficient, $\kappa [m^{-1}]$ for the $B \rightarrow X$ transition in the sulfur molecule as a function of temperature and wavelength. The $S_2$ densities are determined from a full composition calculation (see figure 2.5). The plasma is optically thick between 200 and 400 nm and almost fully transparent above 550 nm. As temperature increases there are less and less molecules in lower rovibrational states and hence the values for $\kappa$ above 5000 K are lower.

The spectral absorption coefficient can be found via the Planck formula and is

$$
\kappa_\nu(r) = \eta_{AB} \frac{c^2 A_{QP}(\nu(r))}{8\pi \nu^2(r)} \frac{4\pi r^2}{|d\nu(r)/dr|} \left[ \exp \left( \frac{-V_P(r)}{k_B T} \right) \right],
$$

(2.10)

where we have omitted the stimulated emission term. The electronic transition probability is given by

$$
A = \frac{16\pi^3 \nu^3}{3e_0 \hbar c^3} |M(r)|^2,
$$

where $M(r)$ is the electronic transition dipole moment as a function of internuclear separation obtained from [8]. In figure 2.4 the spectral absorption coefficient is shown as a function of temperature and wavelength for the $B\Sigma_u^- \rightarrow X\Sigma_g^-$ transition calculated using equation (2.10). The plasma is optically thick for quanta with wavelengths below 400 nm and almost fully transparent for radiation above 600 nm. In between the opacity of the plasma is semi-thick, which has important consequences for the way in which we deal with the transport of radiation. If the radiation produced by the lamp was completely optically open, then the radiative contribution to the energy balance could be treated as a pure loss term. On the other hand, if the radiation was optically thick, the energy balance contribution could be treated as a heat conduction term. However, neither of these is the case and as such the local energy balance will be affected by the non-local production of light and a special approach is needed.
2.4 The Model

Transport of radiation

Since the production of radiation is isotropic whereas the rate of local absorption is dependent on the direction from which the light came from equation (2.3), the transport of radiation is three dimensional for the current case, two spatial coordinates and a frequency coordinate.

In order to deal with this transport irrespective of opacity, we employ a ray tracing method. Rays enter the plasma with \( I_\nu = 0 \), and intensity along them increases due to local emission; transport is realized through absorption, exchanging energy from the ray to the plasma. In fact we integrate along the lines and solve the equation of radiation transfer:

\[
dI_\nu = (j_\nu - \kappa_\nu I_\nu)ds.
\]

The net accumulation of intensity along a ray allows the radiative term in the energy balance to be determined. The absorption term in the energy balance as given by \( \int_\nu \kappa \int_4\pi I_\nu(r)d\Omega \) depends on the action of these rays. Since we have a finite number of rays passing through the plasma, the integration over solid angles is approximated as:

\[
\int_4\pi I_\nu d\Omega \approx \sum_{\text{lines}} I_\nu \Delta \Omega_{\text{line}}.
\]

The subject of radiation generation and transfer is very involved and deserves a dedicated forum. As such we have tried to demonstrate the essence of the techniques we have used and direct the reader to more in-depth discussions on these topics [6, 7].

2.4.5 Boundary conditions

Two boundary conditions are applied in the model. Firstly there is no temperature gradient at \( r = 0 \), i.e. \( \partial T/\partial n = 0 \), where \( n \) is normal to the boundary in question. Secondly, a Neumann condition is applied stating that the heat flux at the wall volume equals that through the wall, i.e.

\[
\lambda_{\text{plasma}} \frac{\partial T}{\partial n}_{\text{wall}} = \frac{\lambda_{\text{wall}}}{\delta_{\text{wall}}} (T_{\text{inner}} - T_{\text{outer}})
\]

where \( \delta_{\text{wall}}, \lambda_{\text{wall}}, T_{\text{inner}}, \) and \( T_{\text{outer}} \) are the wall thickness, thermal conductivity of the wall material and the temperature at the inner and outside wall respectively. We fix the wall temperature to the measured value of 1100 K and wall thickness to 2 mm for all simulations.

2.4.6 Iteration procedure

As we have a non-local radiative energy term in the energy balance, the iteration procedure requires an extra step to determine the local radiative contribution. The simulations proceed as follows:

- Start with a temperature profile which fixes thermal and electrical conductivity.
- Determine the electric field.
Chapter 2: A self consistent LTE model...

![Graph showing density vs temperature]

Figure 2.5: Composition of a 5 bar sulfur plasma with 1 bar of argon buffer gas. Below 3700 K we have essentially a molecular plasma with a very low ionization degree $\approx 10^{-5}$. $S_2^+$ is the dominant ion up to 5000 K.

- Compute $j$ and $\kappa$
  - perform ray tracing in several directions
  - determine $I_\nu$ at each point in the plasma, from a number of directions
  - perform integration over all solid angles
- Determine net contribution of radiation to the energy balance for each control volume
- Solve the energy balance equation itself which provides a new temperature profile
- Determine the electric field ...

2.5 Material properties

Here we discuss how the calculation of the composition, thermal and electrical conductivity of the plasma is carried out. However, we begin by discussing the choice of species and reactions that will be included in the model.

2.5.1 Reactions and species

The wall temperature has been measured with an infrared camera and is always around 1100 K. We do not treat the sulfur trimer, $S_3$, and work from the premise that the heaviest sulfur species is the dimer, $S_2$, which it is the only species responsible for the
2.5 Material properties

Table 2.1: List of reactions we consider and their associated ‘dissociation energies’.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>$\Delta E$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_2 + X$</td>
<td>$2S + X$</td>
<td>4.46</td>
</tr>
<tr>
<td>$S_2 + e$</td>
<td>$S^+ + e + e$</td>
<td>9.36</td>
</tr>
<tr>
<td>$S^- + e$</td>
<td>$S + e$</td>
<td>1.8</td>
</tr>
<tr>
<td>$S + e$</td>
<td>$S^+ + e + e$</td>
<td>10.4</td>
</tr>
<tr>
<td>$S^- + e$</td>
<td>$S + e$</td>
<td>2.0</td>
</tr>
<tr>
<td>$Ar + e$</td>
<td>$Ar^+ + e + e$</td>
<td>15.76</td>
</tr>
</tbody>
</table>

spectrum of the lamp. This limits the model to those pressures where the assumption that the trimer density is negligible is valid. The sulfur atom and dimer are well known electronegative species and the negative ions of each are included in the composition. The ionization of argon is included in the composition calculation although the ion will be of no consequence. We list the reactions considered in the model in table 2.1.

2.5.2 Composition module

Since LTE is assumed, temperature and pressure determine species densities. All possible reactions that occur in the lamp, apart from the molecular excitation, can be written in terms of a generalized dissociation balance

$$AB \rightleftharpoons A + B$$

where $AB$ is the dissociating/ionizing species. The elementary law of mass action, applicable to all reactions taking place in the lamp, implies the following relationship between species densities

$$\frac{n_{AB}}{n_{AB}} = \left(\frac{2\pi \hbar kT}{\mu^3}ight)^{3/2} \exp\left(\frac{-D}{kT}\right), \quad (2.11)$$

where $\eta$ is the density weighted with the partition sum, $D$ is a generalized dissociation energy and $\mu$ is the reduced mass of the combined system $AB$. This relation is valid for the ionization, dissociation and negative ion destruction of atoms as well as diatomic molecules. Equation (2.11) is more commonly know as the Guldberg-Waage or Saha equation for the special cases of molecular dissociation into neutral fragments and ionization.

We solve the system of Guldberg-Waage relations with the state equation and charge conservation constraint using a Levenberg-Marquard minimization routine [9]. The only excited species we deal with is the $B$ state of the sulfur molecule and use the Boltzmann relation to determine the vibrational state densities in relation to the ground state.

The result of such a calculation is presented in figure (2.5) for the sulfur plasma in question. It can be readily seen that below 5000 K the dominant ion is $S^+_2$ and that the ionization degree is of the order of $10^{-5}$. 


2.5.3 Thermal conductivity module

The coefficient of thermal conductivity in a plasma can be written as the sum of two components:

$$\lambda = \lambda_R + \lambda_F$$  \hspace{1cm} (2.12)

where $\lambda_F$ is the so called frozen contribution related to the transfer of kinetic energy and $\lambda_R$ is the reactive term which describes transport due to the release of chemical enthalpy. We ignore the thermal conductivity due to electrons as it is usually of consequence only at temperatures higher than those we expect to find in the lamp.

The frozen component [10] is expressed as the weighted sum of the individual contributions, $\lambda^*_s$, of all the species in the plasma

$$\lambda_F = \sum_s \left( \frac{n_s}{\sum_r n_r M_{sr}} \right) \lambda^*_s$$  \hspace{1cm} (2.13)

where

$$M_{sr} = \sqrt{\frac{2m_{sr}}{m_s}} \frac{Q_{sr}}{Q_{ss}}$$  \hspace{1cm} (2.14)$$

$n_s$ and $m_s$ are the density and mass of species $s$, while $Q_{sr}$ is the momentum transfer cross section for a collision involving species $s$ and $r$. The term in brackets in equation (2.13) represents the magnitude of the contribution of one species based on its mass, density and collisional cross section with all other species. We take the frozen thermal conductivity of a particular species $s$ to be

$$\lambda^*_s = \left[ \frac{15}{8} k_B C_s l_s \right] \left[ \frac{9\gamma_s - 5}{15(\gamma_s - 1)} \right]$$  \hspace{1cm} (2.15)

where $C_s$ and $l_s$ are the mean thermal velocity and the mean free path of the species in a pure gas of itself. The second factor on the right hand side of equation (2.15) is the so-called Eucken correction factor, which corrects for possible rotation and vibration.
The treatment of Butler and Brokaw for the reactive thermal conductivity is used [11], we present only their results necessary to effect a calculation. A system of $\nu$ independent chemical reactions involving $\mu$ chemical species is written as

$$\sum_{j=0}^{\mu} N_{ij} X^j = 0 \quad i = 0, 2, \cdots, j, \nu$$

where $X^j$ represents the $j^{th}$ chemical species, $N_{ij}$ is the stoichiometric coefficient for species $j$ in reaction $i$. Using this formalism for describing reactions, the coefficient for the reactive thermal conductivity is

$$\lambda_R = \frac{1}{RT^2} \begin{vmatrix} A_{11} & \cdots & A_{1\nu} & \Delta H_1 \\ \vdots & \ddots & \vdots & \vdots \\ A_{\nu 1} & \cdots & A_{\nu \nu} & \Delta H_\nu \\ \Delta H_1 & \cdots & \Delta H_\nu & 0 \end{vmatrix}$$

where $\Delta H$ is the enthalpy released in a reaction, in kJ mol$^{-1}$, and the $A_{ij}$ factors are given by

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu} \sum_{l=k+1}^{\mu} \frac{RT}{D_{kl} x_k x_l} \left[ \frac{N_{ik}}{x_k} - \frac{N_{il}}{x_l} \right] \left[ \frac{N_{jk}}{x_k} - \frac{N_{jl}}{x_l} \right]$$

where $D_{kl}$ is the binary diffusion coefficient between species $k$ and $l$ and $x_k$ is the mole fraction of species $k$. Any gas inert to a reaction must be included, but has a stoichiometric coefficient of zero for reactions in which it does not participate.

The influence of pressure on the total thermal conductivity can be seen in figure (2.6). The reactive term has a maximum when the mole fractions of S and $S_2$ are equal and the magnitude of the peak is determined by the enthalpy released and the pressure. As the pressure decreases the temperature at which the mole fractions are equal also decreases.

### 2.5.4 Electrical Conductivity

Again using the mixture rules found in [10], the electrical conductivity $\sigma_e$ is found from

$$\sigma_e = \frac{n_e q^2}{n_e \nu_e H}$$

with $\nu_e H$ the sum of the electron-heavy particle collision frequencies. For the current case the collision frequency is larger than the frequency of the electric field and the imaginary component of the electrical conductivity can be neglected. In figure 2.7 the conductivity for the sulfur-argon plasma mixture is shown as a function of temperature and for several pressures.
Chapter 2: A self consistent LTE model ...

2.5.5 Species interactions

In order to determine the preceeding transport properties we need to be able to describe the interaction between all species in the plasma. We take all neutral-neutral interactions to be hard sphere, using the following rules to determine the collision diameter [12]:

- identical diatomic molecules: \( \sigma_{mm} = \frac{4}{3} \langle R \rangle + c \)
- identical atoms: \( \sigma_{aa} = 2 \langle r_x \rangle + c \)

where \( \langle R \rangle \) is taken to be \( R_e \), the equilibrium atom-atom separation distance and \( \langle r_x \rangle = R_e/2 \) and \( c = 1.6 \text{ Å} \). Collisions between different species are found from: \( \sigma_{am} = (\sigma_{aa} + \sigma_{mm})/2 \). Electron-neutral and ion-neutral collisions are described by the Langevin polarizability model

\[
\sigma_{A^+B} = \left[ \frac{\pi \alpha_B q^2}{\mu \varepsilon_0 C_{AB}^2} \right]^{1/2}
\]

where \( \alpha_B \) is the polarizability of the neutral species. We do not include charge transfer, so this relation is used for all charged-neutral interactions. Finally, charged-charged cross sections are found from

\[
\sigma_{A^+B^+} = 4\pi b_0^2 \ln \left[ 1 + \Lambda^2 \right]^{1/2}
\]

where \( b_0 = Z_A Z_B e^2 / 12 \pi \varepsilon_0 k_B T \) and \( \Lambda = \lambda_D / b_0 \), where \( \lambda_D \) is the Debye length.

2.6 Results

We present here the results of simulations and show the influence of input power and filling pressure on the temperature profile, power balance terms, electric field strength at the wall and the spectrum.
2.6 Results

Figure 2.10: Power balance as a function of radius for a 5.5 bar lamp with 500 W input power. The Ohmic power is coupled in a ring near the center of the lamp. The negative values of the radiated power, \( P_{\text{rad}} \), around \( r = 13 \) mm indicate absorption.

### 2.6.1 Temperature

In figure 2.8 we show the simulated temperature profiles for several input powers. The lamp in this case contains 5.5 bar of sulfur and 1 bar of argon. Two main features can be seen. The central temperature decreases and the profile broadens with increasing power. As the input power is increased the plasma temperature increases and so the mean value of the electrical conductivity increases. The implication of the skin model is clear; more pronounced damping of the field at \( r = 0 \), leading to a lower centre temperature and broader temperature profile.

Figure 2.9 shows the temperature profile as a function of sulfur pressure, for a fixed input power of 500 W. In this case the central temperature increases with pressure while the profile is slightly narrower. Again the influence of the electrical conductivity on the skin effect is responsible for the trend at the centre of the lamp. Since the electrical conductivity is lower at higher pressures, there will be less damping compared to lower pressures with higher conductivities.

### 2.6.2 Power balance

Terms in the power balance are shown as a function of radius in figure 2.10 for a 5.5 bar lamp at 500 W. Each is given as radial power density in \( \text{Wm}^{-1} \), obtained by multiplying the power density by \( 4\pi r^2 \). Ohmic power is coupled close to the centre of the lamp, essentially in a ring, with most power consumed through the radiative term.
Figure 2.11: Ohmic dissipation as a function of input power for a 5 bar lamp. At higher powers the increase in temperature and electrical conductivity causes a reduction in the skin depth and the power input shifts to the wall.

In figures 2.11 and 2.12 the influence of power and pressure on the skin depth and the consequences for the Ohmic input can be seen. In figure 2.11 we see that as input power increases, the dissipated power gets ‘pushed’ further from the centre, and so the temperature and electrical conductivity increase and hence the EM screening effect becomes more dominant. The opposite occurs when lamp pressure is increased while the input power is held constant: the lower electrical conductivity and lesser EM screening allow power to be dissipated closer to the centre of the lamp.

2.6.3 Electric field strength

Figure 2.13 shows the simulated electric field strengths at the wall as a function of input power and pressure. For a fixed power, a higher electric field is required to couple the same amount of power due to the lower electrical conductivity as pressure increases (equation (2.6)). However, this higher field strength does not cause an increase in the centre temperature to dampen the electric field and so the centre temperature increases slightly (see figure 2.9).

As power is increased at constant pressure, the field strength at the wall decreases slightly. As the temperature increases during the iterative process the electrical conductivity rises and thus a smaller field strength is required to couple the desired power. The simulated value of 380 V/cm and the trend of decreasing field strength with power agrees well with the measured value of 440 V/cm and power trend [3] for the 5 bar case.

2.6.4 Spectra

In figure 2.15 spectra are shown as a function of input power (the same input power as used to obtain the measured spectra in figure 2.2).
2.6 Results

Figure 2.13: The electric field strength at the lamp wall as a function of sulfur pressure and power. As the pressure increases the electrical conductivity will decrease which implies a higher electric field.

Figure 2.14: The radiated power as function of the input power. It seems that while the linear trend is followed by the model, the simulated lamp is more efficient.

Figure 2.15: Simulated spectra as a function of power for a 5.5 bar lamp. Two main differences can be observed with respect to the measured spectra in figure 2.2 (the terms in brackets are the simulated radiated power).

Figure 2.16: Simulated spectra as function of sulfur pressure. The spectrum does indeed shift with increased pressure but the shift is not as large as observed from experiment (figure 2.3). Also, the radiated power does not decrease.

While the general shape of the spectra are similar, there are two striking differences. Firstly, the distribution of power over the spectrum is different: the simulated spectra have too much power at shorter wavelengths and too little at longer wavelengths. Secondly, the position of the spectral maximum in the simulated spectra is 515 nm while it should be at 540 nm. Nevertheless, the linear increase in radiated power as a function of input power is well reproduced.
A further judge of the model is to examine the radiated power as a function of input power, which can be found in figure 2.14. While the general trend is followed the lamp we simulate is more efficient, producing consistently 100 - 150 W more light.

### 2.6.5 Sensitivity analysis

Since the spectral emission and absorption coefficients are fixed due to the radiation model we used, we may only vary the material properties in the energy balance (all were increased and decreased by a factor 2):

- electrical conductivity: only a 5% change in the energy balance was observed.
- reactive thermal conductivity: caused a 5% change in the radiated power.
- frozen thermal conductivity: responsible for a 10% change in radiated power.

The energy balance is most sensitive to \( \lambda_F \) due to its influence on heat flux through the lamp wall. Since this term was calculated on the basis of a hard sphere model, basing the calculation on interaction potentials would certainly influence the magnitude of the thermal conductivity at the wall.

### 2.7 Conclusions

The high pressure sulfur lamp is an interesting subject for study, as it is not only an extremely efficient light source but also due to the molecular nature of the radiation. As a first step in understanding the various processes in the lamp, we have described a simple model for the energy balance of such a lamp, which deals the generation of molecular radiation and the consequences of its transport. We validated the model by not only comparing the simulated and experimental spectra but also by showing the radiative efficiency of a real and simulated lamp. Such comparisons are favourable: the simulated spectra do not shift with increased power and the increase in radiated power is linear. The shift to longer wavelengths is also observed in the simulated spectra.

However there are three discrepancies. Firstly, the distribution of power in the spectrum differs with experiment: too much is radiated below 500 nm and too little above 600 nm. Secondly, the simulated radiated power does not decrease with increasing pressure - this may be a consequence of ignoring \( S_3 \) and heavier sulfur polymers, as we have no mechanism for the creation of \( S_3 \) as pressure increases. Thirdly, the radiated power is too large - which after consideration of the sensitivity analysis may be rectified by an improved transport model.

The form of the spectrum is a more serious issue. We employed an approximate technique for the description of the production/destruction of molecular radiation in order to reduce computational effort. The classical approach used has been applied successfully to the determination of spectra produced by \( \text{Na}_2 \). However, in that case the radiation originates from the wings of the internuclear potential and not deep in the well as the situation is here. It may be the case that in the well the vibrational energy levels are too
separated to be considered continuous to allow the line profile to be written as equation (2.8). This would also have a significant influence on the power balance.

To conclude, the simplified energy balance we have presented can predict the trends in spectral behaviour as well as absolute values for radiated power. In the future we will add the presence of $S_3$, improve the species interaction models we use for the transport coefficients and further examine the classical approach to radiation generation used in order to improve the models predictive range.

Acknowledgements

This work is part of the research program of the Dutch Technology Foundation (STW). The authors would like to thank Achim Körber and Johannes Baier of Philips research laboratories in Aachen, Germany for their assistance and provision of experimental spectra.

References


[9] www.netlib.org/lapack/


Temperatures have been measured in a high pressure microwave sulfur lamp using sulfur atomic lines found in the spectrum at 867, 920 and 1045 nm. The absolute intensity of these lines were determined for 3, 5 and 7 bar lamps at several input powers. Temperatures are 4100 K on average and increase slightly with increasing pressure and input power. Direct changes in line intensities are used as conclusive evidence of these trends and the measurements agree well with our simulations. However, the power trend found is contrary to that demonstrated by the model. This might be an indication that the skin depth model for the electric field may be incomplete.

C. W. Johnston, J. Jonkers and J. J. A. M. van der Mullen
Chapter 3: Operational trends ...

3.1 Introduction

The microwave powered, high pressure sulfur lamp is an extremely interesting light source for several reasons: it has good colouring, a long life span and high plasma efficiency. To be specific, its spectrum is molecular in origin and due to the high operational pressure is almost continuous over the range 300 - 900 nm, overlapping well with the eye-sensitivity curve. The plasma is also an efficient radiator - up to 70% of input power can be converted to visible light. Also, in contrast to many contemporary lamps, it neither contains mercury nor requires a phosphor. Other major differences with existing lamps are the magnetron power supply and that the bulb must be rotated.

However, it is precisely these excellent lighting properties and differences to standard lamps that hinder most diagnostic approaches. On one hand, identification of individual transitions in the spectrum is impossible due to the overlap of many thousands of rovibronic lines. And on the other the high spectral radiance, ca. 1.5 W/nm at 532 nm, coupled with the curvature of the bulb and its rotation, effectively rules out active laser diagnostics.

Motivated by these difficulties, we began our studies of the lamp by constructing a numerical model that included Ohmic input balanced by heat conduction and radiation transport [1]. Our principal means of validating this work was through comparison of simulated and measured spectra under different operating conditions of power and pressure. We also compared measured and simulated electric field strengths. Absolute values of the field strengths and the spectral response to different operating conditions were well reproduced. However, the position and magnitude of the spectral maximum were not. Thus, the operational trends produced by the model are encouraging but we are left with several issues that need to be resolved, namely the reproduction of the measured spectrum. Nevertheless, while we are making further studies to improve the model more direct experimental verification of model results is crucial.

The solution to the previously mentioned experimental difficulties came with the discovery of three atomic triplets, all attributable to atomic sulfur. These lines were found at 867, 920 and 1045 nm - all lying in the optically open part of the molecular spectrum. We have measured the absolute line intensities of these lines for several powers and lamp pressures. Since we have limited optical access to the lamp in our current cavity, all such measurements are spatially unresolved and as such we measure average quantities over a line of sight through the centre of the lamp.

The paper is organized as follows: firstly, the experimental setup used to ignite and maintain the discharge is introduced. Secondly, we discuss the origin of the spectrum and how it responds to changes in external parameters such as power and pressure The simulated temperatures profiles from [1] are reviewed. We then present an overview of the measurement procedure, defining the characteristic temperature, and finally we discuss the results and trends in the temperature, comparing them to our simulated values.
3.2 Molecular spectrum and atomic lines

Typical lamp spectra are shown in figures 3.1 and 3.2. They arise from multitudinous rovibrational transitions between the \( B\Sigma_u^- \) excited state and the \( X\Sigma_g^- \) ground state in the \( \text{S}_2 \) molecule. The spectrum is broad and continuous; ranging from 300 nm to more than 900 nm. Radiated power increases linearly as a function of input power, as shown in figure 3.1, and the spectral maximum remains at 514 nm. Figure 3.2 shows that for increasing lamp pressure the spectrum shifts to longer wavelengths and the spectral maximum decreases with respect to lower pressures. In all cases the spectra are extremely dense and identification of individual rovibronic transitions is impossible.

In fact, we have been fortunate enough to find several atomic triplets in the optically open part of the molecular spectrum at 867, 920 and 1045 nm. Transition probabilities, energy level data and statistical weights of the transitions and states are listed in table 3.1. These lines can be used to determine a temperature. However, since our optical access to the lamp is restricted, we measure these along a line of sight through the centre of the lamp.

3.3 Experimental setup

The apparatus we use to ignite and maintain a sulfur discharge is similar to the one described in [3] and shown in figure 3.4; a magnetron introduces EM radiation at a frequency of 2.45 GHz into a waveguide onto which a resonator is attached. The bulb is fixed on a rod which allows it to be rotated from outside the cavity. Tuning is facilitated by stub tuners and a movable short. Despite some differences with the commercial system from Fusion Lighting, the Solar 1000, the two systems are essentially the same, the main difference being the resonator used. In our case it is a hemi-ellipse which supports a \( \text{TM}_{101} \) mode while the Fusion lamp employs a cylindrical cavity and resonates in the \( \text{TE}_{111} \) mode. Our cavity, shown in figure 3.4, is essentially a metal box with some holes
Table 3.1: List of lines and their energies and transition probabilities [4]. In our calculations, we group each of the triplets.

<table>
<thead>
<tr>
<th>Line [nm]</th>
<th>Energy [eV]</th>
<th>A \left[ 10^8 s^{-1} \right]</th>
<th>Stat weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>921.28</td>
<td>7.869</td>
<td>3.0</td>
<td>7</td>
</tr>
<tr>
<td>922.81</td>
<td>7.867</td>
<td>0.22</td>
<td>5</td>
</tr>
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<td>923.75</td>
<td>7.866</td>
<td>0.22</td>
<td>3</td>
</tr>
<tr>
<td>1045.83</td>
<td>8.0456</td>
<td>0.22</td>
<td>1</td>
</tr>
<tr>
<td>1045.96</td>
<td>8.0452</td>
<td>0.22</td>
<td>3</td>
</tr>
<tr>
<td>1046.22</td>
<td>8.0456</td>
<td>0.22</td>
<td>5</td>
</tr>
<tr>
<td>867.065</td>
<td>9.2958</td>
<td>0.087</td>
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</tr>
<tr>
<td>869.316</td>
<td>9.2956</td>
<td>0.075</td>
<td>7</td>
</tr>
<tr>
<td>869.471</td>
<td>9.2954</td>
<td>0.11</td>
<td>9</td>
</tr>
</tbody>
</table>

at the sides that allow limited optical access to the bulb.

A SBIG CCD camera is used in combination with a crossed Czerny turner monochromator to measure spectra. Light is guided from the lateral aperture in the cavity to the spectrograph by means of an optical fibre. The resolution of the system is 0.05 nm at all wavelengths measured.

### 3.3.1 Bulb characterization

The bulbs themselves are quartz spheres fixed to the end of a quartz rod. The internal diameter in our lamps is 32 mm and the wall thickness is 2 mm. A typical bulb filling is 26 mg sulfur powder and 100 mbar argon (at room temperature). The total pressure in the lamp is taken to be the sum of pressure of an ideal sulfur gas, consisting only of $S_2$, and the argon gas pressure. Both are evaluated at 2500K which is taken to be a typical plasma temperature, $T_P$. The sulfur gas pressure, $P_{S_2}$, and the argon gas pressure, $P_{Ar}$, are given by

\[
P_{S_2} = \frac{mRT_P}{VM} \tag{3.1}
\]

\[
P_{Ar} = \frac{T_P P_{Ar}^{Fill}}{T_{Fill}} \tag{3.2}
\]

where $V$ is the bulb volume in m$^3$, $R$ is the gas constant in J mol$^{-1}$K$^{-1}$, $M$ the molar mass of $S_2$ in kg mol$^{-1}$, while $m$ is the amount of the sulfur powder in the bulb in kg. $P_{Ar}^{Fill}$ and $T_{Fill}$ are the pressure and temperature of the argon buffer gas when added to the bulb (room temperature). The typical operating pressure is 6 bar, 5 bar due to sulfur and 1 bar due to argon. However, from now on when we refer to a lamp we do this by the sulfur pressure alone at $T_P$.

So, when we refer to a 3, 5 or 7 bar lamp, it is a lamp filled, at room temperature, with 15.5, 26 and 37 mg of sulfur powder respectively. The argon pressure is the same for all lamps. Rather than acting as a buffer gas as it does in other lamps, argon forms a precursor plasma which allows sulfur to take over as the main plasma constituent.
3.3 Experimental setup

Figure 3.3: Energy diagram of the sulfur system. Here we show the energy levels of the molecule on the left relative to the atom on the right.

Figure 3.4: Sulfur lamp setup used to ignite and maintain the discharge. Light from the bulb is fed to the spectrograph via a fibre optic at the side of the cavity. Optical access is granted to the cavity through an aperture at one side whose position is indicated by the crossed box. The bulb is positioned so that its center lies in the middle of this aperture. The cavity is closed with an aluminium plate and the bulb is rotated from outside the cavity via its stem.

Krypton or xenon can also be used but the fields generated in the cavity are insufficient for ignition and a Tesla gun is needed.
3.4 Model results

3.4.1 Temperature profiles

In order to compare experimental results with our model, we reproduce here simulated temperatures for various input powers and lamp pressures, presented and discussed in [1]. Figure 3.5 shows the variation in radial temperature as a function of input power. Two distinct features of the profile vary: firstly the centre temperature, at \( r=0 \), decreases as the power is increased. Secondly, the mid-radius temperature, around 9 mm, increases. In short, the temperature profile becomes lower and broader with increased power. Figure 3.6 shows the temperature response to pressure. Again, variations can be characterized by the change in the centre and mid-radius temperatures. Here, higher pressures correspond to higher centre and lower mid-range values.

The behaviour of the profiles can be explained in terms of the skin effect model used to describe the electric field, the spherical nature of the lamp and the electrical conductivity of the plasma. Firstly, as power increases for a fixed powder content, the plasma heats up, the electrical conductivity rises and the electric field is shielded from the centre of the lamp. Thus, the profile broadens and lowers. Secondly, as the pressure increases, the electrical conductivity falls. Since the input power is a model input and remains fixed, the temperature has to rise to compensate. However, the conductivity does not increase enough to cause significant damping of the field and hence the temperature rises without the profile broadening. In all cases the small change in mid-radius temperature has a large influence on the power coupling; the large increase in volume moving towards the lamp wall means that only a small increase in temperature is required to couple significantly more power. So the difference in mid-radius temperature between 400 and 1000 W of input power need only be 400 K (see figure 3.5).
3.5 Spectral line interpretation

Here we discuss two approaches to using spectral lines to determine plasma parameters. Firstly, since it is such a common technique, we construct a Boltzmann plot. Secondly, we determine relations to relate the absolute intensity of a spectral line to a temperature, which is characteristic of the radiating state.

3.5.1 Boltzmann plot

The standard way to determine plasma parameters from spectral lines is to plot relative intensities against excitation energy. Here, one exploits the fact that the Boltzmann relation between an excited state and the ground state can be expressed in the form of a linear equation

$$\ln(I^*_{\lambda} \lambda_{\text{g} \rightarrow \text{e}}) = \frac{E^*}{k_B T_{\text{exc}}} + \ln(\eta_{\text{gs}})$$  (3.3)

where the ground state density $\eta_{\text{gs}}$, is the intercept and $-(k_B T_{\text{exc}})^{-1}$ is the slope. Since the ground state density is a constant for all measurements it is unnecessary for the determination of the excitation temperature $T_{\text{exc}}$. As such finding the slope of a plot of the level densities against excitation energies leads to the excitation temperature

$$\frac{\partial \eta^*}{\partial E^*} = -(k_B T_{\text{exc}})^{-1}$$  (3.4)
The density of a radiating state, $\eta^*$, is proportional to the measured (relative) line intensity $I$, via

$$\eta^* \propto \frac{4\pi I g^*}{A h \nu s};$$

(3.5)

where $s$ is the optical depth of the plasma and $A$ the transition probability. This is plotted against excitation energy in figure 3.7 using the lines found. As can be seen, the radiating states cover only a small range of excitation energies which permits a large range of temperatures. Using a least squares fit to the data we find an excitation temperature of around 30,000 K while plotting the steepest line that the errors will allow provides a more reasonable 7800 K. The fact that a large spread in excitation energies is needed to obtain precise results is well known. We could perhaps use the ground state density to provide a better estimate of the temperature. However, some knowledge of the radial dependency is needed.

### 3.5.2 Dissociation degree

While we are chiefly interested in the temperature profiles for comparison with experiments the plasma composition needs to be considered. In Figure 3.8 we have plotted the dissociation degree as a function of radius as found from simulations. We define the dissociation degree as being $n_S/(n_{S_2} + n_S)$. At the centre of the lamp there is at most 60% dissociation for all pressures. Moving towards the wall there are ever more molecules where association is, as is to be expected, larger for higher pressures. The model shows that plasma is molecular throughout most of the lamp, apart from the centre where the plasma is slightly more atomic in nature. Thus, rather than extending the Boltzmann slope approach and the assumption of homogeneity we chose to measure the absolute line intensities.

### 3.5.3 Absolute line measurements

Integrating over the line of sight through the centre of the plasma we measure the total intensity of a spectral line

$$I(\nu) = \frac{h \nu A}{4\pi} \int_0^s N^*(x) dx \quad [\text{Wm}^{-2}\text{sr}^{-1}]$$

(3.6)

where $s$ is the optical path length, $A$ is the transition probability and $N^*$ is the density of the radiating state. In order to determine the relationship between the radiating state density and the spectrograph signal the absolute sensitivity of the detector needs to be found as a function of the appropriate frequency. The signal recorded by the CCD camera, $S_{pl}$ is related to the intensity integrated over the line profile via the absolute sensitivity of the spectrograph $Q_\lambda$

$$I = \int_{\nu_1}^{\nu_2} S_{pl} Q_\nu d\nu$$

We measured $Q_\nu$ by placing a tungsten ribbon lamp, whose emissivity is known, where the lamp is fixed in the cavity. By assuming that the excited state densities are governed
3.5 Spectral line interpretation

Figure 3.8: Dissociation degree as a function of lamp radius for several pressures at 800 W. As one moves from the center to the wall the dissociation degree remains at around 60% at all pressures until 4 mm when the molecules truly begin to dominate.

Figure 3.9: $T_{CE}$ as found from the 920 and 1045 nm lines along with the values determined from numerical results all taken at 400 W. While there is an increase of 200 K for 3 to 7 bar in the simulated result the experimental results remain quite constant.

by Boltzmann, equation (3.6) can be written in terms of the ground state density $n_{gs}$

$$I = \frac{h \nu A}{4\pi} \int_0^s n_{gs}(r) \frac{g^*}{g_{gs}} \exp \left( \frac{-E}{k_B T(r)} \right) dr$$

(3.7)

where $g^*$ and $g_{gs}$ are the statistical weights of the excited and ground states and $E$ is the energy of the radiating level. However, we cannot easily progress from here. Since we have no information regarding $n_{gs}(r)$ and have limited optical access to the lamp we have two options. One method could be to invert the experimental data by using a temperature profile parameterized as a function of the central temperature. A direct radial comparison with modelled temperature profiles would then be possible. However, aside from assuming the shape of the profile, the simulated profiles are not simple functions of the radius.

Secondly, and this is the approach we take, we can assume that the plasma is homogeneous. The density and hence line emission is represented by a temperature which is characteristic of the radiating volume and uniform throughout. In this case what is found from experiment is a characteristic temperature $T_{CE}$, an average over the line of sight and is found from

$$T_{CE} = -\frac{\nu}{k_B} \ln \left( \frac{4\pi I}{\hbar \nu A n_{gs}(T_{CE}) g_{gs}} \right)^{-1}$$

(3.8)

In order to compare results a similar characteristic temperature must also be determined from the model temperature profiles. Assuming homogeneity really means that

$$n^*(T_{CE})s = \int_0^s n^*(r)dr$$
which, again relating the excited state density to that of the ground state via Boltzmann, allows the definition of $T_{CE}$ in terms of the radial density profile

$$T_{CE} = -E \left[ k_B \ln \left( \frac{1}{2} \int_0^R \eta_{gs}(r) \exp \left( \frac{-E}{k_B T(r)} \right) dr \right) \right]^{-1} \quad (3.9)$$

In both cases, equations (3.8) and (3.9) have to be solved iteratively: an initial $T_{CE}$ is chosen and modified until the right hand sides are equal to the seed temperature. The atomic ground state density is required for this calculation, and is available from our modelling results.

### 3.6 Results

Here the experimental and simulated characteristic temperatures are compared as functions of power and pressure and we finish by examining the line profiles themselves for conclusive proof.

#### 3.6.1 Characteristic temperatures

Figures 3.9 and 3.10 show $T_{CE}$ determined from the 920 and 1045 nm triplets at 400 and 600 W respectively as functions of pressure along with the values determined from simulation. At both powers and all pressures both lines provide almost the same temperatures, within 50K of each other.
3.7 Conclusions

In this paper we have presented the first, to our knowledge, direct measurement of temperatures in a high pressure, microwave powered sulfur lamp. This was achieved by the absolute measurement of three atomic triplets found in the optically open part of the molecular spectrum. Due to the limited optical access to the bulb, we defined a temper-
ature characteristic of the radiating state and determined it as a function of pressure for 400 and 600 W input power.

This temperature was found to be 4100 K on average, increasing slightly with increased pressure and power. Trends observed in the measurements were confirmed by the line spectra themselves since the radiating states are close to the ionization potential and also very sensitive. The increase in plasma temperature with increasing pressure is confirmed by the fact that the 867 nm lines could only be detected at 5 bar and above. Characteristic temperatures determined from our previous modelling efforts were found to be 150-200 K lower than those from experiment, but pressure trends were well reproduced. Despite the averaging nature of the characteristic temperature approach, we have exposed a problem with our model where the power trend is reversed. This is due to our use of a skin effect description of the electric field in our numerical model and requires further study.

Acknowledgements

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References


An existing LTE model [1] of a high pressure sulfur discharge is improved upon by the more accurate and complete treatment of each term in the energy balance. The simulation program PLASIMO [2, 3], which is an integrated environment for the construction and execution of plasma models, has been used to define and solve all aspects of the model. The electric field is treated as being DC and the temperature dependent nature of species interactions is incorporated in the determination of transport coefficients. In addition to the main radiative transition, the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$, several others in $S_2$ are included. These are $B^3\Pi_u \rightarrow X^3\Sigma_g^-$, $B^3\Pi_g \rightarrow \{A^3\Sigma_u^+, A^3\Delta_u\}$ and $e^3\Pi_g \rightarrow e^3\Sigma_u^-$. The $S_3$ molecule is also included in the composition as an absorbing particle. Furthermore, radiation production is treated quantum mechanically. The principle improvement over the previous work is that both the position of the spectral maximum and the pressure shift are quantitatively described by the current model. Both are chiefly due to the presence of $S_3$. 
Chapter 4: An improved LTE model . . .

4.1 Introduction

The sulfur lamp is known mainly for its radiative efficiency and good colour rendering. It is a high pressure discharge that produces white light without the need for a fluorescent powder to convert UV photons into visible light.

The lamp is by any standard an unusual system. It is powered by microwaves and comprises a rotating bulb, inside a resonant cavity, that uses a high pressure sulfur discharge as the radiating medium. We have chosen to study the system with the help of a 1D LTE energy balance constructed with the help of PLASIMO [2, 3]. Rotation is ignored in order that we might concentrate on the most important aspect of the lamp, namely the spectrum.

The distribution of power in the spectrum, which matches the eye sensitivity curve very well, is so important that any attempt to understand and model the lamp should not only include the energy balance in global terms but also the relative power distribution in the emitted spectrum. In a previous article [1], referred to as paper I from now on, we presented a 1D LTE model of the lamp which was validated by comparison of the simulated and measured spectra. In the present paper we improve upon this model by enhancing the treatment of each term in the energy balance and the influence of radiation generation from various species.

The reason that a high pressure sulfur plasma possesses such desirable lighting properties is a result of several factors. Firstly the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition is very strong. The transition probabilities for many of the vibronic transitions are large for a molecule, namely in the order of $10^5 \text{ s}^{-1}$. Secondly, the high pressure and temperature ensures that all vibrational states are substantially populated which allows them to contribute to the spectrum. The fact that only visible light is produced is due to the fortuitous positioning of the $B$ and $X$ electronic states with respect to each other, which also determines the shape of the spectrum. A further property of sulfur is that the atomic transition associated with the molecular one is optically forbidden.

Paper I was based on a simplified energy balance comprising three terms: Ohmic input balanced by conductive and radiative losses. All species interactions were assumed to be hard sphere and the transport coefficients were found using mean free path methods. The generation of radiation was attributed to only one electronic transition — the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ in $S_2$ and the semiclassical Franck Condon approach was used to describe the spectral distribution. The plasma-electric field interaction was described with a skin model.

We found that at high pressure the single transition in the dimer was a good candidate when seeking to explain the spectrum and the high radiative efficiency. Furthermore the general shape and extent of the spectrum were reproduced quite reasonably. Moreover, both the measured linear increase in radiated power with increasing input power and shift of the spectrum to the red with increasing pressure were reproduced by the model. In addition, the electric field strengths were found to be within a factor 2 of the experimentally determined values. However, there were three chief discrepancies. Firstly, the position of the spectral maximum lay too far to the blue, secondly there was too little light in the red part of the spectrum and finally the decrease in radiated power as a function of increasing pressure was not reproduced.

In a subsequent article [4], referred to as paper II from now on, we measured a tem-
temperature from absolute measurements of several atomic lines we found at 920 and 1046 nm. A temperature of 4100 K was found which agreed well with the value determined from the model results. However, while the model predicted the measured increase in temperature as a function of pressure, it also predicted a decrease of the temperature with increasing power — contrary to the measurements. In conclusion: we have thus constructed a picture of the sulfur lamp in which the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition does not produce sufficient red light and self absorption at shorter wavelengths is too insubstantial to quantitatively explain either the position of the spectral maximum or the spectral shift of the maximum with pressure.

In their series of articles on the generation and transport of molecular sulfur spectra [5, 6, 7] van der Heijden and van der Mullen have shown that one has to take fine structure into account in order to correctly describe the transport of the spectrum. It was shown that in comparison to the semiclassical treatment [5] a quantum-mechanical description produces less blue and more UV [6]. It has been known for some time already that $S_3$ absorbs in the UV. Döll and Lapatovich [8] suggested that the former could be responsible for the spectral shift which was later demonstrated by Körber [9].

With respect to the deficiency in the red there are several excited states in $S_2$, observed in emission, that may redress this. On the other hand van der Heijden et al advanced the idea that a departure from LTE may be responsible. Assuming LTE, the ionization degree is $10^{-5}$ which can be too low to maintain Maxwell and Boltzmann equilibria. While it may be ultimately necessary to investigate LTE departure we consider the previous LTE model presented in paper I to have performed well enough that the next step should be to improve it, add the trimer, and determine whether other states in $S_2$ may contribute to the spectrum.

The article is laid out as follows: section 4.2 presents a brief review of the model and explains the lamp nomenclature. Section 4.3 reports the plasma composition and the transport property calculations. Section 4.4 deals with radiation transport and the extra contributions to spectrum calculation. The results of the model are presented in section 4.5, discussed in 4.6 and we finish with our conclusions in section 4.7.

## 4.2 Model Review

In an LTE model plasma composition and material properties are established once quantity of material and temperature are known. There is then one equation that needs to be solved for the temperature. As in paper I Ohmic input is balanced by conductive and radiative losses. Ignoring convection the steady state balance is

$$Q_{\text{Ohm}} + \nabla \cdot (\lambda_c \nabla T) + Q_{\text{rad}} = 0$$

(4.1)

where $\lambda_c$ is the thermal conductivity and $Q_{\text{Ohm}}$ and $Q_{\text{rad}}$ are the power source terms for Ohmic input and radiation. Since the plasma emits a significant proportion of the input power $Q_{\text{rad}}$ is typically negative. Positive values of this term indicate that absorption outweighs local emission.

In paper I the plasma-electric field interaction was treated with a skin effect model. This time however, the electric field will be treated as DC. There are three reasons for this. Firstly, in paper II we observed trends in the simulated temperature profiles that
Table 4.1: LTE balances considered in the composition calculation.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_3 \rightarrow S_3^* + e$</td>
<td>10.6</td>
</tr>
<tr>
<td>$S_3^* \rightarrow S_3 + e$</td>
<td>2.1</td>
</tr>
<tr>
<td>$S_3 \rightarrow S_2 + S$</td>
<td>0.8</td>
</tr>
<tr>
<td>$S_2 \rightarrow S_2^* + e$</td>
<td>9.36</td>
</tr>
<tr>
<td>$S_2^* \rightarrow S_2 + e$</td>
<td>1.67</td>
</tr>
<tr>
<td>$S_2 \rightarrow S + S$</td>
<td>4.46</td>
</tr>
<tr>
<td>$S \rightarrow S^* + e$</td>
<td>10.36</td>
</tr>
<tr>
<td>$S^* \rightarrow S + e$</td>
<td>2.1</td>
</tr>
</tbody>
</table>

conflicted with measurements. The discrepancy was attributed to the use of a skin effect model. Secondly, van Dongen et al [10] have demonstrated that an electric field with a frequency of 2.45 GHz impinging on a plasma with an electrical conductivity of 1 Sm$^{-1}$ is hardly damped at all. Finally, and most compelling of all, we have observed that the lamp produces exactly the same spectrum when maintained by a 27 MHz RF field [11].

So, an approach which is simpler approach is to assume a uniform electric field, $E$, which is determined at each iteration to ensure that the total input power is maintained:

$$E^2 = P_{\text{Ohm}} \left[ 2\pi \int_0^R \sigma(r)r^2dr \right]^{-1}$$

(4.2)

where $\sigma(r)$ is the radially dependent electrical conductivity.

The solution of equation (4.1) is sought iteratively. The radiation and ohmic terms are determined from the current temperature profile. The profile for the next iteration is found by solving equation (4.1). This procedure is repeated until the difference between subsequent iterations is smaller than a pre-determined residue.

In paper I we assumed a characteristic temperature of 2500 K in order to determine the sulfur pressure given the quantity of powder in the bulb. This time however, the pressure is found through the iterative process. Thus the local pressure constraint ignoring charged species

$$\frac{p}{k_BT} = n_S + n_{S_2} + n_{S_3}$$

(4.3)

is now subject to an additional non-local constraint

$$\frac{M_{\text{fill}}}{m_S} = \int_V (n_S + 2n_{S_2} + 3n_{S_3} + \ldots) dV$$

(4.4)

where $M_{\text{fill}}$ is the mass of powder placed in the bulb and $m_S$ is the mass of the sulfur atom. We model three lamps - containing 15, 26 and 37 mg sulfur powder. In papers I and II these were referred to as 3, 5 and 7 bar respectively - the sulfur partial pressure during operation. In all cases the argon pressure is 100 mbar at room temperature and the lamp radius is 16 mm.
4.3 Composition and transport properties

The difference between the plasma composition described in this paper and that in paper I is the inclusion of $S_3$ and its positive and negative ions. Thus the number of species in the plasma mixture rises from 8 to 11 and the number of reaction balances from 6 to 10. The composition calculation is straightforward due to the generic way in which we treated the equilibrium relations in paper I. The reactions considered are shown in Table 4.1. The density of each particle is found by solving the Guldberg-Waage equations for each balance, constrained by charge neutrality and mass conservation.

The neutral and charged particle densities are shown as functions of temperature in figures 4.1 and 4.2. In both cases the total pressure is 6 bar, 5 due to sulfur and 1 due

Figure 4.1: Neutral species densities as a function of temperature. The sulfur dimer is the dominant neutral from 1000 K up to 4500 K. The trimer density is only significant below 1000 K.

Figure 4.2: Charged particle densities as a function of temperature. The positive $S_2^+$ ion is the principal charged particle. The electron density is very low leading to an ionization degree $\lesssim 10^{-5}$ at 4500 K.

Figure 4.3: Thermal conductivity as a function of temperature for two pressures. The argon pressure is 1 bar.

Figure 4.4: Electrical conductivity as a function of temperature and pressure. The argon pressure is 1 bar.

4.3 Composition and transport properties

The difference between the plasma composition described in this paper and that in paper I is the inclusion of $S_3$ and its positive and negative ions. Thus the number of species in the plasma mixture rises from 8 to 11 and the number of reaction balances from 6 to 10. The composition calculation is straightforward due to the generic way in which we treated the equilibrium relations in paper I. The reactions considered are shown in Table 4.1. The density of each particle is found by solving the Guldberg-Waage equations for each balance, constrained by charge neutrality and mass conservation.

The neutral and charged particle densities are shown as functions of temperature in figures 4.1 and 4.2. In both cases the total pressure is 6 bar, 5 due to sulfur and 1 due
to the argon buffer gas. At temperatures above 1000 K the neutral densities are as they were reported in paper I. Just above 1000 K $S_2$ is the dominant neutral while atomic sulfur only begins to play a role above 4500 K. It is only at low temperatures that a significant $S_3$ density builds up. In fact the trimer will only play a role at 1000 K — the wall temperature. Aside from the addition of $S_3$ the rest of the composition is identical to the one presented in paper I.

The accurate determination of the transport properties on the other hand is more complex. Not only do we need to describe species interactions in more detail, the number of unique species interactions rises from 36 to 66.

A full discussion of species interactions and their influence on transport properties are discussed in chapters 8 and chapter 9. In this approach transport properties of LTE mixtures are found via the Chapman Enskog expressions using only model potentials based solely on properties of the collision partners.

The result of using this approach for the thermal conductivity is shown in figure 4.3. For the temperature ranges found in the sulfur lamp, an error of ca. 10% can be expected. The differences between the thermal conductivity from paper I and the current improved calculation are significant. While the maximum value attained at the dissociation of $S_2$ is essentially the same, the high temperature behaviour above 5000 K is entirely different. However, temperatures higher than these are not reached in the plasma. The low temperature behaviour is slightly different although the contribution of $S_3$ is that the thermal conductivity at 1000 K is twice that in paper I.

The electrical conductivity is found using Devoto’s second order expression [12]. Cross section data for the electron-sulfur and electron-argon atom collisions are available from Saha [13] and Devoto [14]. Since no data is available for sulfur, the electron-O$_2$ data from Capitelli [15] is used for the electron-$S_2$ interaction. The result of the calculation is shown in figure 4.4. Compared to the result from paper I the electrical conductivity here is a factor of 2 lower at 4000 K. This provides further justification for our DC treatment of the electric field.

### 4.4 Radiative contribution to the energy balance

#### 4.4.1 Radiation generation and transport

The energy balance used to describe the lamp is one dimensional and the Ohmic and conductive contributions depend only on the local magnitude and gradient in the temperature. This is not true for the radiative contribution - emission at any point may contribute to absorption elsewhere in the plasma.

Thus the local radiative contribution is in a sense aware of the rest of the plasma and the energy balance must reflect this accordingly. In order to describe the radiation transport we exploit the point symmetry of the system - several parallel probe lines are sent through the plasma along which the equation of radiation transport is solved for several frequency values. These probe lines traverse different lengths of the plasma and allow the calculation of the total emitted spectrum as well as the local radiative energy sources. This technique to handle radiation transport is discussed in further detail in [6, 7].

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4.4 Radiative contribution to the energy balance

This method was used to treat radiation transport in paper I and is retained here. However, radiation generation will be treated in a different way. As argued before, a full quantum mechanical treatment of the spectrum is out of the question. There are 41 vibrational levels in the B and 63 in the X state where all levels have rotational sublevels.

Performing radiation transport on the ca. $10^6$ rovibrational lines that arise is computationally expensive. Since we are more interested in the general shape of the spectrum and its overlap with the eye sensitivity curve rather than the ultra fine detail which a full quantum mechanical treatment would eventually provide, we employed a semiclassical technique in paper I. In that approach the radiation produced between electronic states in a molecule is treated as a two level system — a single line profile was used to describe the transition. The line has a shape that is related to the transition frequency on the internuclear distance $r$, as provided by the state potentials and reads

$$
\phi(\nu) \propto r^2 \exp \left( \frac{-V(r)}{k_B T} \right) \left| \frac{d\nu}{dr} \right|^{-1},
$$

where $V(r)$ is the potential function of the lower electronic state. The radial change in frequency is found from the state potentials. The power of this approach is that only a very limited number of frequency points is needed, and it is thus computationally cheap. In addition the data demands are moderate.

However, applying this method in paper I we found that the self absorption in the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ system was insufficient to explain the observed position of the spectral maximum. A detailed comparison of the semiclassical (SC) and quantum mechanical (QM) approaches as they apply to the sulfur spectrum shows that while on average the SC cross section for radiation absorption seems to agree with the QM value [5], the influence of fine structure increases absorption in the blue [6].

As a result the spectrum is shifted as required. So, while we are not interested in fine structure it is necessary to include it. Nevertheless, the situation remains that we do not wish to include a full quantum mechanical radiation transport calculation inside an iterative model for the energy balance. Van der Heijden et al [7] have shown that a full QM spectrum can be modelled to within 5% accuracy by taking 40 clusters throughout the frequency spectrum, each of which contains 250 frequency points. In this way the correct average of the absorption cross section is found at each frequency and the full spectrum is found by interpolation.

The QM absorption cross section is first calculated for all possible transitions and those that fall within our desired range are grouped to provide the cross section as a function of frequency. Aside from potential and spectroscopic data two pieces of information are required: the Franck-Condon table and the electronic transition dipole moment (ETDM) for the transition. In order to calculate the vibrational wavefunctions we use the SCHROED program [16] and employ the integration routines provided by the GNU Scientific Library [17] to determine the overlap. The BX transition has been studied extensively and its ETDM is available [18, 19, 20].
4.4.2 Heavier polymers

While the introduction of QM radiation goes some way to increasing self absorption in the blue, shifting the spectrum, it is still not large enough to reproduce the experimental maximum [6]. Moreover, it has been proposed that the presence of S\textsubscript{3} will have a significant influence on the shape of the spectrum. Döll and Lapatovich reported the presence of the trimer in low pressure discharges [8].

There are two principal sources for S\textsubscript{3} absorption data. Krasnopolsky [21] determined the cross section from the absorption spectra data of Braune et al [22]. More recently Billmers and Smith found the cross section from their own measurements [23]. In Figure 4.5 the absorption cross section as a function of wavelength is shown for S\textsubscript{2} at 1000 K [5] and for the trimer from both sources. Firstly, S\textsubscript{3} absorbs far more effectively in the UV and into the visible than S\textsubscript{2} and ought to have quite some influence on the spectrum. Secondly, there is only a slight difference between the S\textsubscript{3} cross sections. However, the data from Krasnopolsky extends to 600 nm and for this reason we use that data.

Of course with absorption comes emission. With the wall temperature fixed at 1000 K and the rapid decrease of S\textsubscript{3} density with increasing temperature it will be restricted to a thin layer at the bulb wall, perhaps no more than 1 mm thick. In order to investigate the possibility of emission from S\textsubscript{3} will we consider the two extremes of the absorption cross section.

At 400 nm, the cross section has its maximum with a value of \(\sim 1 \text{ Å}^2\). Given the density at the wall, which is \(\sim 10^{20} \text{ m}^{-3}\), the absorption coefficient, \(\kappa\), is \(10^5 \text{ m}^{-1}\). As a consequence the optical depth, that is the distance into the discharge that we can look, is approximately 10 \(\mu\)m. Thus the trimer is an optically thick surface radiator and the intensity of emission is determined by the Planck intensity \(B_\nu\) and temperature.

\[
B_\nu = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/k_BT) - 1} \quad (4.5)
\]
4.4 Radiative contribution to the energy balance

At 400 nm for an elevated temperature of 1400 K the intensity is $10^{-17}$ W m$^{-2}$ Hz$^{-1}$ sr$^{-1}$. The energy radiated from the surface of the plasma under these conditions, $4\pi^2 B_0 R_0$, provides less than $10^{-6}$ W nm$^{-1}$. Thus emission from S$_3$ at 400 nm is insignificant compared to that from S$_2$.

At 600 nm the absorption coefficient is $10^2$ m$^{-1}$ which provides and optical depth of 10 mm. The S$_3$ layer is thus fully transparent. Again due to the low temperature and its limited thickness, the layer simply cannot contribute to the spectrum in any way that may be discerned from radiation produced in the rest of the lamp volume. In short, the S$_3$ layer is too cold to radiate at short wavelengths and too thin to contribute to the spectrum at longer wavelengths. Thus the trimer is included only as an absorbing particle.

4.4.3 Additional S$_2$ states

There were two chief discrepancies in the distribution of power between the simulated and measured spectra in paper I. Firstly, there was too much blue and secondly there was too little red. We have increased the chance that the former will be solved by the introduction of S$_3$ and the QM description of radiation. That there was too little red in the simulated spectra can be related to the radial dependence of the ETDM. Figure 4.6 shows the ETDM for the $B^3\Sigma_u^{-} \rightarrow X^3\Sigma_g^{-}$ transition as a function of internuclear separation along with the state potentials. At the separation where the system might be expected to produce the missing red radiation we miss, that is beyond 3 Å, the ETDM falls to zero. This asymptotic behaviour is consistent with the fact that the atomic transition associated with the $B^3\Sigma_u^{-} \rightarrow X^3\Sigma_g^{-}$ one is forbidden. As such there is no way in LTE that this transition can produce the missing part of the spectrum and we must look to other processes and the most logical place to start is S$_2$ itself. The ground states of the sulfur atom give rise to 13 bound states [20, 24]. Optical transitions between several of these have been reported [25]. The most well known are the $B^3\Sigma_u^{-} \rightarrow X^3\Sigma_g^{-} \rightarrow X^3\Sigma_g^{-}$ and $B^3\Pi_u \rightarrow X^3\Sigma_g^{-}$ which have been studied extensively. The other transitions, $e^1\Sigma_g^{-} \rightarrow e^1\Sigma_u^{-}$ and $B^3\Pi_g \rightarrow \{A^3\Sigma_u^+, A^3\Delta_u\}$, have only been identified. In order to quantify the influence of these transitions and
include them in the model we require both spectroscopic and ETDM data. The former is available for all the states although the ETDM is only available for the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $B^3\Pi_u \rightarrow X^3\Sigma_g^-$ transitions. The quantum chemistry package MOLPRO2000.3 was used to calculate all state potentials and ETDMs for all radiating states [27]. Figure 4.7 shows the potential energy curves for the states involved in the optical transitions. These agree with published PECs [20, 24] except that the asymptotes of the $e^1\Pi_g$ and $B^3\Pi_g$ lie at the $^1D$ and $^3P$ rather than the $^1S$ and the $^1D$. The consequence is that these states are bound over a smaller range of separation than has been previously reported. In figure 4.8 the ETDMs of all the radiating states are shown as a function of wavelength. The $B^3\Pi_u \rightarrow X^3\Sigma_g^-$ transition will only contribute to the spectrum at very short wavelengths. The $e^1\Pi_g \rightarrow c^1\Sigma_u^-$ transition radiates only at 500 nm where the ETDM for the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ is four times larger. Thus the only transitions that may generate additional radiation in the red are the $B^3\Pi_g \rightarrow \{A^3\Sigma_u^+, A^3\Delta_u\}$. However, the ETDMs are no larger than that for the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$. It is then doubtful whether these will greatly influence the spectrum. Nevertheless, we will include these states in the radiative transfer calculation.

4.5 Results

In this section the model output that can be validated is presented. The modelled spectrum is compared to those measured and found previously in paper I. The effect of calculating the pressure is not so substantial - the sulfur partial pressures are found to be 2.9, 5.1 and 7.2 bar for the 15, 26 and 37 mg lamps. Thus we will stick to the previous nomenclature when referring to lamps by the sulfur pressure as determined at 2500 K. The bulb radius remains 16 mm.

4.5.1 Spectra

In figure 4.9 simulated and experimental spectra are shown for the three main lamps that we have studied - the 3, 5, and 7 bar bulbs. In each case the input power is 800 W. The main result is that the position of the spectral maximum is in good agreement with measurement. This lies at 490, 510 and 536 nm for the 3, 5 and 7 bar lamps respectively. The model predicts the maximum exactly for the 3 and 5 bar bulbs but the 7 bar spectra lies at a slightly shorter wavelength. Nevertheless, the results are far superior to the previous model.

In paper I the simulated spectra were deficient in the red and there was a surplus of radiated power in the blue. As can be seen in figures 4.9(a), 4.9(b) and 4.9(c) the red deficit is still present but there is also less blue. This decrease was obtained by adding $S_3$. The extra transitions in $S_2$ that were added contribute little to the spectrum as predicted - the flat feature at 700 nm is due to the $B^3\Pi_g \rightarrow \{A^3\Sigma_u^+, A^3\Delta_u\}$ transition. However, in total the supplementary levels contribute less than 20 W to the radiated power which is too little to raise the emission to the experimental level. In figure 4.9(d) the simulated and measured radiated power is shown as a function of input power for the 3 and 7 bar lamps. In paper I the simulated radiated power increased linearly with input power with the same rate of increase as the experimental. The simulated lamp was more efficient than the real one, radiating 20% too much.
This time however, while the simulated trend is linear and the results match at 400 W, the rate of increase is not as strong as the experimental results.

A final disagreement with measurement is the pressure trend. As figure 4.9(d) shows, the model predicts that the 7 bar lamp should be a better radiator than the 3 bar which is contrary to measurement.

While our improved treatment of the lamp still does not fully reproduce the experimental spectra the simulated efficiencies agree well with experimental values. Furthermore, the fact that the position of the spectral maximum and the shift of the spectral maximum to longer wavelengths with increasing pressure are almost exactly modelled is a very positive result. This success is entirely due to the improved treatment of radiation production/transport and the inclusion of absorption in $S_3$. In figure 4.10 simulated spectra are shown that result from treating the emission in the model - semiclassically (SC) as
Figure 4.10: Simulated spectra for a 3 bar lamp using three different approaches for radiation generation. The semiclassical (SC) result from paper I radiates the most. The quantum mechanical (QM) spectrum is shifted only slightly and produces less blue and more UV than the SC approach. The QM approach including $S_3$ cuts off the spectrum below 400 nm and determines the final shape.

was done in paper I, quantum mechanically (QM) and finally quantum mechanically with $S_3$ absorption. While the differences between SC and QM spectra has been investigated before [6], it is useful to review the main points here to highlight the influence of $S_3$. We divide the spectral range into three regions: I which extends up to 400 nm, II lies between 400 nm and 550 nm and region III beyond this. The ‘blocky’ appearance of the QM spectra can be removed by increasing the number of frequency points.

First examining the spectra without $S_3$: in region I the SC spectrum is fully trapped while the QM absorption coefficient varies considerably with frequency and the wings of vibronic lines can escape. In region II the situation is reversed; the SC spectrum is almost fully open while absorption of the central frequencies of transitions in the QM description are still strongly absorbed - hence the QM approach provides less light. In region III the plasma is fully optically open and both spectra are essentially equal. Including $S_3$ in the QM calculation decreases the extent of region II. Absorption at short wavelengths means that the spectrum behaves semiclassically up to 450 nm but with a much lower intensity. It is clear that $S_3$ absorption dominates the short wavelength behaviour and determines the position of the spectral maximum.

4.5.2 Temperature

In figure 4.11 simulated temperature profiles are shown for a 3 bar lamp for several input powers. In contrast to the profiles reported in paper I, the central temperature increases
with increasing power. The central temperature is 4000 K for an input power of 200 W and increases by around 50 K for every extra 100 W input power. The difference in the profiles towards the wall is more pronounced, particularly so for the 200 W case. In figure 4.12 the temperature profiles for two different pressures, 3 and 7 bar, are shown. The input power in both cases is 800 W. The profiles are identical at the wall but at the centre the temperature is lower for the 7 bar lamp due to the enhanced emission caused by a greater radiating state density. In paper II a temperature characteristic of the (atomic) radiating volume was determined from the absolute measurement of the intensities of several atomic sulfur lines. In that article the measured value was compared to that determined from the simulated temperature profiles. The absolute values were found to be very close to each other - 4200 K from the measurement as compared to 4000 K from the model. An increase in this temperature was found by experiment as a function of increasing pressure which was reflected in the model results also. However, while an increase in this characteristic temperature was found with increasing power, the model demonstrated the opposite behaviour. This behaviour was entirely due to the use of a skin effect model for the plasma/electric field interaction which permits a higher central temperature for a lower input power.

Table 4.2: Characteristic temperatures, both measured (left) and simulated (right). Values are given in kK

<table>
<thead>
<tr>
<th>Power [W]</th>
<th>3 bar</th>
<th>5 bar</th>
<th>7 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.0/4.2</td>
<td>4.1/4.1</td>
<td>4.1/4.0</td>
</tr>
<tr>
<td>600</td>
<td>4.15/4.3</td>
<td>4.2/4.2</td>
<td>4.3/4.1</td>
</tr>
</tbody>
</table>
Mid-radius temperatures on the other hand are higher for larger input powers; as one would expect. This subject is more fully dealt with in paper II.

In table 4.2 the measured characteristic temperatures are presented, along with those found from the current model. At all pressures the temperature increases with power, as required, but this time it is the pressure trend for a fixed input power that is contrary to the experimental results. The higher the pressure the greater the radiative efficiency the model predicts.

4.6 Discussion

4.6.1 Energy balance

Deeper insight into the operation of the lamp can be gained by examining the radial dependence of the terms in the power balance. In figure 4.15 the Ohmic, radiative and conductive contributions are plotted as a function of lamp radius for a 5 bar lamp with 800 W input power. What one notices immediately is that the radiative term at the wall is very large and positive. This gain in energy is due to absorption in $S_2$ and $S_3$ which must be conducted away. Since the thermal conductivity is very low at 1000 K (figure 4.3) a high temperature and large temperature gradient can be maintained near and at the wall (figure 4.12). The other point of note is that the power is coupled mid-radius where the radiative contribution is negative due to (locally) escaping radiation. This is entirely due to the spherical geometry of the bulb. At the centre of the bulb there is very little volume that can influence the overall energy balance. The temperature at the wall, where there is significant volume, is too low to maintain an appreciable electron density. Therefore power can only be coupled in between where the volume and temperature are both large.

4.6.2 Origin of the spectrum

In the current model the improved radiative contribution to the spectrum and energy balance is determined by two processes. Firstly, there is emission from the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ transition in $S_2$ and secondly, absorption by $S_3$. In figure 4.16 the spectral source terms are shown as a function of wavelength and radius. The most intense emission occurs at 4 mm from the centre of the lamp at 450 nm. This was the position of the spectral maximum provided by the semiclassical approach (figure 4.10) where $S_3$ absorption was omitted. However, towards the wall from 12 mm there is significant absorption between 350 and 480 nm. This is due to $S_2$ and $S_3$ which are responsible for the shift in the maximum in emission. We also see that emission decreases towards longer wavelengths which is the reason for the red deficit.

4.6.3 Species densities

The neutral particle densities are shown in figure 4.13 as a function of the lamp radius. The sulfur dimer is the most abundant and its density is quite uniform throughout. Since the temperature never exceeds 4500 K, the dissociation degree is everywhere less than 50%.
We have identified absorption in S\textsubscript{3} as having a significant influence on the spectrum and in figure 4.1 we have seen that its density is very sensitive to temperature at 1000 K - the wall temperature in the simulations. This is confirmed in figure 4.13 where the density is only significant at the wall. Since the temperature increases rapidly towards the centre, S\textsubscript{3} is confined.

Figure 4.13: *Neutral species density as a function of bulb radius. The density of S\textsubscript{2} is almost uniform throughout. On the other hand the S\textsubscript{3} density is only significant at the wall.*

In figure 4.14 the charged particle densities are also shown as a function of radius. The dominant ion species is S\textsuperscript{2+}. Due to the fact that the temperature profile is quite flat its density is maintained in the direction of the wall before decreasing rapidly at 12 mm. The S\textsuperscript{-} density is also quite substantial being 60% of the S\textsuperscript{2+} density. The ionization degree is low and never exceeds 10\textsuperscript{-5}.

### 4.6.4 Influence of the wall

The trends observed in the spectra and temperatures can be related to what occurs at the wall. In reality the temperature that is established at the wall is a function of the lamp filling and input power and we have found that the model is highly sensitive to the wall temperature. The absorption data for S\textsubscript{3} from taken from Krasnopolsky was measured at 800 K. At higher temperatures the cross section for absorption will be lower. In fact the behaviour of the measured spectrum at 400 nm can be reproduced exactly by the model at all pressures if the wall temperature is set to 1400 K. Furthermore, the radiative efficiency increases, improving the model’s agreement with experiment. However, at such a temperature the quartz wall would melt [28]. Increasing the temperature is simply a means to decrease absorption by reducing the S\textsubscript{3} density.
Chapter 4: An improved LTE model...

Figure 4.15: Contributions to the energy balance as a function of bulb radius. Each term has been multiplied by $4\pi r^2$ so that the quantities have the units of W/m.

Figure 4.16: Spectral source terms shown as a function of wavelength and lamp radius. A negative number indicates local emission and a positive one local absorption.

4.7 Conclusions

In this paper we have substantially improved each term in a previously published LTE model of the high pressure sulfur lamp. Radiation production is treated quantum mechanically which improves the description of the absorption of blue radiation at low temperatures. In search of other transitions that might produce more red where the $B^3\Sigma_u^- \rightarrow X^3\Sigma_u^-$ transition is incapable of doing so, several other transitions in $S_2$ have been added. The most significant improvement to the simulation of the spectrum is the inclusion of $S_3$ and its influence on the spectrum through absorption.

With the addition of $S_3$ and QM radiation production we have resolved several issues outstanding from our first model. Not only can we predict the position of the spectral maximum, the pressure shift and simulated temperatures agree very well with measurement. Of the remaining discrepancies between the model and experiment we have demonstrated that the fixed wall temperature and absorption in $S_3$ are responsible. Remedyng the former is straightforward but the latter will be more difficult as there is as yet little known about the electronic energy levels in the trimer.

Having gained new insights into the transport and generation of dense molecular spectrum, the influence of various states in $S_2$ and absorption in $S_3$, we have constructed a model that reproduces spectra and operational trends very well. The chief remaining issue is that of the missing red. However, in LTE $S_2$ cannot radiate any more around 800 - 900 nm than it has done so far.

At the internuclear separations where long wavelengths can be produced the fact that the atomic transitions are forbidden means that the ETDM is very small in the same region. Thus producing more red within an LTE description of the discharge is impossible. The only way that the high vibrational states in the $B$ state could radiate more is if there was a significant deviation from a Boltzmann distribution. The influence of such a scenario has been investigated [7] where an non-Boltzmann distribution was...
shown to reproduce the measured spectra.

We conclude from the results of the model in paper I, the measurements in paper II and the improved model presented here that the power balance and response of the spectrum to operational parameters can be very adequately understood via LTE. However, we feel that any further refinement of our understanding of the discharge will require the consideration of non-equilibrium processes.

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References


Bibliography


[22] Braune H, Steinbacher E, Adv. Space Res. 7a, 486 (1952)


[27] T. Kiljunen, private communication

The power supplied to a high pressure sulfur plasma sustained by microwaves is inter-
rupted on short times scales. The response of the molecular spectrum between 400 and
900 nm is measured during this interruption. Characteristic decay times of around 20
ms are found and are due chiefly to the large heat capacity of the reacting mixture. The
results of a time dependent LTE model of the interruption, including radiation transport
of the entire molecular spectrum and heat conduction, are also presented. The simu-
lated signal decay agrees with experiment not only in magnitude but also as a function
of wavelength.
5.1 Introduction

The ability to manipulate the internal states of atoms and molecules through the application of an external electric field means that partially ionized plasmas can be used in many applications. In many cases the most important goal of any study is the establishment of direct relationships between external control parameters and the principal plasma quantities. However, the enormous degree of freedom afforded by plasmas, which makes them so attractive from an industrial as well as a scientific point of view, complicates matters considerably.

Due to their small size and hence the presence of steep gradients artificial plasmas can often deviate from local thermal equilibrium (LTE). As such the laws of statistical mechanics no longer relate particle densities to each other and species temperatures can decouple. The most well known example of such a case is the low pressure mercury discharge [1]. The low collision frequency and large mass difference permits the electron temperature to decouple from that of the heavy particles. Since excitation and emission are dominated by electrons, any passive spectroscopy performed under the mistaken assumption of LTE would lead to an erroneous picture of the plasma. As a consequence such diagnostics must be carried out with care. On the other hand measurement of more variables, for example via active (laser) techniques, will certainly provide a more detailed insight into the discharge. However, a full understanding of the equilibrium status of the discharge as a whole is required. In the case of a molecular plasma where the high pressure engages many rovibronic channels this is not straightforward.

The microwave powered sulfur lamp is a high power, high pressure discharge which has the appealing property that it can radiate up to 70% of input power into the visible [2]. Furthermore, the resultant spectrum appears continuous and overlaps the eye sensitivity curve well. As is suitable for primary investigations into such a new plasma we have reported several studies of the system from the viewpoint of LTE. In two papers the energy balance of the lamp including heat conduction and radiative transfer of the molecular spectrum is studied by means of a one dimensional LTE model [3, 4]. The spectra found agreed well with measurement and the influence of increasing pressure and power were well modelled.

In an experimental study the central temperature was determined from absolute measurements of sulfur atomic lines found in the near infra-red [5]. These also agreed well with the values predicted by the models. Nevertheless, while we have demonstrated the effectiveness of an LTE approach in describing the global properties of the plasma there are some remaining concerns. The most important of these is related to the source(s) of emission towards longer wavelengths, above 700 nm, which the model cannot reproduce. Van der Heijden et al have demonstrated that a non-Boltzmann distribution over the vibrational states in the $B$ state can reproduce the entire spectrum [6]. Finally, the general concern remains as to whether a plasma that radiates such a significant proportion of the input power can achieve LTE conditions.

In order to investigate the possible deviation from LTE the influence of power interruption on the spectrum is studied in this chapter. Evaluating observed responses with respect to LTE will expose any non-LTE behaviour. First proposed by Gurevich et al in the 1960’s [7], power interruption techniques were initially applied to DC arc discharges in the early 1980’s [8]. Bydder and Miller [9, 10] recognized the role and influence of the elec-
tron temperature on emission in inductively coupled plasmas and examined the response of spectral lines on microsecond timescales. Since then power interruption has largely been used as a means to study open flowing argon plasmas used for spectrochemical analysis. Fey established a link between the delayed response of spectral lines to convection and thus determined the velocity field in an ICP [11]. Timmermans used the technique to study the influence of the heavy particle temperature on line emission from metals in microwave torches [12]. De Regt [13] and van de Sande [14] investigated the behaviour of the electron gas with the help of Thomson scattering during the power interruption.

Relaxation techniques, and power interruption in particular, can be useful to unravel the dependence of various balances on plasma parameters. A variation in the density of a particular radiating state that results from a power interruption, which is communicated by a change in the observed spectrum, can assist in exposing the dominant production and destruction channels of that state. However, given the high pressures in the sulfur lamp and the large number of states involved, describing the response of the observed spectrum in terms of excitation temperatures is more appropriate than explaining responses in terms of densities.

In particular, removing the input power to the lamp is a simple and elegant way to gain insight into the role of the electron and heavy particle temperatures $T_e$ and $T_h$. Indeed, the different timescales on which electron and heavy particle temperature influenced phenomena respond to the interruption is the key to the technique.

In most laboratory plasmas heavy species are heated by collisions with electrons which initially gain energy from the electric field. The inefficient transfer of this energy to the heavy particles, due to the large mass difference, leads to a common conclusion that $T_e$ is higher than $T_h$. However, such reasoning is usually applied to low pressure or atmospheric plasmas. The sulfur lamp on the other hand is a high pressure system, with operating pressures of 3 bar and up, where we assume that density and temperature are strongly coupled. Moreover, the enhanced collision frequency may assist in equilibration of the electron temperature.

All interpretation of results is carried out assuming LTE. As such, deviations from this picture will be readily apparent. In as much as $T_e$ and $T_h$ dominated balances will be exposed by the interruption experiment, the vibrational temperature can be also probed. If there is indeed a deviation from a Boltzmann occupation of the vibrational levels in the $B$ state it will be reflected in the relative decay of radiation from different levels.

The chapter is laid out as follows: in section 5.2 the apparatus used to ignite and maintain the discharge is presented. The setup for the interruption experiment is also introduced. Section 5.3 reviews the types of responses displayed by spectral lines in interruption experiments and some nomenclature is introduced. The results of the experiments on the atomic lines and for molecular wavelengths are given in section 5.4. A general discussion and quantification of characteristic decay times is presented in section 5.5. In section 5.6 temperature decay times are determined from the experimental results and from global considerations of the plasma in section 5.7.

In sections 5.8 and 5.9 decay times are evaluated from studies of the electron energy balance and that for heavy particles dominated by heat conduction respectively. In section 5.10 the results of a time dependent LTE model of the energy balance including radiation transport are presented. The chapter finishes with our conclusions.
Chapter 5: Measured and simulated response ...

2.45 GHz Magnetron Circulator Triple stub tuner Movable short Rectangular waveguide HV-power supply Reflected power meter Parabolic cavity Quartz bulb 80 mm Water cooling Rectangular waveguide Movable short

Figure 5.1: Sulfur lamp setup used to ignite and maintain the discharge. Light from the bulb is fed to the spectrograph via a fibre optic at the side of the cavity. Optical access is granted to the cavity through an aperture at one side whose position is indicated by the crossed box.

5.2 Experimental setup

The apparatus used to ignite and maintain the discharge is shown in figure 5.1. A magnetron introduces EM radiation at a frequency of 2.45 GHz into a waveguide onto which the resonator is attached. The bulb is a quartz sphere with an inner diameter of 32 mm and a wall thickness of 2 mm. It is attached to a quartz rod which allows it to be rotated from outside the cavity. The rotation frequency is fixed at 8 Hz for all measurements. Matching is facilitated by stub tuners and a movable short. Once the lamp is ignited, optimal matching is achieved and the steady state reached, the discharge is ready for interruption. The lamp filling is fixed for all experiments. The bulb contains ca. 15 mg sulfur powder and the argon fill at room temperature is 100 mbar. Simple estimations as well as our models indicate that the total operational pressure is approximately 4 bar - 75% of which is due to sulfur.

The spectrum produced by the lamp in the setup is shown in figure 5.2. It is broad, ranging from 300 to 900 nm, and appears continuous. It arises mainly from the radiative

Figure 5.2: A typical spectrum produced by the sulfur lamp.

Figure 5.3: Potential energy curves for the $X$ and $B$ states in $S_2$. 

66
decay of vibrational levels in the \( B \) state to the ground \( X \) state in \( S_2 \).

In figure 5.3 the potential energy curves for these states are shown together with the ‘vertical’ wavelength as a function of internuclear radius. Moving from small towards larger internuclear separations the system produces increasingly longer wavelengths. The atomic lines that we will study lie at 869 and 920 nm. Their excitation energies are 9.29 and 7.87 eV above the atomic ground state [15].

The setup for the interruption experiment is shown in figure 5.4. A Stanford Research Systems DG-535 pulse generator is used to trigger the microwave power supply, model MW-GIR2M130-2K from Muegge which has been modified to guarantee full switch-off after 2 \( \mu \)s. We have found that full switch-off is in fact achieved within 1 \( \mu \)s although the switch-on behaviour is much less reliable. There is always a delay of several milliseconds before power returns after being triggered and it also takes ca. 100 ms for the forward power to return to 100\%. This is most likely due to a change in the impedance matching caused by the electrical conductivity of the plasma during the interruption. Therefore, this study will be confined to the responses of the spectrum during switch-off.

Radiation from the plasma is focused onto the entrance slit of a 1 m monochromator and the signal generated by a Hamamatsu side-on RS666 photomultiplier, which is sensitive between 200 and 930 nm, is recorded before, during and after the interruption. The signal is averaged over several shots and we have found that a repetition rate of less than 1 Hz is needed to prevent the lamp from extinguishing.

5.3 Typical responses

In this section responses most often displayed by interrupted systems are briefly explored. Both non-LTE and LTE perspectives are examined in order to anticipate responses.

![Diagram of experimental setup](image)

Figure 5.4: Setup for the interruption experiments.
Figure 5.5: Typical spectral line responses to power interruption. In contrast to the sudden decrease typical for a Boltzmann response an upward jump is seen in a Saha response.

Figure 5.6: Typical responses occurring under quasi-steady state conditions. The transition temperature, $T_{\text{Trans}}$, separates the molecular and atomic reservoirs.

5.3.1 Non-LTE responses

One possible aspect of non-LTE that might be present in the lamp is an inequality between the electron and heavy particle temperatures. Such a disparity is created by the energy flow from the electromagnetic field to the plasma and its interaction with the environment. This can be depicted by the following scheme:

\[
\text{EM field} \rightarrow [e] \rightarrow [h] \rightarrow \text{environment.} \tag{5.1}
\]

In the steady state electrons are heated by the electric field and transfer this energy to the heavy species which are subsequently cooled by the environment. The large electron-heavy particle mass difference means that this elastic energy transfer is not very efficient which leads to the temperature difference. Switching off the power supply will allow $T_e$ to decay to $T_h$. The cooling time will be shorter the higher the pressure, which in atmospheric plasmas, such as argon, was found to be on the order of several microseconds. In the sulfur lamp where pressures are approximately 4 bar we may expect that the electron cooling time will approximately be 4 times shorter due to enhanced collision frequencies. Moreover, the manifold inelastic loss channels available will enhance electron cooling and we can expect a shorter cooling time than predicted by elastic energy transfer. Therefore, if a temperature inequality is indeed present it will be eliminated in a time shorter than the switch-off time of our set-up, which is 2 microseconds. In any case, such a sudden cooling will result in an immediate response in those excitation channels which are ruled by electron kinetics. In an effort to understand the influence of such cooling on emission it is useful to review the results of previous power interruption experiments. These have been chiefly performed on atmospheric argon plasmas in open flowing ICP or microwave torches [11, 12]. The interruption of such experiments was facilitated by distinguishing two typical reactions: the so-called Boltzmann and Saha responses.

The excitation and de-excitation of a radiative state from and to the ground state is
5.3 Typical responses

ruled by the Boltzmann balance

\[ X + e + [E_{ex}] \rightleftharpoons X^* + e. \] (5.2)

If the balance is in equilibrium the population of the excited state is given by

\[ \frac{n_{X^*}}{g_{X^*}} = \frac{n_X}{g_X} \exp \left( \frac{-E_{ex}}{k_B T_e} \right). \] (5.3)

where \( n \) and \( g \) represent the density and statistical weights of the levels.

If the electron temperature changes from \( T_e \) to \( T_h \) one can expect that the density and thus the emission from \( X^* \) will decrease during cooling. Thus, the signal from a species dominated by the Boltzmann balance will fall due to electron cooling — a very natural result. However, lines in argon have been found to react in a manner contrary to this. At the moment of the power interruption the signal has been observed to increase or ‘jump up’ rapidly. This counter-intuitive behaviour, called a Saha response, can be explained as follows: if the radiating level is ruled by the Saha balance of ionization and recombination

\[ X^* + e + [I_p] \rightleftharpoons X^+ + 2e \] (5.4)

the removal of power drives the balance from right to left which indeed leads to an increase in the density of the excited state \( X^* \). While pure temperature considerations demonstrate the existence of a Saha response, the decoupling of density and temperature provide more justification. Argon, which readily displays Saha responses, recombines poorly. After the removal of power the electron density remains constant while the temperature decreases. During the stepwise decay of highly excited states the de-excitation of the first excited state forms a bottleneck. The combination of constant electron density, decreasing temperature and slow de-excitation result in the increase of density of highly excited states and hence a jump in emission. Once the electron density begins to decay so do the radiating states and emission decreases. Thus, the signal from a species determined by a Boltzmann balance is characterized by a decay, and a Saha balance by an upward jump. These typical responses are depicted in figure 5.5.

5.3.2 LTE responses

In the sulfur lamp high pressures may lead to a close to LTE situation. Here density and temperature do not decouple and with a low ionization degree it is unlikely that increases in emission during an interruption will be observed. However, ‘Saha-like’ responses are a possibility. Rather than being due to ion recombination, association of sulfur atoms is responsible. As will be demonstrated here the shift from one particle reservoir to another, or not as the case may be, provides a means to determine an upper temperature.

In figure 5.6 the steady state composition of an molecular plasma in equilibrium is depicted as a function of single ruling temperature. Here the molecular and atomic ground states are the main density reservoirs and are related via Guldberg-Waage. The excited state density is determined by its Boltzmann relationship with the ground state. As the temperature increases the atom and excited state densities increase at the cost of the ground state. Above a particular temperature the atom dominates and the ground as well as excited state densities decrease.
Chapter 5: Measured and simulated response …

We identify the dissociation transition temperature, $T_{\text{trans}}$, at which the atom and molecule densities are equal, as the division between the type of responses (Boltzmann or Guldberg-Waage) that the radiating state demonstrates. Below $T_{\text{trans}}$ the molecular ground state is the main density reservoir and a decrease in temperature results in a lower excited state density, hence reduced emission — a Boltzmann response. Above $T_{\text{trans}}$ the opposite is true, the ion state is the dominant particle reservoir. A decrease in temperature leads to an increase in the state density and thus increased emission — a ‘Saha-like’ or Guldberg-Waage response. Both of these responses are indicated in figure 5.6.

In considering responses in this quasi steady-state approach a shift between two main particle reservoirs can provide certain insight into the plasma conditions. The interruption signal can be used to indicate which particle reservoir is dominant and in which temperature range the radiating state can be found — above or below the transition temperature. The lack of a Guldberg-Waage response is an indication that the temperature of the system is lower than $T_{\text{trans}}$.

This general discussion can be applied to sulfur and quantitative estimates of an upper temperature found. In figure 5.7 the LTE composition of a dissociating sulfur plasma is shown (neutral fragments only). The molecular and atomic ground state densities are presented as well as those for two vibrational levels in the $B$ state of $\text{S}_2$. These lie at 4.3 and 5 eV in the molecular energy scheme shown in figure 5.3 and radiate at 600 and 900 nm respectively. The maximum in both excited state densities is shifted with respect to the transition temperature due to the competition between decreasing $\text{S}_2$ ground state density and increasing Boltzmann factor.

---

**Figure 5.7:** Density of sulfur atomic and molecular ground states as a function of temperature. Also shown are the densities of two vibrational levels in the $B$ state, both multiplied by $10^{10}$. The energies of the $v' = 5$ and $v' = 10$ levels are 4.3 and 5 eV respectively.

**Figure 5.8:** Ratio of state occupations of vibrational levels in the $B$ state after a 200 K decrease in temperature (PI) from two steady state (SS) values. The increase in state occupation from 6000 to 5800 K can be understood from the high temperature branch in figure 5.7.
Above 5000 K the densities of both excited states decrease. If the removal of power leads to a decrease in temperature the increase in the excited state densities results in enhanced emission. On the other hand, below the transition temperature a decrease in density occurs and a Boltzmann response will be observed. To further demonstrate this, the ratio of the $B$ state vibrational level occupations after a temperature decrease to that in the steady state is shown in figure 5.8. Two steady state temperatures have been chosen, one on either side of the transition value. Decaying from 4000 to 3800 K leads to a decrease of the radiating state densities while a decrease from 6000 to 5800 K to an increase.

There are two pieces of information that the interrupted signal immediately communicates. Firstly, rapid responses indicate differences between $T_e$ and $T_h$. Secondly, since assuming LTE simplifies the interpretation and prediction of spectral responses as temperature and density are linked, the dominant particle reservoir can be identified by the presence or otherwise of an increase in the interrupted signal. The fact that the excitation energy of the first vibrational level in the $B$ state is so close (indeed is less than) the dissociation energy of the ground state means that the interruption can probe the transition temperature itself. However, as shown in chapters 2 and 4 the spectrum is optically open above 600 nm. This corresponds to radiation originating from $\nu' \geq 5$. The density of the $\nu' = 5$ level is shown in figure 5.7. Thus, if no ‘Saha-like’ response is demonstrated by the molecular spectrum the temperature is less than the transition value which in the case of a 4 bar lamp is ca. 4500 K.

## 5.4 Results

### 5.4.1 Atomic lines

In figures 5.9 and 5.10 the relative response of the 920 nm and 869 nm lines are shown for two input powers, 600 and 800 W. The interruption starts at 10 ms and lasts 7 ms. For both lines and at both powers the response is indeed instantaneous. However, there is no sudden decay to indicate rapid cooling. At the switch-on there is approximately a 3 ms
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Figure 5.11: Response of the atomic lines at 800 W. The lesser energetic level, which produces the 920 nm wavelength, decays the faster which is contrary to expectation.

delay before the signal starts increasing and returns to its steady state value. The reason for this and the fact that the steady state is not reached until almost 70 ms after the power has been switched on, is due to the slow response of the magnetron. This means that the repetition frequency of the interruption must be quite low. For both lines signal decay is more rapid for the lower power. When the responses are compared, as shown in figure 5.11, the lesser energetic state responds more swiftly at the switch off. In all cases a very small overshoot, that is the signal is greater than the steady state value, is seen at 70 ms.

5.4.2 Molecular bands

In figures 5.12 and 5.13 the response of the molecular spectrum is shown at several wavelengths. The measurements were performed at 800 W only and the interruption settings are the same as for the atomic lines. The 400 nm signal decays the most rapidly, falling to 60% of the steady state value by the end of the interruption. The 600 and 700 nm signals respond more or less in an identical manner and decay by 25% of the steady state signal by the end of the interruption. The signals at 500, 800 and 900 nm lie in between these extremes — having fallen to 65% of the initial signal. Again it takes 70 ms after power is switched on before the steady state is reached. Overshoots are again seen here, but are only appreciable at 400 and 800 nm.

Returning to the main discussion, we may state that for both atomic and molecular lines no sudden changes were found at the onset of the power interruption. Moreover, all signals decrease in time. Therefore, the first conclusion is that the system is ruled by the molecular ground level. There is no shift from an upper to a lower particle reservoir. The investigations to follow will be guided by the hypothesis that the response observed
5.5 Characteristic decay times

The response of the atomic and molecular spectra are the same: all signals are decaying functions of time. Here we define characteristic decay times in order to establish a relationship between signal and temperature decay.

The decay time of a particular plasma quantity $Q$ can be derived from a general time dependent production/destruction balance which is applicable in many situations:

$$\frac{dQ}{dt} = P - QD$$

(5.5)

where $P$ is the production term and $D$ is the destruction factor. If the power interruption leads to a complete and abrupt removal of the production, such that $P = 0$ at time $t = 0$, the quantity $Q$ will decay according to the differential equation

$$\frac{dQ}{dt} = -QD.$$  

(5.6)

This means that $Q$ can be described by an exponential function $Q(t)$ in terms of an initial steady state value $Q_0$ and a time $\tau_Q$ which is characteristic of the decay,

$$Q(t) = Q_0 \exp \left(-t/\tau_Q\right).$$

(5.7)

The decay time $\tau_Q$ is directly related to the destruction factor

$$\tau_Q = \left| \frac{d \ln Q}{dt} \right|^{-1} = \frac{1}{D}.$$  

(5.8)
Another important property of equation (5.5) is that steady state quantities can be used to estimate the decay time. In the steady state we simply have

$$P = QD.$$  \hspace{1cm} (5.9)

Using (5.8) the decay time is given as the fraction of the content to the production

$$\tau_Q = D^{-1} = Q/P$$ \hspace{1cm} (5.10)

which also shows that the content $Q$ can be obtained by applying the power during the period $\tau_Q$. These simple forms provide insight into the relation between plasma properties once steady state properties are known and will be used in the study of the energy balance of the electrons and heavy particles.

**5.5.1 Signal decay time**

We shall now use the above equations to explore the various decay times found in the spectral responses. This analysis is carried out assuming that a single temperature rules the system. Here, all radiating state densities are related to the ground state via Boltzmann so we write the time dependent intensity as

$$I(t) = I_0 \exp\left(-\frac{E}{k_B T}\right)$$ \hspace{1cm} (5.11)

where $E$ and $T$ are the excitation energy and temperature respectively. The primary time dependent quantity in this equation is the temperature so that all the different signal decay times must be related to that of the temperature. The challenge is to deduce the temperature decay time from the spectral responses since any deviations will point to the existence of more than one temperature. In this way we might find out to what degree the power interrupted lamp behaves as a decaying LTE plasma. To get the relation between the characteristic time of a spectral signal and that of the temperature we differentiate equation (5.11) with respect to time and obtain:

$$\tau_I = \left|\frac{d \ln I}{dt}\right|^{-1} = \left|\frac{E}{k_B T} \frac{d \ln T}{dt}\right|^{-1} = \frac{k_B T}{E} \tau_T.$$ \hspace{1cm} (5.12)

Here, the temperature decay time, $\tau_T$, is defined as

$$\tau_T = \left|\frac{d \ln T}{dt}\right|^{-1} = \left|\frac{1}{T} \frac{dT}{dt}\right|^{-1}.$$ \hspace{1cm} (5.13)

Thus, for a given temperature decay time, the larger the excitation energy the shorter the signal decay time. By the same token: the lower the temperature the shorter the decay time. We now have the means to relate the decay of a temperature to that demonstrated by a radiating state.
5.6 Measured decay times

From equation (5.12) we can establish the decay time, $\tau_I$, for the various spectral lines. Since we report only the relative change in the emission the decay time is simply $\tau_I = -t/\Delta \ln I(t)$ where $t$ is the time after the interruption. The decay times for the atomic lines and molecular wavelengths deduced from the first 5 ms of the interruption are shown in table 5.1. The atomic lines decay time is between 11 and 15 ms depending on the input power. The molecular decay times are the shortest (14 ms) at 400 nm rising to a maximum (25.2 ms) at 600 nm and subsequently decrease towards longer wavelengths.

Plotting the signal decay time, $\tau_I$, versus the inverse excitation energy allows the quantity $k_B T \tau_I$ to be found from the experimental data. If the entire atomic/molecular system is ruled by one temperature then a straight line through all data points should be found. However, in order to present the atomic and molecular results on the same graph an appropriate zero energy has to be chosen. In this case the molecular ground is suitable. The effective excitation energies of the atomic states then have to be found.

The density of the molecular ground electronic state is related to the atomic one via the Guldberg-Waage law

$$n_{S_2} = n_S^2 \frac{Z_{S_2}^2}{Z_S^2} V \exp \left( \frac{D_e}{k_BT} \right)$$

(5.14)

where $V$, $Z_M$ and $D_e$ are the de Broglie volume, the partition sum of the molecular ground state and the dissociation energy of the molecule respectively. The density of an excited atomic state, $n^*$, is related to the atomic ground state via Boltzmann and inserting this into equation (5.14) a direct relationship is found with the molecular density:

$$n^* = \left[ n_{S_2} \frac{Z^*}{VZ_{S_2}} \right]^{1/2} \frac{Z^*}{Z_S} \exp \left( \frac{-E^* - D_e/2}{k_BT} \right)$$

(5.15)

where $E^*$ is the excitation energy of the atomic state relative to the atomic ground. This pseudo-Boltzmann expression shows that the effective excitation energy of an atomic
Figure 5.14: Signal decay times plotted as a function of inverse excitation energy. The molecular bottom and atomic top of the system is governed by a single temperature. The energies of the atomic and molecular ion states are indicated along with the dissociation energies, $D_e$, of the molecular states.

state relative to the molecular ground is $E^* + D_e/2$ (thus, the effective excitation energy of the atomic level as seen from the molecular ground state is $E^* + D_e/2$). In table 5.1 the effective excitation energies of the states considered are presented. Our simulations have shown that absorption in $S_3$ is by and large responsible for the short wavelength behaviour of the spectrum. In order not to cloud the discussion with such considerations we focus on radiation produced at 600 nm and for which the plasma is optically open. In figure 5.14 the signal decay time is plotted as a function of inverse excitation energy. The dissociation energies of the X and B states are indicated in the graph along with the ionization energies of $S_2$ and S.

According to equation (5.12), plotting the signal decay time versus the inverse of the excitation energy should begin at the origin — an infinitely highly excited state will demonstrate an infinitely small decay time. In figure 5.14 the best fit line to the data through the origin is also shown. The slope of this line is $\sim 100$ ms eV. For an excitation temperature of 4000 K a temperature decay time of 290 ms is found.

The decay of the molecular spectrum at 600 and 700 nm lies close to the best fit line while the response of the rest of the spectrum slightly less so. Since the measurement of the signal responses is a relative one, the error on the data is negligible. Thus, there is some indication that the excitation temperatures ruling high lying vibrational states in the $B$ state and the atomic states are different to the rest of the system.
5.6 Measured decay times

5.6.1 Molecular response above 700 nm

The response of the 800 and 900 nm wavelengths do not lie near the best fit line. In fact they decay faster than they ought. The previous analysis, in equation (5.12), shows that a lower temperature or higher excitation energy leads to a shorter decay time. For the latter to be true, the radiation would have to originate from 5.7 eV up in the system. This is in excess of the dissociation energy of the $B$ state. However, as we have seen in section 4.4.3 no other state in $S_2$ is more energetic than the $B$ state and radiates at these wavelengths. The other possibility is that the excitation temperature for the vibrational states that produce these wavelengths is lower than that which determines the distribution in the rest of the system. If we assume that the decay time is universal the excitation temperature is

$$\hat{T} = E \frac{T_I}{T_e}$$

where $\hat{T}$ is the temperature in units of electron volt. We find an excitation temperature of ca. 3200 K. In this view of the system the excitation temperature for large vibrational quantum numbers in the $B$ state is only $\sim 20\%$ lower than that governing the rest of the system. While a non-LTE discussion of the possible reasons for the extra red and faster decay of the spectrum is beyond the scope of this work, some processes are discussed in appendix B.

5.6.2 Atomic line response

On the other hand the atomic lines decay more slowly than expected from equation (5.12). Moreover, the more highly excited state of the two decays the slower which is a further contradiction. In this case it may be possible that we are observing a mixture of Boltzmann and Saha responses. Since the density of atomic states with small ionization potentials is less than that of the ion, recombination into these may slow down the overall Boltzmann response. For states with a smaller ionization energy, whose density is also lower, the effect will be more pronounced. In the formalism of equation (5.5) the time dependent density of the excited state, $X^*$, is given by

$$\frac{dn_{X^*}}{dt} = P^S + P^B - n_{X^*} \left( D^S + D^B \right)$$

where the superscripts $S$ and $B$ refer to Saha and Boltzmann processes. When power is removed, only the Boltzmann production and Saha destruction paths are removed. The density decay time is thus

$$\tau_{n_{X^*}} = \left| \frac{1}{n_{X^*}} \frac{dn_{X^*}}{dt} \right|^{-1} = \left[ \frac{P^S}{n_{X^*}} - D^B \right]^{-1}.$$

Thus, the addition of an extra (but not dominant) particle source increases the decay time of the state density. Subsequently, emission lags behind the expected LTE value and a longer decay time is observed. While this is a purely qualitative view the fact that three particle recombination can decrease the destruction rate and hence slow down the decay in density is demonstrated.
To conclude, while almost all of the excitation energy space is ruled by a single temperature, which has a characteristic decay time of 290 ms, the ‘red’ part of the spectrum is ruled by a different excitation temperature.

### 5.7 Global study of the response of energy balances

We will now use the general equation (5.10) to explore the relaxation times for the plasma as a whole and for the various subgroups the electrons \([e]\) and heavy particles \([h]\). Our strategy is to begin with a general exploration and to then proceed to more in-depth considerations.

Firstly, we assume that the plasma is in full LTE. Then \(P\) and \(Q\) in equation (5.10) refer to the power density and energy density respectively. For a total input power of 800 W and lamp radius of 16 mm, \(P\) is \(\sim 5 \times 10^7\) W m\(^{-3}\). The energy content of the plasma is the product of the specific heat and the temperature. Thus, we understand that the relaxation time found for the energy content is that of the corresponding temperature. For \(Q\) we take \((70/2)p\) which as we will show in section 5.9.2 is a reasonable value for a chemically reactive sulfur plasma at 4000 K. Then we find that \(\tau_T = Q/P \sim 300\) ms which agrees very well with the time found from the experimental data where the temperature was taken to be 4000 K.

Secondly, we assume that the plasma is a two temperature plasma ruled by the energy chain

\[
\text{EM field} \rightarrow [e] \rightarrow [h] \rightarrow \text{environment}.
\]

Here we assume that \(T_e \gg T_h\) and that the power along the links is the same. Since \(D_e = P_e/Q_e\) and \(D_h = P_h/Q_h\) the electron destruction factor can be written as \(D_e = D_h(Q_h/Q_e)\).

If we now use \(D_h \sim 3\) s\(^{-1}\) (the value found above), the relation \(Q_h/Q_e = (70/3)p_h/p_e\), and the value of the ionization degree \(p_e/p_h\) of \(10^{-5}\), we find the decay rate of the electron gas \(D_e = 7 \times 10^6\) s\(^{-1}\). This implies a \(\tau\) value of about 0.1 \(\mu\)s. Knowing the decay time and the destruction factor, the heat content of \([e]\) and the electron temperature can be estimated. Employing equation \(Q_e = P_e/D_e\) and taking a value of the electron density \(n_e = 10^{20}\) m\(^{-3}\) we find \(T_e = 3400\) K. This is too low and in violation of the assumption that \(T_e \gg T_h\).

Although it has some shortcomings the global approach provides some insight. In particular it shows that electrons will respond much faster since the heat capacity is so much smaller that of the heavy particles. However, the assumption that \(T_e \gg T_h\) proves to violate itself. In fact the total energy reservoir of \([e]\) does not drain into \([h]\) but only a fraction \(\mathcal{F} = (T_e - T_h)/T_e\). The smaller this is, the faster the electron temperature will react and (using \(\mathcal{F}Q = P/D\)) the smaller \(\mathcal{F}\) will be. To break this vicious circle and to get more information in the actual value of electron response time we need a more in-depth study for which the energy balances have to be consulted.
5.8 Electron temperature decay

The rapid and large jumps of spectral lines in response to power interruption was in the past attributed to the substantial difference between the electron and heavy particle temperature. And indeed, in the (atomic) argon ICP large differences between $T_e$ and $T_h$ were found. Since we do not detect any sudden responses (in the order of $\mu$s) in the sulfur lamp we might conclude that $(T_e - T_h)$ is small in this plasma. This is the subject of this section in which we study the electron energy balance which expresses the relationship between the ohmic input, $\epsilon$, and the power lost per unit volume by electrons to heavy species in elastic and inelastic collisions:

$$0 = \epsilon - n_e n_{S_2} \left[ \langle \sigma_{em} v_e \rangle \frac{3 m_e}{M} k_B (T_e - T_h) + \langle K \rangle \langle E \rangle \right].$$  \hspace{1cm} (5.20)

Here $\langle \sigma_{em} v_e \rangle$ is the rate coefficient for momentum transfer between electron and molecule averaged over the Maxwellian electron energy distribution function while $\langle K \rangle$ and $\langle E \rangle$ are the mean values of the rate coefficient for electron excitation and the excitation energy respectively. We assume that all inelastic losses are associated with electron impact excitation from the $X$ to the $B$ state. In order to make this study possible $\langle K \rangle$ and $\langle E \rangle$ must be determined in an averaging procedure which will be discussed at the end of this section and in the appendix.

Comparing the electron energy balance with the general formulae, equations (5.5) to (5.9), shows that two destruction terms are present; one associated with elastic and the other with inelastic processes. We will start with the elastic rate. Since the loss term of the corresponding decay equation clearly scales with the energy difference $(T_e - T_h)$ we can use the elastic term directly in a simplified balance (see equation (5.6)) to describe the decay of the temperature difference $(T_e - T_h)$

$$C_v \frac{dT_e - T_h}{dt} = -n_e n_{S_2} < \sigma_{em} v_e > \frac{3 m_e}{M} k_B (T_e - T_h).$$  \hspace{1cm} (5.21)

Using $C_v = 3/2 m_e k_B$ for the specific heat of the electron gas leads to the following decay rate:

$$D = n_{S_2} \left[ \langle \sigma_{em} v_e \rangle \frac{2 m_e}{M} \right].$$  \hspace{1cm} (5.22)

The elastic decay rate can now be estimated using the mass of the sulfur molecule, (64 a.m.u.) while the rate for elastic processes, $\langle \sigma_{em} v_e \rangle$, is replaced by a simple product of the electron velocity, $v_e = 10^6$ ms$^{-1}$ and a cross section of 1 Å$^2$. Inserting for the ground state $n_{S_2} = 10^{25}$ m$^{-3}$ we get a decay frequency of $\sim 10^6$ s$^{-1}$. An estimate of the steady state value of $(T_e - T_h)$ can now be found by calculating the temperature increase of the electron gas due to application of a power density of $5 \times 10^7$ W m$^{-3}$ during 1 $\mu$s. Applying equation (5.9) leads to a value of $(T_e - T_h)$ around 3000 K; a value which is neither realistic nor observed. Note that the decay rate and the corresponding temperature difference are comparable to the values found in an atmospheric argon ICP. But this is not surprising since the elastic processes in the Ar-ICP are very important while the collision rates and pressure are of the same order as that in the sulfur lamp. The reason that we do not see the comparable $(T_e - T_h)$ value in the sulfur lamp must be due to the the large inelastic losses.
The inelastic term does not have a clear \((T_e - T_h)\) factor in it. That makes the description of the decay of the temperature difference less trivial. However, employing a Taylor expansion around \(T = T_e\) leads to the following expression

\[
C_e \frac{dT_e - T_h}{dt} = -n_e n_{S_2} \langle E \rangle \frac{d\langle K \rangle}{dT_e} (T_e - T_h) \tag{5.23}
\]

where we used the assumption that the variation in \(h E_i\) due to the changing temperature is much smaller than that in \(\langle K \rangle\). Since the latter has the structure \(\langle K \rangle = K_0 \exp(-\langle E \rangle/kT)\) we may write

\[
\frac{d\langle K \rangle}{dT_e} = \frac{\langle K \rangle \langle E \rangle}{k_B T_e^2} \tag{5.24}
\]

We find for the decay of \((T_e - T_h)\) due to inelastic processes

\[
\frac{dT_e - T_h}{dt} = -D_{inelas}(T_e - T_h) \tag{5.25}
\]

where

\[
D_{inelas} = \frac{2}{3} n_{S_2} \frac{\langle K \rangle}{k_B T_e} \left[ \frac{\langle E \rangle}{k_B T_e} \right]^2 \tag{5.26}
\]

Employing the values \(n_{S_2} = 10^{25} \text{ m}^{-3}\), \(\langle E \rangle = 4.2 \text{ eV}\), \(kT_e = 0.35 \text{ eV}\) and \(\langle K \rangle = 8 \times 10^{-19} \text{ m}^{-3}\), it is found that \(D = 10^9 \text{ s}^{-1}\).

Using the same reasoning as before we find the temperature difference is more in the order of 3 K rather than 3000 K. Thus the inelastic processes are far more important than elastic processes. They are responsible for the fact that the decay rate is so large and the temperature difference is so small.

The value of \(\langle K \rangle\) used in the estimation was found using the cross sections for vibrational excitation between the electronic states employing the impact parameter approach from Hazi [16] in the improved form developed by Redmon et al [17]. Details of the calculation are provided in the appendix. The state-to-state vibrational level averaged rate coefficient for electron excitation from \(X\) to \(B\) levels is given by

\[
\langle K \rangle = \frac{\sum_i (\sum_f K_{if}) \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \tag{5.27}
\]

where \(i\) and \(f\) range over the vibrational states of the \(X\) and \(B\) states respectively. The energy eigenvalues of the vibrational levels is denoted by \(E_i\). The mean excitation energy \(\langle E \rangle\) is found in a similar manner. For a temperature of 4000 K, we find that the rate coefficient is \(8 \times 10^{-19} \text{ m}^3\text{s}^{-1}\) and the excitation energy is 4.2 eV.

In our attempt to estimate the extent to which the electron temperature is larger than that of the heavy species we have not only determined that the enormous inelastic losses prevent such a difference from establishing, but also encounter one of the reasons for the lamps efficiency. In atomic plasmas the production of the first excited states is the chief bottleneck to the further manufacture of excited states. The inelastic losses are thus comparable to the elastic and the overall inefficiency of energy transfer from the electric field to the heavy species results in a high electron temperature.
In a molecular discharge the rovibrational structure provides manifold excitation channels. A system such as \( \text{S}_2 \) has, on the one hand, rather large transition probabilities for radiative decay, namely on the order of \( 10^5 \text{ s}^{-1} \) for most of the vibronic transitions, which are quite large for a molecule. On the other hand the high pressures in the lamp engage all possible excitation channels. In short, the energy transfer from the electric field to the internal levels of the molecular electronic states via the electron gas is highly efficient. It is a favourable side effect that the vibronic states produced have the property that they radiate so rapidly and at such useful wavelengths.

### 5.9 Heavy particle temperature decay

As demonstrated by the experimental decay times and the calculations presented in the previous section we may assume that a single temperature approach provides a good approximate means to describe the plasma and its response to power interruption. This means that we can confine ourselves to the study of the LTE energy balance. In this section we will examine in how far this energy balance can describe the observed phenomena.

The energy balance expresses that the Ohmic input power is equal to that lost by heat conduction and radiation losses

\[
0 = \epsilon + \nabla \cdot (\lambda \nabla T_h) + Q_{\text{rad}} \quad (5.28)
\]

where \( \lambda \) is the thermal conductivity and \( Q_{\text{rad}} \) is the radiation term. By convention local absorption leads to a positive \( Q_{\text{rad}} \) value whereas pure emission means that \( Q_{\text{rad}} \) is negative.

Here again we see that there are two loss terms and it is seductive to follow the strategy of the previous section by determining two decay rates; one associated to the heat conduction the other to the radiative losses. However, due to its non-local character (the influence of absorption) it will not be easy to transform the \( Q_{\text{rad}} \) to a destruction rate; instead we have to use computer simulations. This will be treated in section 5.10

To determine the role of the heat conduction we may use the simplified destruction balance

\[
C_v \frac{dT}{dt} = \nabla \cdot (\lambda \nabla T) = -\frac{\lambda T}{\Lambda^2} \quad (5.29)
\]

where \( \Lambda \) is the gradient length. The conduction decay time is thus

\[
\tau_T^C = \frac{C_v \Lambda^2}{\lambda} \quad (5.30)
\]

Even in this simplified form there are some issues to overcome, namely the gradient length, the heat capacity and thermal conductivity in a reacting molecular gas.

### 5.9.1 Gradient length

The gradient length is often set to the plasma radius. This is in general allowed for plasmas with Gaussian density or temperature profiles. The sulfur lamp is on the other
hand a relatively large closed system and as our LTE models show a temperature gradient is only supported towards the wall. At the centre of the lamp the temperature gradient is very small. We therefore need to calculate a radially averaged value for $\Lambda$. By definition

$$\Lambda = \left[ \frac{1}{T} \frac{dT}{dr} \right]^{-1}. \quad (5.31)$$

From our LTE models we have found the temperature profile to be reasonably approximated by the following function of lamp radius

$$T(r) = T_A - (T_A - T_W) \left( \frac{r}{R} \right)^4. \quad (5.32)$$

The lamp radius is given by $R$ and $T_A$ and $T_W$ are the centre and wall temperatures respectively. The gradient length can then be expressed as a function of radius

$$\Lambda(r) = \frac{r}{4} \left( \frac{1}{T_A - T_W} \right) \left[ T_A \left( \left( \frac{r}{R} \right)^4 - 1 \right) + T_W \right]. \quad (5.33)$$

The radially averaged value is found from

$$\langle \Lambda \rangle = \frac{\int_0^R r^2 \Lambda(r) dr}{\int_0^R r^2 dr} \quad (5.34)$$

which gives a gradient length of 90 mm, more than 5 times the lamp radius. If conduction dominates throughout the lamp this is the value taken. Otherwise, the gradient length is determined from the edge of the region where most power is coupled. This inevitably results in a shorter gradient length.

### 5.9.2 Heat capacity

The heat capacity of a reacting molecular gas is more complex and greater in magnitude than simply the sum of the translational and internal contributions from the various
species in the mixture. One must take into account an additional component due to the release of enthalpy when species associate. Thus the total heat capacity, $C_T^v$, can be expressed as the sum of two components

$$C_T^v = C_F^v + C_R^v. \quad (5.35)$$

where $C_F^v$ and $C_R^v$ are the so-called frozen and reactive contributions. The former encompasses the internal and translational contributions and the latter deals with the reactive part. The internal contributions are straightforward to calculate and we can make use of Butler and Brokaw's expression to find the total heat capacity [21]. This relates the total and frozen heat capacities at constant pressure to the frozen, $\lambda^F$, and total thermal conductivities, $\lambda^T$:

$$C_T^p = C_F^p \frac{\lambda^T}{\lambda^F}. \quad (5.36)$$

For our purposes we require $C_v$ and write, using $C_p = C_v + p/T$

$$C_T^v = \frac{\lambda^T}{\lambda^F} C_F^v + \frac{p}{T} \left( \frac{\lambda^T}{\lambda^F} - 1 \right) \quad (5.37)$$

where $p$ is the total pressure. Using the LTE plasma composition and assuming that all rotational and vibrational levels are engaged, the internal heat capacity is

$$C_F^v = \left[ \frac{3}{2} n_S + \frac{7}{2} n_{S_2} + 6n_{S_3} \right] k_B \quad (5.38)$$

where the densities of the atom, dimer and trimer are found from [4].

We have also calculated the thermal conductivity of the plasma. The total value, $\lambda^T$, can be written as the sum of three terms

$$\lambda^T = \lambda^R + \lambda^I + \lambda^E \quad (5.39)$$

where $\lambda^I$ and $\lambda^E$ are the internal and electronic contributions respectively. However, at the temperatures found in the sulfur lamp the latter is negligible. The internal contribution is determined from the expressions of Muckenfuss et al [19] and Eucken [20]. The reactive contribution, $\lambda^R$, due to chemical reactions which in this case is the dissociation of $S_2$ is found from Butler and Brokaw's expressions [21, 22]. The elastic cross sections required and an evaluation of the accuracy with which they can be used to determine the transport properties of reacting plasmas are provided in chapters 8 and 9 respectively. The total value and the frozen contribution are shown in figure 5.15 along with the ratio $\lambda^T/\lambda^F$. One can see that at 4000 K the latter is ca. 10 and will lead to a great enhancement in the heat capacity.

In figure 5.16 the contributions of the various species to the frozen heat capacity are shown. The total value found from equation (5.37) is also presented. The reactive component does indeed result in a greatly enhanced heat capacity particularly at 1000 and 4000 K. This will certainly influence the temperature decay time.
Figure 5.17: Decay times of the molecular spectrum as found from experiment and the LTE model of the decay. The model provides not only accurate values for $\tau_i$ but also as a function of wavelength.

5.9.3 Conduction decay time

Returning to equation (5.30) the decay time resulting from heat conduction can be found. The radially averaged temperature in the lamp is 2700 K providing a thermal conductivity of 0.14 Wm$^{-1}$K$^{-1}$ and a heat capacity of ca. $(28/2)p/T$. Together with a gradient length of 90 mm the decay time is 116 s. This is more than two orders larger than the measurements or the global approach of section 5.7. However, this is appropriate when conduction dominates the energy balance from the centre of the lamp. However, as shown in figure 4.15 this is only true 1 mm from the wall. The decay time with this substantially smaller gradient length is 15 ms. Thus, the decay of the entire plasma through conduction, influenced by the flat temperature gradient at the centre, takes too long. On the other hand, decay dominated by conduction near the wall is too fast.

Reproducing the measured decay times requires the radiative contribution to be taken into account; where radiative loss in the centre and absorption at the wall will respectively shorten and lengthen decay times.

5.10 Decay times including radiation transport

If there were indeed a significant difference between electron and heavy particle temperatures, we have demonstrated that signal decay times would occur on microsecond timescales. On the other hand the very large heat capacity of the sulfur plasma and large gradient length indicate that signal decay through pure heat conduction is likely to occur on a timescale of tens of seconds.

The measured decay times are right in the middle of these estimates. So as one
might expect, the influence of radiative losses cannot be excluded from a study of the behaviour of the plasma during power interruption. We are dealing with a highly efficient light source after all. However, as stated above, the influence of radiation on the energy balance cannot be treated simply. Fortunately we can profit from our previous steady state models to investigate the relaxation of the system.

In two previous papers we have presented steady state LTE models of the discharge. In the first, radiation generation and transport were treated semi-classically. Here, the manifold vibronic transitions in the BX system in $S_2$ were treated with a two state approach. A single line profile was used to describe the emission and absorption from the plasma. In the second paper we showed that UV absorption in $S_3$ and a quantum mechanical description of the spectrum were required to achieve a more satisfactory agreement between the measured and simulated spectra.

Both of these models were constructed and executed in PLASIMO, a plasma simulation platform developed in our group [23, 24, 25]. One of the many strengths of PLASIMO is its modular design — the description of particular mechanisms is separated from the physico-chemical details of any given problem. We can benefit greatly in this from the features that this design provides. The time dependent relaxation of the system from the steady state after the power has been removed can be treated in PLASIMO as a relatively simple extension of our existing model. The time dependent part of the governing equation

$$C_v \frac{dT_h}{dt} = \nabla \cdot (\lambda \nabla T_h) + Q_{rad}$$

(5.40)

is treated with an implicit Euler discretizer. Ohmic input has been set to zero and all variables are initialized with steady state results. The radiation generation and transport is treated quantum mechanically, $S_3$ is included as are the five other transitions in $S_2$ identified in [4]. The specific heat calculation has already been dealt with and we can easily model the decay of the system including radiation transport.

In figure 5.17 the measured and simulated characteristic decay times are shown as a function of wavelength. The main result is that the modelled times are in reasonable agreement with the experimental results — the inclusion of radiation decreases the decay time from some hundreds of seconds in the case of pure heat conduction to tens of milliseconds.

Not only that, but the measured increase from 400 nm to 600 nm and the subsequent decrease with increasing wavelength is reproduced as well. The temperature decay time can also be found from the model. In figure 5.19 the steady state temperature is shown together with the profile after 5 ms. What is immediately apparent is that the drop in temperature is very small - from 4460 to 4290 K at the centre of the bulb. The reason for the high central temperature, above the transition value shown in figure 5.7, is that the simulated pressure is slightly greater than 4 bar. From figure 5.18 we see that emission is strongest at 9 mm from the centre of the lamp. As figure 5.19 shows the temperature drops 97 K in 5 ms at this radius — a decay time of 200 ms. This is within 50% of the experimental decay time of 290 ms (see section 5.6).
Chapter 5: Measured and simulated response ...

![Figure 5.18](image1.png)  
**Figure 5.18:** Energy balance contributions as a function of lamp radius.

![Figure 5.19](image2.png)  
**Figure 5.19:** Radial temperature profiles before the interruption and 5 ms into the interruption.

### 5.11 Conclusions

The relaxation of molecular and atomic spectra from a high pressure sulfur discharge have been observed before and during a time in which power input has been removed. Characteristic decay times have been determined and the influence of various temperatures/processes have been studied.

All observed responses, whether in the atomic or molecular spectra, are gradual. The lack of a sudden response indicates that $T_e$ is approximately equal to $T_h$. Since all signals decay there is no shift in particle reservoirs. The indications are thus that the molecular ground state is the chief reservoir and that the temperature is less than the dissociation transition temperature. In the current case of a 4 bar sulfur-argon mixture this is $\sim 4500$ K.

The decay of the spectrum points to a single ruling temperature. However, there is a indication that around 800 and 900 nm the vibrational states radiating in this range are ruled by an excitation temperature slightly lower than that for the rest of the system. The response of the atomic lines is contrary to expectation on two counts: they decay more slowly than expected and the lesser excited of them decays the faster. We have attributed this to a possible mixing of Saha and Boltzmann responses.

We have shown that the difference between electron and heavy particle temperatures is only several Kelvin. This is due to the extremely large inelastic losses incurred in producing vibrational levels in the $B$ state. The decay time of the electron temperature was shown to be less than 10 ns.

We have also demonstrated that conduction dominated processes cannot explain the observed decay times. An existing steady state model of the lamp which includes radiation transport has been adapted to simulate the relaxation of the system after power has been removed. The decay of the molecular spectrum found from the simulation agreed very well with experiment being within 40% of measured values.

Until now only what occurs inside the power interruption has been studied. Due to the switch-on behaviour of the magnetron/plasma system the response of the spectrum
Conclusions

after the interruption has been left. Nevertheless, the overshoots observed at 400 and 800 nm and in the atomic lines is worth noting and returning to in future investigations.

The technique of power interruption has proved to be very useful in increasing our understanding of the sulfur lamp. This study was initiated by several questions regarding the LTE status of the discharge and has answered several of them. One of the chief concerns is the behaviour of the spectrum towards longer wavelengths. Our LTE models have proven reasonably effective in all regions of the spectrum except in the ‘red’. In this article we have seen that the excitation temperature through the $B$ state is likely to be a function of the vibrational level. This points to a possible non-LTE route to enhance emission in this range.

Acknowledgements

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Appendix A — rate coefficients

First developed by Hazi [16] and extended by Redmon [17] the impact parameter method for the calculation of inelastic cross sections for molecular excitation is used very much in contemporary works. Most recently it has been used to determine the excitation cross sections of a small number of vibronic transitions in $O_2$ and $S_2$. In the approach, the cross section is written as the product of two terms: a structural factor that encompasses the specifics of the interacting levels and a dynamical factor, which deals with the electron behaviour. Thus,

$$\sigma_{\nu_i\nu_f}^{\alpha_i\alpha_f}(E) = S_{\nu_i\nu_f}^{\alpha_i\alpha_f} D_{\nu_i\nu_f}^{\alpha_i\alpha_f}(E) \quad (A.1)$$

where $\alpha$ and $\nu$ indicate the electronic and vibrational states involved, and the subscripts $i$ and $f$ discriminate between initial and final states. The structural factor is given by

$$S_{if} = \frac{m_e^2 e^2}{12\pi\epsilon_0 g_i \hbar^3} |\langle \psi_i | M | \psi_f \rangle|^2 \quad (A.2)$$

where $\psi_i$ and $\psi_f$ are the wavefunctions for the initial and final vibrational states, $g_i$ is the statistical weight of the electronic state and $M$ the electronic transition dipole moment (ETDM). The dynamical factor is an involved function and for completeness is reproduced here from [17]

$$D_{if}(E) = \frac{2\pi\hbar^2}{m_e^2 u_i^2} \left[ \gamma_i \left( K_0(\gamma_i)K_1(\gamma_i) - \frac{\pi^2}{4} S_0(\gamma_i)S_1(\gamma_i) \right) + \gamma_f \left( K_0(\gamma_f)K_1(\gamma_f) - \frac{\pi^2}{4} S_0(\gamma_f)S_1(\gamma_f) \right) + \gamma \left( K_0(\gamma_i)K_1(\gamma_f) + K_0(\gamma_f)K_1(\gamma_i) + \frac{\pi^2}{4} S_0(\gamma_i)S_1(\gamma_f) + \frac{\pi^2}{4} S_0(\gamma_f)S_1(\gamma_i) \right) \right]$$

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where $K$ and $S$ are the modified Bessel and Struve functions. The initial and final electron velocities $u_i$ and $u_f$ are given by

\[
\begin{align*}
    u_i &= \sqrt{\frac{2E}{m_e}} \\
    u_f &= \sqrt{\frac{2(E - \Delta E_{i,f})}{m_e}}
\end{align*}
\]

where $\Delta E_{i,f}$ is the energy difference between the vibrational levels. The $\gamma_i$, $\gamma_f$ and $\gamma$ terms are defined as

\[
\begin{align*}
    \gamma_i &= \frac{\rho |\Delta E_{i,f}|}{\hbar u_i} \\
    \gamma_f &= \frac{\rho |\Delta E_{i,f}|}{\hbar u_f} \\
    \gamma &= \frac{\rho |\Delta E_{i,f}|}{\hbar} \frac{2u_i}{u_i^2 + u_f^2}
\end{align*}
\]

where $\rho$ is the so-called cut-off parameter - a length required to prevent a divergent cross section. The cutoff parameters are given by [26] as 0.921 and 0.974 Å for oxygen and sulfur respectively. Energy gap details are found from the potential curves from figure 5.3. The vibrational wavefunctions were calculated using the SCHROED program [27] and the Franck-Condon factors found using the quadrature routines supplied with the Gnu Scientific Library [28]. The electronic transition dipole moments for the transitions were found in the literature [29]. Once the elementary cross sections have been found the rate coefficient is easily calculated from

\[
K_T^R(T_v, \epsilon) = \int_0^\infty \sigma^R(T_v, \epsilon) f^M(\epsilon) v_e(\epsilon) d\epsilon
\]

where $f^M(\epsilon)$ is the Maxwellian electron energy distribution function and $v_e(\epsilon)$ is the electron velocity.

## Appendix B — the missing red problem

In this section a non-LTE process is presented as a possible solution to the missing red problem and the too rapid decay of the long wavelength range of the spectrum.

In order for the $B^3\Sigma_u^{-} \rightarrow X^3\Sigma_g^{-}$ transition to produce more red an overpopulation of the appropriate vibrational levels with respect to equilibrium is needed (the vibrational levels $v' > 15$ radiate at 800 nm and beyond). This applies to the steady state and which ever process is proposed must be consistent with the temporal behaviour of the spectrum during an interruption — a more rapid decay must be seen.

Taking the dissociation-association balance as the sole cause of vibrational non-equilibrium, the main point is that densities can remain greater in space and decay more rapidly in
time than LTE predicts. The density of the atomic state is very important in this picture. However, before discussing the process some basic information is needed.

The reaction cross-section, $\sigma_R$, for the dissociation

$$S_2(B) + M \rightleftharpoons S^* + S^* + M$$

(B.1)
can be taken as a fraction of the elastic cross-section [30]. We assume that this fraction is unity and set the cross-section to 1 $\text{A}^2$. The rate coefficient for dissociation, $k_{\text{diss}}$, is to a first approximation the product of $\sigma_R$ and the velocity. The latter is taken to be $10^3 \text{ ms}^{-1}$. In equilibrium the number of forward processes equals the number of reverse processes and the three particle (3p) association rate, $k_{3p}$, is found from

$$k_{3p} = k_{\text{diss}} \frac{n_{S_2(B)}}{n_{S^*}}.$$  

(B.2)
The ratio of the molecular to atomic densities is found from the Guldberg-Waage relation given in equation (5.14). Thus,

$$k_{3p} = k_{\text{diss}} \frac{Z_{S_2(B)} Z_{S^*}}{Z_{S^*}^2} V \exp \left( \frac{E_a}{k_B T} \right).$$

(B.3)

Here $Z_{S_2}/Z_{S^*}^2 V$ is effectively constant ($10^{-30} \text{ m}^3$) and $E_a$ is the activation energy. This is taken to be 1 eV, the dissociation energy of the vibrational level $v' = 15$ which radiates at 800 nm. The rate $k_{3p}$ is effectively constant with temperature and is $10^{-46} \text{ m}^6 \text{s}^{-1}$.

In the steady state the temperature is $\sim 4000 \text{ K}$ at the centre of the lamp. The atomic (LTE) density is $1 \times 10^{23} \text{ m}^{-3}$ and the association frequency is 1.8 s$^{-1}$. This is extremely slow. Moreover, towards the wall the temperature and atom density decreases and association slows down further. This slow production of vibrational levels is one possible mechanism for the production of extra red. The higher atom density maintained by poor association, can lead to a higher population of the vibrational levels in $S_2(B)$.

Once power is removed the decay of the spectrum is due to vibrational relaxation and three particle association. However, a higher atom density and slow association does not help in explaining the rapid decay of the spectrum. A possible explanation could be that the vibrational levels relax on different timescales; higher levels redistributing more quickly due to the smaller energy gaps.

While molecular non-LTE is a complex subject, both broad and deep, what we have presented here is one possible means to explain deviations and may serve as a starting point for future investigations. Nevertheless, the conclusion remains that the discharge can be described to a very great extent by LTE.

References


Bibliography

[4] Chapter 4 of this thesis


A scaling rule for molecular electronic transition dipole moments: application to asymptotically allowed and forbidden transitions

Guided by the work of Woerdman [1] and Monyakin [2, 3], we propose rules that allow the electronic transition dipole moment for a transition in one molecule to be determined from that of a similar one in an isovalent species. The rule can be applied to asymptotically allowed and forbidden transitions. We have tested it by applying it in two specific cases: the moments for the $A^1\Sigma \rightarrow X^1\Sigma$ and $X^1\Sigma \rightarrow B^1\Pi$ transitions in Na$_2$ are found from those in Li$_2$, which are asymptotically allowed and the moments for the $B \rightarrow X$ transition in O$_2$, Se$_2$ and Te$_2$ which are asymptotically forbidden, are found from moment data for S$_2$. Transition moments calculated with this rule are within 15% of the available literature values and behaviour as a function of internuclear separation is well described.

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Chapter 6: A scaling rule for ETDMs …

6.1 Introduction

The electronic transition dipole moment (ETDM) is an especially important term in the spectroscopy of diatomic molecules as it determines the strength of a particular transition. Detailed knowledge of it can be useful not only in diagnostics but also in discharge modelling where it can be employed in the simulation of spectra as well as the determination of electron impact excitation cross sections. While ETDM data is available in the literature, certainly not all transitions that might be of interest are represented and even then often only over a limited range of internuclear distance.

The ETDM for a particular transition may be found from experiment by the optimized fitting of simulated to measured spectra [4]. However, due to often limited discharge conditions only a small part of the band system is observed. Thus the ETDM is often only recovered for a small range of internuclear separation. On the other hand, the entire ETDM can be found by calculating it \textit{ab initio}, which is however an involved and specialized task. As such, possessing the means to reliably estimate the ETDM before recourse to theoretical or experimental measures can be of great use.

We are currently studying the high pressure sulfur lamp numerically as well as from an experimental point of view [5, 6]. The system is an efficient visible light radiator and produces a seemingly continuous spectrum from 300 to 900 nm. In short, the spectrum can be attributed to radiative transitions between all vibrational levels in the BX system of the sulfur dimer. Thus quanta are produced over the complete range of internuclear distance. This is a situation where full knowledge of the ETDM is required and a rare one where the data is in fact available [7]. However, two other group VI elements, selenium and tellurium, display similar high pressure spectra to the sulfur, also attributable to BX radiation, and we expect to verify and perhaps enhance our understanding of the sulfur lamp by studying these systems. For these dimers ETDM data has only recently appeared in the literature although only over a limited range of separation, centered around the equilibrium separation. So here is a specific case where the full ETDM is needed to describe the physical behaviour of a system but where it is lacking and a semi-empirical approach would be valuable.

To this end we have sought and found two such approaches in the literature. Firstly, there is the direct approach of Woerdman [1] in which the ETDM is determined as a function of internuclear distance using the transition frequency to provide its shape. Furthermore, asymptotic correctness is ensured by establishing the magnitude of the molecular oscillator strength in terms of that of the associated atomic absorption as \( r \to \infty \). A second method, inferred from the work of Monyakin [2, 3], uses the ETDM of a reference transition in one molecule to find that in an isovalent species, that is one with the same number of valence electrons. Here, a radial scaling is performed to allow the mapping between different sized molecules. The former approach is not applicable to asymptotically forbidden transitions while there is no particular objection to this in the Monyakin method.

The article is laid out as follows: we first introduce relevant terms and examine the two empirical approaches. After discussing their efficacy we propose a new scaling rule which uses a reference ETDM to determine that for an identical transition in an isovalent molecule, much like Monyakin’s method but which also ensures asymptotic correctness, the importance of which we learn from Woerdman’s approach. We provide an appropriate
6.2 Empirical methods

As opposed to atomic spectroscopy where the oscillator strength plays a large role, it is the ETDM that is significant in molecular spectroscopy. That this is the case is due to the spatial extent of an electronic state in a molecule which would require the oscillator strength and hence dipole polarizability to be determined as a function of frequency. The ETDM for a transition between two electronic states, $A$ and $B$ is defined as follows

$$M(r) = \langle \psi_A \left| \sum e r_i \right| \psi_B \rangle,$$  
(6.1)

where $r$ is the internuclear distance, $\psi_A$ and $\psi_B$ are the electronic wavefunctions and the moment operator sum extends over all electrons, with the electron position vector given by $r_i$.

6.2.1 Direct approach

The oscillator strength, $f$, for a given transition in a molecule is given in terms of the ETDM, $M(r)$:

$$f(r) = \frac{g_A 8\pi^2 m_e \nu(r)}{g_B 3\hbar} M^2(r),$$

where $m_e$ is the electron mass, $\nu(r)$ is the frequency of the transition and the statistical weights for the upper and lower states are given by $g_A$ and $g_B$ respectively. What Woerdman did was to turn this expression around so that the ETDM depends on the oscillator strength

$$M(r) = \left( \frac{3\hbar^2}{8\pi^2 m_e \nu_{AB}(r) g_A} f(r) \right)^{1/2}. \quad (6.2)$$

Since everything is known once we are in possession of the state potential energy curves the problem becomes one of finding the oscillator strength. If a semi-empirical way can be found to estimate it, the problem is solved. In considering the $X^1\Sigma^+_g \rightarrow A^1\Sigma^+_u$ and the $X^1\Sigma^+_g \rightarrow B^1\Pi_u$ absorptions in the lithium and sodium dimers, Woerdman estimated the asymptotic magnitude of the molecular oscillator strength for these transitions by ensuring asymptotic correctness. The potentials for the states considered are shown in figure 6.1 and as can be seen, both the A and B states share the same asymptote. Woerdman proposed that since either the A or B state could be responsible for the transition at $r \rightarrow 1$, the sum of the molecular oscillator strengths is twice that of the atomic transition

$$f_{X \rightarrow B} + f_{X \rightarrow A} = 2F,$$

where $F$ is the atomic value. Furthermore, he states that as $r \rightarrow \infty$ the molecular wavefunctions are essentially atomic so that the ETDMs should be equal. If that is the
Figure 6.1: Potential energy curves for the \(B^1\Pi_u, A^1\Sigma^+\) and \(X^1\Sigma^+\) states in \(Li_2\) and \(Na_2\).

The results of using these values in equation (6.2) for \(Li_2\) are shown in figure 6.2 along with the literature data for the ETDMs. For both transitions the ETDMs found with equation (6.2) are within 8% of the reference values but for \(Na_2\) Woerdman reports errors up to 30%. The principal reason for the success of this approach is the fact that if the oscillator strength is constant then equation (6.2) demands that \(M^2(r) \times \nu(r)\) is also a constant - a property that the alkali dimers do display. This means that the radial shape of the ETDM is determined solely by the transition frequency. In figure 6.2 we show the ETDM for the AX transition in \(Li_2\) along with the transition frequency. It is immediately clear that the position of the maximum in the ETDM lies at the same position as the minimum in the frequency and we can rely on it to provide the correct shape of the ETDM.

This approach cannot be used for asymptotically forbidden transitions since there is no way we can relate oscillator strength behaviour inside of a molecule that radiates to that in the corresponding atom state that does not. Furthermore, the method has been criticized [9] as not being able to reproduce the local minima and maxima that can be found in the ETDMs of alkali dimers.

### 6.3 Scaling approach

Another method can be drawn from the work of Monyakin. After observing some regularities in the ETDMs of tin halides he proposed a scaling rule, in which the ETDM in
6.4 Asymptotically correct scaling rule

Our stated goal is to arrive at rules for the ETDM that are applicable to asymptotically allowed as well as forbidden transitions. Given the preceding approaches we can follow two paths - the direct or scaling one. The main problem, as mentioned before, with a direct approach is that it is unclear how to proceed when the associated atomic transition is forbidden. We can illustrate this by examining the BX transition in the sulfur dimer. In figure 6.3 we show state potentials and the ETDM for the transition [7] along with the

\[ M^A(r_{00}^A) = M^B(r_{00}^B) \left( \frac{\omega^B}{\omega^A} \right)^{1/2}, \]  

(6.3)

where \( A \) and \( B \) denote the desired and reference transitions, \( \omega_e \) is the vibrational spectroscopic constant for the lower electronic state in the transition and \( r_{00} \) is the r-centroid for the (0,0) vibrational transition.

The latter is the mean radius at which a vibrational transition takes place and is defined as

\[ r_{v'v''} = \frac{\langle \psi_{v'} | r | \psi_{v''} \rangle}{\langle \psi_{v'} | \psi_{v''} \rangle} \]  

(6.4)

where \( \psi \) is the vibrational wavefunction. The rule has been tested extensively but proves too unreliable. Since neither information about the upper state in the transition nor the frequency appear in equation (6.3) its accuracy will be and indeed is hit or miss. Furthermore, it provides the ETDM at one radial position only. Nevertheless, we see how a radius scaling can be achieved via the r-centroid.

### 6.4 Asymptotically correct scaling rule

Our stated goal is to arrive at rules for the ETDM that are applicable to asymptotically allowed as well as forbidden transitions. Given the preceding approaches we can follow two paths - the direct or scaling one. The main problem, as mentioned before, with a direct approach is that it is unclear how to proceed when the associated atomic transition is forbidden. We can illustrate this by examining the BX transition in the sulfur dimer. In figure 6.3 we show state potentials and the ETDM for the transition [7] along with the
Chapter 6: A scaling rule for ETDMs ...

Figure 6.3: On the left the potential energy curves for the B and X states in the sulfur dimer are shown. On the right the ETDM (solid line) and the transition frequency (dashed line) are plotted. The shape of the dipole is not related to that of the transition frequency.

frequency as a function of internuclear distance. The ETDM rises at first from 1 Å to 2 Å but with larger separations it falls to zero. In contrast to the situation in \( \text{Li}_2 \), the frequency does not reflect the radial behaviour of the moment. It could be argued that up to 2 Å a direct approach may work, but beyond this the ETDM falls while \( \nu(r)^{-1} \) rises to reach a plateau at large separations. The trick then would seem to be to find a means of interpolating the ETDM from the maximum to large values of \( r \). Even so we are not certain to be able to identify the maximum, if indeed there is one, from the frequency data. Thus, a direct approach seems unlikely to be fruitful.

In light of this we are forced to choose a scaling approach, which can have distinct advantages. It has been argued before that since the electron distributions in bound atoms are highly localized, it is the valence or bonding electrons that dominate the dipole moment operator. If this is the case, then diatomic species with the same number of valence electrons will have similar moment operators, scaled only for the size difference between systems. Here, a scaling approach, using a reference ETDM may be successful if we can find a suitable radial and magnitude scaling factors. The idea being that if the reference ETDM falls to zero with increasing internuclear separation, we are sure that the desired moment will do the same.

6.4.1 Asymptotically allowed transitions

We will first test this hypothesis by constructing a rule for allowed transitions and test it on \( \text{Li}_2 \) and \( \text{Na}_2 \). Taking the ratio of two ETDMs for a desired transition \( A \) and a reference one \( B \), we have from equation (6.2)

\[
\frac{M^A(r)}{M^B(r')} = \left( \frac{\nu^B(r') f^A}{\nu^A(r) f^B} \right)^{1/2}
\]

(6.5)

where the statistical weights of the upper states in the transition are equal and \( r' = g(r) \) is a radial scaling function which we have yet to define. Thus, the magnitude of the reference
ETDM is modified by the ratio of the frequencies and oscillator strengths and the radial extent is shifted by the function $g(r)$. What this might be follows from Monyakin - using the r-centroid allows a correct comparison between equivalent vibrational transitions and hence radii. Nevertheless, one cannot simply map the r-centroid for each transition from one system to another as it is highly unlikely that both will have the same number of vibrational levels. Furthermore, the effort in calculating a somewhat substantial mapping cannot be justified by the simplicity of equation (6.5). Thus, we choose the simplest mapping possible - between the (0,0) transitions. Thus we find that

$$r' = r \times \frac{r_{B0}^A}{r_{A0}^B}$$  \hspace{1cm} (6.6)

which is intuitively correct. If the reference molecule $B$ is larger than the desired molecule $A$, then the ratio of the r-centroids ensures that the reference ETDM is compressed, and vice-versa. The final problem is that of the oscillator strengths. Since there is already long range information present in the reference ETDM, simply using the atomic oscillator strength values seems reasonable. Thus we arrive at the following rule for asymptotically allowed transitions

$$M^A(r) = M^B(r') \left( \frac{\nu^B(r)}{\nu^A(r')} \frac{F_A}{F_B} \right)^{1/2}.$$  \hspace{1cm} (6.7)

The frequency for each transition is determined from the vertical energy gap between the states.

**Validation**

To test this rule we will determine the ETDM for the $A^1\Sigma \rightarrow X^1\Sigma$ and $X^1\Sigma \rightarrow B^1\Pi$ transitions in Na$_2$ from those in Li$_2$.
Chapter 6: A scaling rule for ETDMs ... 

The dipole moments for both are available in the literature [9] and the radial frequencies are found from the state potentials which we generate using Jhungs universal approach [10]. The atomic oscillator strengths are 0.753 for lithium [11] and 0.982 for sodium [12]. In order to calculate the r-centroid we use the SCHROED program [13] which provides the wavefunctions and employ the integration routines provided by the GNU Scientific Library (GSL). The values can be found in Table 6.1 (a quicker way to find the zeroth r-centroid is to find the halfway point between the equilibrium distances of the two states. This is just as accurate as using equation equation (6.4)).

The results of applying the new rule for finding the sodium moments are shown in figure 6.4. The difference between the literature values and derived ones is less than 10%, more accurate than Woerdman’s approach, and the asymptotes are well described, although there is a slight shift in the peak position.

6.4.2 Asymptotically forbidden transitions

The situation here is less straightforward. There is little we can do to anticipate, in general, what happens inside the molecule when the atomic state does not radiate. Nonetheless, we can rely on the reference ETDM to fall to zero and allow the atomic oscillators strengths to be equal. The radial scaling takes place as before, though now the transition frequencies are solely responsible for the magnitude scaling. Thus the rule for forbidden transitions becomes

\[ M^A(r) = M^B(r') \left( \frac{\nu^B(r')}{\nu^A(r)} \right)^{1/2} \]  

(6.8)

Validation

We now examine the B→X transition for several group VI molecules to demonstrate this rule. The radial frequencies and r-centroids for these molecule were calculated as before and the latter can be found in table 6.1. In figure 6.5 we show the literature values of the transition moment for O₂ [15], S₂ [16] and Te₂ [17]. Also shown are the results of applying equation (6.8) to find the moments for O₂, Se₂ and Te₂ using the S₂ data [7] a reference. The data derived from the sulfur moment gives not only an extremely good value but the radial behavior is very well described. The largest error of 15% is found in

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>( r_{00}[\text{Å}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂</td>
<td>( A^1\Sigma \rightarrow X^1\Sigma )</td>
<td>2.891</td>
</tr>
<tr>
<td>Na₂</td>
<td>&quot;</td>
<td>3.354</td>
</tr>
<tr>
<td>O₂</td>
<td>( B^3\Sigma \rightarrow X^3\Sigma )</td>
<td>1.387</td>
</tr>
<tr>
<td>S₂</td>
<td>&quot;</td>
<td>2.016</td>
</tr>
<tr>
<td>Se₂</td>
<td>&quot;</td>
<td>2.304</td>
</tr>
<tr>
<td>Te₂</td>
<td>&quot;</td>
<td>2.678</td>
</tr>
</tbody>
</table>

Table 6.1: r-centroids for the test species
6.5 Conclusions

In this work we have critically reviewed two existing empirical techniques for the determination of the electronic transition dipole moment or ETDM in diatomic molecules. We have achieved our goal of establishing rules for determining the ETDM for an unknown transition. As a result of examining Woerdman’s and Monyakin’s work we have found that a direct approach, one where only information about the transition of interest is used, is unlikely to work unless one can relate the atomic oscillator strength to that inside the molecule, which is an unlikely prospect. Understanding the importance of establishing asymptotic correctness and recognizing the usefulness of the r-centroid approach as means to scale between systems, we have been able to propose new scaling rules for finding the ETDM. This method requires a reference ETDM for a transition in a molecule that is isovalent to the desired one together with the transition frequency. There are two versions for the rule, one for asymptotically allowed and one for forbidden transitions. We have tested the former by finding ETDMs in Na$_2$ for the AX and BX transitions from those in Li$_2$. The rule for asymptotically forbidden transitions was tested by finding the ETDM for the BX transitions in O$_2$, Se$_2$ and Te$_2$ from that in S$_2$. In all cases the derived Se$_2$ data where it would seem that the radial scaling was not quite sufficient. Nevertheless, the radial shape is well described.

Figure 6.5: Literature values for ETDMs for the BX transitions in O$_2$, Se$_2$ and Te$_2$ are shown (symbols) along with the values derived from the ETDM from the sulfur dimer, taken from figure 6.3, using equation (6.8).
derived values agreed within 15% of the literature values. The strength of the approach
is that we use the reference ETDM to describe that in a species where it is unknown and
use readily available data - the transition frequencies and atomic oscillator strengths to
ensure that the magnitude is correct. Furthermore, the r-centroid scaling we employ is
readily performed. We find the accuracy of the new approach more than sufficient given
its simplicity. Finally, while all examples here treated homonuclear molecules, extension
of the rules to hetero-nuclear species should be possible.

References

242, 253 (1999)
2578 (2002), Chapter 3 of this thesis
(1977)
(1996)
A simple power scaling law is reported between the quadrupole, octupole polarizabilities and the dipole values of neutral atoms which has been deduced from the tabulations of Patil [1]. The values 1.553 and 2.238 are found to relate the dipole to quadrupole and dipole to octupole. The scaling is applied to molecules and proves to be within 20% of literature values.


7.1 Introduction

The accurate treatment of molecular collisions is important in many fields of chemistry and physics. Knowledge of the interactions and especially the corresponding potential is for example critical to modelling of trajectories needed in Monte-Carlo modelling. Furthermore, elastic cross sections can be calculated and subsequently transport properties found. However, the principle issue to be overcome lies not in the description of the potential but in the underlying fundamental data, particularly the polarizabilities. For atoms the dipole, quadrupole and octupole polarizabilities are well known and can be obtained for example from the tables of Patil [1]. However, for molecules this data is decidedly lacking. Thole[2] provided a straightforward means to determine the dipole polarizability of any molecule given the location of atoms in it and their dipole values. So with the tables of atomic values from Patil the dipole polarizabilities of very many molecules can be found [3, 4]. Unfortunately, the approach cannot be applied to higher order polarizabilities. This paper reports a power law scaling we have found between the dipole and higher order polarizabilities found in Patil’s tables. Whether this atomic scaling can be applied to molecules is investigated.

7.2 Scaling in atomic polarizabilities

In figure 7.1, the dipole, quadrupole and octupole polarizabilities of the neutral atoms from Patil[1] are plotted as a function of Z. The peaks and troughs correspond to the alkali metals and the noble gases respectively. The reason is that the sole electron in the outer shell of the former is more easily perturbed in an external field than those in the closed shells of the latter.

In search of a power law relationship between the \( L^{th} \) and first (dipolar) polarizability
7.3 Application to molecules

Table 7.1: Quadrupole polarizabilities, $\alpha_2^S$, for several diatomic molecules found with the simple power law relationship from the dipole values, $\alpha_1$. Literature values are also shown, $\alpha_2^R$ [5, 6, 7]. The agreement with the literature values is remarkable, given the simplicity of the scaling.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\alpha_1$</th>
<th>$\alpha_2^S$</th>
<th>$\alpha_2^R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>8.85(11.57)</td>
<td>50.6(85.6)</td>
<td>80.2</td>
</tr>
<tr>
<td>CO</td>
<td>13.95</td>
<td>100.7</td>
<td>106.9</td>
</tr>
<tr>
<td>HCl</td>
<td>19.3</td>
<td>124.6</td>
<td>117.8</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>33.62</td>
<td>307.9</td>
<td>371.1</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>21.92</td>
<td>243.6</td>
<td>229</td>
</tr>
</tbody>
</table>

we plotted

$$\eta_L = \frac{\ln \alpha_L}{\ln \alpha_1}$$

(7.1)

as a function of Z. The quadrupole and octupole polarizabilities are denoted by $\alpha_2$ and $\alpha_3$. Indeed more or less constant values of $\eta_2$ and $\eta_3$, the scaling from dipole to quadrupole and octupole respectively, were found. The best fit to the data provides the following relationships

$$\alpha_2 = \alpha_1^{1.553}$$

(7.2)

$$\alpha_3 = \alpha_1^{2.238}$$

(7.3)

which works reliably above $Z = 20$. Below this individual relationships are required, rather than the standard 1.553/2.238 powers. For nitrogen, oxygen, carbon and fluorine and chlorine we find 1.8/3.09, 1.75/2.99, 1.77/2.9, 1.78/3.13 and 1.63/2.54 respectively.

7.3 Application to molecules

Data to confirm these scaling relationships for molecules is unfortunately sparse. We have been only able to find quadrupole polarizability data for five molecules; N$_2$, CO, HCl, Cl$_2$[5] and SF$_6$[6, 7] - see table 7.1. None of the atoms in this list obey the scaling (7.2) so it is unlikely that the molecules will also. Thus for the homonuclear species, N$_2$ and Cl$_2$, $\eta_2$ is 1.8 and 1.63 respectively. For the hetero-nuclear species the scaling factor of the atom that is most likely to dominate the polarizability is used. In the case of HCl, the scaling factor of the chlorine atom, $\eta_2 = 1.63$ is used, and the scaling factor of the fluorine atom is employed for SF$_6$.

The literature values for these molecules are shown in table 7.1 with the dipole values and the quadrupole values found using the individual scalings just described. For CO, HCl, Cl$_2$ and SF$_6$ the scaling rule provides the quadrupole polarizability to within 20% of the reference values. For N the dipole value reported by Patil is 5.43 $a_0^3$ while a more accepted value is 7.5 $a_0^3$ [8]. Using the latter value to determine the dipole polarizability of N$_2$ provides a value of $\alpha_2$ of 85.6 $a_0^3$ rather than 50.6 $a_0^3$. 

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7.4 Conclusions

In this paper we have reported the existence of a simple power law scaling between the quadrupole and octupole polarizabilities and the dipole value for atoms. This has been shown to be effective in reproducing the quadrupole polarizability for several diatomic species to within 20%. The simplicity of the method means that it can be used readily and at least in the first instance provides a reasonably reliable first guess value for the higher order polarizabilities of molecules.

References

The model potential of Tang and Toennies [1] is used to determine the Born-Mayer parameters for arbitrary atomic and molecular interactions. Several existing empirical relations are collected in order to calculate the necessary data. The dispersion coefficients for any atom-atom interaction are found from Patil’s tabulations of atomic hyperpolarizabilities [2]. Thole’s modified dipole approach [3] provides a means to determine the dipole polarizability of any molecule and our own scaling law (chapter 7) permits the quadrupole and octupole polarizabilities of any molecule to be found from the dipole value. Together with the empirical expressions of Cambi et al [4] which relate the potential well parameters to the dipole polarizabilities of the colliding pair the repulsive part of the interaction is recovered.

The potential parameters found with this approach are tested by comparing results with literature values for several noble gases interactions and collision integral data for the interactions of nitrogen and oxygen atoms, molecules and ions. In all cases the computed cross sections and collision integrals are within 10% of the literature values.
8.1 Introduction

The transport properties of a dilute (ionized) gas mainly depend on the elastic interactions between the gas particles. In principle the properties of these interactions can be established experimentally; in beam experiments for instance. However, if the objective is to obtain insight into plasma properties as function of their chemical composition an experimental approach is a difficult one. The huge diversity of the plasma state means that the number of interacting pairs that might require treatment is vast. Therefore, a theoretical approach would appear to be more promising. In particular, the ease of use of semi-empirical methods can be attractive, especially so when one is interested in rapid prototyping of plasma transport properties. Currently the common practice is to use a hard sphere model to estimate cross sections when nothing is known about a particular interaction. However, the approximate and temperature independent nature of this cross section is far from realistic. In this chapter we show that there is a readily tractable alternative.

The transport properties of ionized plasmas are the result of the interaction of many different types of species. For example, in a molecular plasma the interactions between molecules, molecules and atoms, charged and neutral species and between charged species can all play important roles. In this chapter we confine ourselves to van der Waals interactions and their description; in chapter 9 the influence of these and other interactions on the transport properties as a whole are discussed.

By and large, most heavy particle collisions, including those between ions and neutrals, are characterized by a van der Waals interaction potential. These are closed-shell interactions, which means that the collision partners neither change their identity nor form a molecule during the collision. In general a van der Waals interaction potential consists of an attractive part and at smaller internuclear distances, a repulsive branch. Under most partially ionized plasma conditions the majority of such interactions are determined by their repulsive nature. This is best described by an exponential function

\[ V(r) = Ae^{-br} \]  

where \( A \) and \( b \) are the so-called Born-Mayer parameters. The only empirical means that we are aware of to find these in an accurate way is via the full van der Waals potential described by the Tang and Toennies [1]. The advantage of using this potential is that there are no fit parameters. For each interacting pair the potential can be constructed using properties of the collision partners solely. These properties turn out to be the polarizabilities and the effective number of electrons of each of the interacting particles. Another advantage of the Tang and Toennies potential is that an algorithm is available to find \( A \) and \( b \) [5] from these fundamental properties. The principal idea is that once the attractive part of the interaction is known accurately, the repulsive part can be found as well. The goal of this chapter is to collect existing empirical formulae that will allow the Born-Mayer parameters to be found for any atomic or molecular interaction via the model potential function of Tang and Toennies.

The chapter is laid out as follows: in section 8.2 some basic definitions are introduced. The Tang and Toennies potential is presented in section 8.3 and the parameters required to recover the repulsive part of the potential are identified. In section 8.4 Cambi’s relations to determine the potential well-depth parameters are presented and their efficacies
are considered. Ultimately, all that is required are the dipole, quadrupole and octupole polarizabilities of the interacting pair and how these are found for atoms and molecules is discussed in section 8.5.

The sensitivity of cross sections to errors in the input parameters is explored in section 8.6. The potential parameters for several noble gases, molecular oxygen and nitrogen potentials are calculated and compared to available literature data. The cross sections and collision integrals that result are also shown as a graphical confirmation of the success of the approach. Finally, section 8.7 is devoted to our conclusions.

8.2 Definitions

For any type of interaction the related transport properties are determined by the collision integral:

\[ \Omega^{(l,s)}(T) = \left( \frac{k_B T}{2 \pi \mu} \right)^{1/2} \int_0^\infty e^{-\gamma^2 \gamma^{2s+3} Q^{(l)}(g)} d\gamma \quad [m^3 s^{-1}] \]  

(8.2)

Here \( \gamma^2 = \mu g^2 / 2k_B T \) is the normalized kinetic energy, associated with relative velocity \( g \) while \( \mu \) is the reduced mass. The \( l^{th} \) moment collision cross section \( Q \) is given

\[ Q^{(l)} = 2 \pi \int_0^\infty (1 - \cos^l \chi) \beta d\beta \quad [m^2] \]  

(8.3)

where \( \beta \) is the impact parameter. Setting \( l = 1 \) yields the diffusion cross section while \( l = 2 \) defines the so-called viscosity cross section. The scattering angle is found from

\[ \chi = \pi - \int_{r_0}^\infty \frac{\beta dr}{r^2 \left[ 1 - \frac{\beta^2}{r^2} - \frac{2V(r)}{\mu g^2} \right]^{1/2}} \]  

(8.4)

where \( r_0 \) the distance of closest approach found from setting the denominator to zero. All that is needed further to determine the scattering angle \( \chi \) is the interaction potential \( V(r) \).

Examination of equation (8.4) reveals the circumstances under which the different parts of the potential play an important role. Only when \( k_B T / V(r) < 1 \) does the attractive part of the potential contribute significantly to scattering. Most interactions give rise to a potential minimum of at most several meV. In plasmas where the heavy particle temperature is 1000 K and above the bound and long range behaviour will therefore be insignificant as compared to the repulsive part. This implies that any model potential we would wish to use needs to accurately and reliably reproduce the short range behaviour.

8.3 Tang and Toennies potential

The Tang and Toennies (T&T) model potential [1] is given by

\[ V(r) = A e^{-br} - \sum_{n=3} \frac{f_{2n}(r)}{r^{2n}} C_{2n} \]  

(8.5)
which is an addition of two terms. The first is an repulsive exponential function the second an attractive part given in the form of a power expansion. The first term is known as the Born-Mayer potential and \( A \) and \( b \) are the so-called Born-Mayer (BM) parameters. The \( C_{2n} \) coefficients in the attractive part are the so-called the dispersion coefficients. The summation in principle extends towards infinity but in practice it can be limited to \( n = 12 \). Moreover, \( C_6, C_8 \) and \( C_{10} \) are the only independent parameters. The higher order coefficients are related to those of lower order by means of a recursive relation \([6]\):

\[
C_{2n+4} = \left( \frac{C_{2n+2}}{C_{2n}} \right)^3 C_{2n-2}.
\] (8.6)

The factors \( f_{2n} \) are damping functions and given by

\[
f_{2n} = 1 - \left( \sum_{k=0}^{2n} \frac{(br)^k}{k!} \right) e^{-br}
\] (8.7)

and only depend on the BM range parameter \( b \). Their function is to turn off the attractive part of the potential at small separations so that the close encounters are determined the repulsive BM part solely.

Details of the algorithm to determine \( A \) and \( b \) from equation (8.5) can be found in \([5]\). The procedure is based on the fact that \( V(r_m) = \epsilon_m \), and that the second derivative of the potential at \( r_m \) is zero. This provides a closed relation between the BM parameters and the potential well parameters. Given the discussion above, there are five essential parameters needed to determine the whole potential. These are the well-depth \( \epsilon_m \), well-depth position \( r_m \) and the dispersion coefficients \( C_6, C_8 \) and \( C_{10} \).

While we now have a method for finding the entire potential for any binary van der Waals interaction in principle, we do not necessarily have the means - the five parameters. Thus in order to be able to present the T&T potential as a universal tool to determine BM parameters, a generic means to determine these parameters is needed. In the next section we will explore the empirical rules and tabulations already available that will allow use to equation (8.5). It will be shown that all parameters can be deduced from the properties of the individual colliding particles. Apart from the (hyper) polarizabilities of the individual atoms the number of effective electrons plays an important role as well.

### 8.4 Potential parameters

#### 8.4.1 Potential minimum: \( r_m \) and \( \epsilon_m \)

Cambi et al \([4]\) have provided empirical rules for the potential parameters \( r_m \) and \( \epsilon_m \) in terms of the dipole polarizabilities and the effective number of electrons of each of the interacting pair. The following formula was provided for the well position

\[
r_m = 1.767 \frac{\alpha_1^{1/3} + \alpha_2^{1/3}}{(\alpha_1^{1/3} \alpha_2^{1/3})^{0.095}} \text{[Å]}.
\] (8.8)

Here, the dipole polarizabilities, \( \alpha_1 \), of the interacting particles \( A \) and \( B \) are in units of \( \text{Å}^3 \). Both numerical coefficients, the factor 1.767 and the exponent 0.095, were found.
by averaging over reference data for several noble gas interactions. Using equation (8.8) the \( r_m \) values for 104 atom-atom, atom-molecule and molecule-molecule pairs have been reproduced to within 7\% or better [4]. Using a similar procedure they provided the following formula for the well depth

\[
\epsilon_m = 0.72 \frac{C_6}{r_m^6} \quad \text{[eV]} \quad (8.9)
\]

However, this rule is less accurate than that for the well position. Cambi reported that this can in some cases lead to errors in the order of 30\%.

### 8.4.2 The dispersion coefficient

Equation (8.9) shows that the well depth depends on the dispersion coefficient \( C_6 \). This in turn is determined by the dipole polarizabilities and the effective electron numbers of the collision partners. To recover the whole potential we still need \( C_8 \) and \( C_{10} \), formulae for which are given in the appendix. Apart from the dipole polarizability and the effective electron number, \( C_8 \) and \( C_{10} \) depend on higher order polarizabilities. The quadrupole polarizability \( \alpha_2 \) is needed to find \( C_8 \) and for \( C_{10} \) we need the octupole polarizability \( \alpha_3 \).

The value of the dispersion parameter \( C_6 \) is given by the Slater-Kirkwood formula

\[
C_6 = 15.7 \frac{\alpha_1^A \alpha_1^B}{\left( \frac{\alpha_1^A}{N_{eff}^A} \right)^{1/2} + \left( \frac{\alpha_1^B}{N_{eff}^B} \right)^{1/2}} \quad \text{[eVÅ]^6]} \quad (8.10)
\]

In the original formulation the \( N_{eff} \) were simply the number of electrons in the outer shell of the atoms. However, it has long been known that the internal structure can cause the atom to behave as if it had more outer shell electrons than actually present.

Cambi et al [4] also took this into account and provided the following formulae for the effective number of outer electrons in atoms

\[
N_{eff} = N_{ext} \left[ 1 + \left( 1 - \frac{N_{ext}}{N_{int}} \right) \left( \frac{N_{int}}{N_{tot}} \right)^2 \right]. \quad (8.11)
\]

Here, \( N_{ext} \) and \( N_{int} \) are the number of valence and inner shell electrons respectively. For molecules the \( N_{eff} \) is

\[
N_{eff} = N_{tot} \left( 1 - \frac{N_b}{N_{tot}} \right) \quad (8.12)
\]

where \( N_b \) is the number of bonding electrons, \( N_{nb} \) the number of non-bonding valence electrons and \( N_{tot} \) is the sum of the two.

### 8.5 Atomic and molecular polarizabilities

In the preceding it was shown that the construction of a T&T interaction potential needs information on the well depth parameters and three dispersion coefficients. Moreover, it was demonstrated that these five parameters can be deduced from the properties of the collision partners. What is needed essentially is the dipole, quadrupole and octupole polarizabilities, \( \alpha_1 \), \( \alpha_2 \) and \( \alpha_3 \). In this section we outline how to determine the polarizabilities. We first address atoms after which the molecules will be dealt with.
8.5.1 Atoms

All the potential parameters required to use equation (8.5) can be found for all atomic collisions with $2 \leq Z \leq 92$. The dipole polarizabilities are available from the tabulations of Patil [2]. Thus the potential parameters for 4186 atomic collisions can be found. The higher order dispersion coefficients, $C_8$ and $C_{10}$, follow from the quadrupole and octupole polarizabilities that Patil also provides.

8.5.2 Molecules

The situation for molecules is more complex. The essentially limitless number means that there can never be a compendium equivalent to that provided by Patil. Here we discuss how to determine the dipole polarizabilities from structural data. Once these are known we apply our own scaling law to find the quadrupole and octupole values.

Dipole polarizabilities

The dipole polarizability describes the response of a charge distribution in an electric field in terms of induced dipole moment

$$\mu = \alpha_1^{\text{mol}} E \quad (8.13)$$

In the first instance, one might think that the dipole moment due to a molecule might simply be the sum of the individual atomic moments

$$\mu = \sum_i (\alpha_1)_i E \quad (8.14)$$

such that the dipole polarizability of the molecule would be given by the sum, $\alpha_1^{\text{mol}} = \sum_i (\alpha_1)_i$, where $i$ runs over all atoms in the molecule. However, this simple addition is questionable since the field inside the molecule will be inhomogeneous due to the disturbance of local (atomic) charge distributions. Thus the simple additive approach is incorrect. Doing so for cyclohexane and Cs$_2$ we would find 15.76 and 130.5 Å$^3$ whereas the true values are 11.06 Å$^3$ and 104 Å$^3$ respectively. So while it may seem that simply adding the atomic polarizabilities gets us in the ‘ball park’, the approach is too unreliable.

Several authors have allowed the atoms in a molecule to interact as point dipoles and built in geometrical data so that

$$\mu_\text{mol} = \sum_i \mu_i = \sum_i (\alpha_1)_i \left[ E - \sum_{i \neq j} T_{ij} \mu_{ij} \right] = \alpha_1^{\text{mol}} E \quad (8.15)$$

where $T_{ij}$ is a dipole-dipole interaction tensor. The molecular polarizability can be salvaged from the atomic polarizabilities and is

$$\alpha_1^{\text{mol}} = \sum_i \sum_j \left[ (\alpha_1)_i + T_{ij} \right]^{-1} \quad (8.16)$$

Thole proposed the following dipole tensor [3]

$$T_{ij} = \frac{4v^3_{pq} - 3v^4_{pq}}{r^3_{pq}} \delta_{pq} - \frac{3v^4_{pq}r_{pq,i}r_{pq,j}}{r^5_{pq}} \quad (8.17)$$
8.6 Validation

Table 8.1: Dipole polarizabilities of several molecular species found with Tholes model, $\alpha_1^T$, compared with literature values, $\alpha_1^R$. All the reference values are from [7].

<table>
<thead>
<tr>
<th>Species</th>
<th>$\alpha_1^T$</th>
<th>$\alpha_1^R$</th>
<th>Species</th>
<th>$\alpha_4^T$</th>
<th>$\alpha_4^R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1.71</td>
<td>1.77</td>
<td>Cs$_2$</td>
<td>103.2</td>
<td>104</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.34</td>
<td>1.57</td>
<td>H$_2$O</td>
<td>1.65</td>
<td>1.49</td>
</tr>
<tr>
<td>CO</td>
<td>2.07</td>
<td>1.95</td>
<td>CO$_2$</td>
<td>2.36</td>
<td>2.63</td>
</tr>
<tr>
<td>NO</td>
<td>1.58</td>
<td>1.74</td>
<td>NH$_3$</td>
<td>2.62</td>
<td>2.22</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>4.98</td>
<td>4.61</td>
<td>CH$_3$OCH$_3$</td>
<td>5.83</td>
<td>5.24</td>
</tr>
<tr>
<td>Na$_2$</td>
<td>37.8</td>
<td>40.0</td>
<td>CH$_4$</td>
<td>2.96</td>
<td>2.64</td>
</tr>
<tr>
<td>K$_2$</td>
<td>61.0</td>
<td>77.0</td>
<td>C$<em>6$H$</em>{12}$</td>
<td>11.86</td>
<td>11.06</td>
</tr>
</tbody>
</table>

where $v$ is a dimensionless parameter which relates the internuclear distance $r_{pq}$ to that of a gauge distance $s_{pq}$. It is defined as $v = r_{pq}/s_{pq}$ if $r_{pq} < s_{pq}$, and $v_{pq} = 1$ otherwise. While there are several definitions, we will use Thole’s original $s_{pq} = 1.662(\alpha_1^R\alpha_1^T)^{1/6}$.

The power of Thole’s approach is that it is readily programmed and once the necessary structural and polarizability data of the constituent atoms is known, the dipole polarizability of any molecule can be found.

The method is tested by finding the polarizabilities of several molecules. The results are given in Table 8.1. The difference between the computed and reference values is in most cases below 20% and is often better.

Molecular hyperpolarizabilities

The procedure sketched above makes it possible to fill the gap created by the severe lack of molecular dipole polarizability data in literature. However, the situation is even worse for higher order values polarizabilities. To solve this problem we have found an interesting correlation between the magnitudes of the atomic polarizabilities in chapter 7 and applied the results to molecules. A simple power law is sufficient to reproduce the quadrupole and octupole polarizabilities, $\alpha_2$ and $\alpha_3$ from the dipole value for all atoms covered by Patil’s tables. Specifically,

$$\alpha_2 = \alpha_1^{1.553} \quad (8.18)$$

$$\alpha_3 = \alpha_1^{2.238} \quad (8.19)$$

which works reliably above $Z = 20$. Below this individual relationships should be established, rather than the standard 1.557/2.238 powers. For nitrogen, oxygen, carbon and chlorine we find 1.8/1.72, 1.75/1.67, 1.77/1.64 and 1.63/1.56 respectively. We have applied these scalings to several molecules and compared the quadrupole values and found the method to be accurate within 20%. 

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Table 8.2: Potential parameters as found from the various approaches outlined here. The terms in brackets are experimental data or have been found from mixture rules [5].

<table>
<thead>
<tr>
<th>System</th>
<th>( \epsilon [\text{meV}] )</th>
<th>( r_m [\text{Å}] )</th>
<th>( C_6 [\text{eVÅ}^6] )</th>
<th>( C_8 [\text{eVÅ}^8] )</th>
<th>( C_{10} [\text{eVÅ}^{10}] )</th>
<th>( A [\text{eV}] )</th>
<th>( b [\text{Å}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne Ne</td>
<td>4.50 (3.66)</td>
<td>3.13 (3.08)</td>
<td>5.93 (4.10)</td>
<td>18.7 (12.53)</td>
<td>71 (51)</td>
<td>2373 (3413)</td>
<td>4.22 (4.46)</td>
</tr>
<tr>
<td>Ne Xe</td>
<td>6.14 (6.19)</td>
<td>3.88 (3.89)</td>
<td>29.38 (26.91)</td>
<td>154.26 (156.96)</td>
<td>880 (1118)</td>
<td>2746 (4725)</td>
<td>3.35 (3.46)</td>
</tr>
<tr>
<td>Ar Ar</td>
<td>11.00 (12.30)</td>
<td>3.73 (3.76)</td>
<td>39.79 (40.12)</td>
<td>201.49 (247.10)</td>
<td>1039 (2009)</td>
<td>4304 (10^4)</td>
<td>3.46 (3.60)</td>
</tr>
<tr>
<td>Kr Kr</td>
<td>15.80 (17.2)</td>
<td>4.02 (4.01)</td>
<td>92.52 (84.72)</td>
<td>565.63 (531.06)</td>
<td>3304 (4215)</td>
<td>5916 (24180)</td>
<td>3.19 (3.57)</td>
</tr>
<tr>
<td>Xe Xe</td>
<td>21.3 (24.3)</td>
<td>4.23 (4.36)</td>
<td>176.26 (202.98)</td>
<td>1300.93 (1736.80)</td>
<td>8861 (17860)</td>
<td>6411 (13,512)</td>
<td>3.00 (3.00)</td>
</tr>
</tbody>
</table>

8.6 Validation

It was shown in the preceding sections how the various properties of the colliding particles leads to the dispersion coefficients and the well-depth parameters of the interaction potential. In particular the important role of the polarizabilities of the interaction partners is evident. However, there are uncertainties in the determination of these. Therefore, the validation of our approach should start with a sensitivity analysis that demonstrates how the uncertainties in the basic parameter works out in that of the potential parameters and collisions integrals. This sensitivity analysis is a substantial undertaking given the number of input parameters and the fact that the collision integral is related to the potential via a triple integral.

Monchick [8] has provided tables for the cross section and collision integral for BM potentials of the form given. Using these, spares us the effort of performing the triple integral in equation (8.2). Furthermore, the analytical relations provided permit a limited sensitivity analysis so that we can concentrate on the influence of the uncertainties in the BM parameters \( A \) and \( b \) on that of the collision integrals. The collision cross section can be shown to be related to the BM parameters:

\[
\sigma \sigma^* \propto \ln\left(\frac{A}{k_B T}\right)^2 b^{-2},
\]

where \( \sigma^* \) is the dimensionless quantity is a measure of the deviation of the actual \( \Omega \) from that related to cross section of the hard sphere. As shown by equation (8.20) the cross section will be quite sensitive to changes in \( b \) whereas the appearance of \( A \) in a logarithm will strongly reduce the influence of any variations in its value. A further analysis is needed to determine the sensitivity of BM parameters to input parameters. If we take the polarizabilities to be exact, and hence the dispersion coefficients, it can be shown that the calculation of \( b \), is
quite insensitive to changes in the potential parameters. On the other hand $A$ can be shown to be exponentially sensitive to changes in $b$:  

$$A(b + \Delta b)/A(b) \propto e^{\Delta br_m} \tag{8.21}$$

Thus, any variation in $b$ appears in an exponent and furthermore is amplified $r_m$, the parameter we can determine with the least accuracy. Nevertheless, the situation is a fortunate one: errors in the parameter that we can determine with the least accuracy, $A$, are strongly damped by its appearance in a logarithm.

From now on, for the lack of a better acronym, we will refer to the set of rules that we have outlined to determine the atomic and molecular polarizabilities and the potential parameters as the CTS (Cambi, Thole, Tang and Toennies, Scaling) approach.

### 8.6.1 Noble gases

We proceed with the validation by employing the CTS approach to the interaction of noble gas atoms. The interaction potentials between these are among the best known and most intensively studied and are a good place to start validating our approach since we can verify not only potential parameters but also cross sections. In Table 8.2 all the potential parameters required found using the CTS approach for several interactions are shown along with experimental values. The potential well parameters are found to be within 2% of the reference values. The results for $C_{10}$ are the least accurate, being generally within a factor two of the actual values. The BM parameter, $b$, is found to within 6% with the CTS approach. As predicted, the value of $A$ deviates the most, being consistently a factor two smaller than experiment provides. However, as we have established as well, this should have a limited influence on the derived quantities.

In figure 8.1 viscosity cross sections as functions of the centre of mass collision energy for several noble gas interactions are shown using the BM parameters given in Table 8.2. Reference data, calculated by partial wave methods [10], are also presented. At very low collision energies (low temperature) the two approaches differ since we exclude the
Table 8.3: Comparison of potentials parameters for several neutral-neutral interactions as found using the rules laid out in this article with data from other sources. The un-bracketed values are the results of the CTS approach applied to the interaction. The quantities in brackets are the literature data. All Born-Mayer parameters are from Cubley and Mason [12] and the other potential parameters are from Brunetti et al [13, 14]. Blank entries indicate that there is no reference data available.

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon$ [meV]</th>
<th>$r_m$ [Å]</th>
<th>$C_6$ [eVÅ$^6$]</th>
<th>$C_8$ [eVÅ$^8$]</th>
<th>$C_{10}$ [eVÅ$^{10}$]</th>
<th>$A$ [eV]</th>
<th>$b$ [Å$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ O$_2$</td>
<td>13.9</td>
<td>3.80</td>
<td>46.64</td>
<td>287</td>
<td>2327</td>
<td>1.77(3)</td>
<td>3.01</td>
</tr>
<tr>
<td>(11.4)</td>
<td>(3.94)</td>
<td>(46.62)</td>
<td>(260)</td>
<td>(1898)</td>
<td>(1.27(3))</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>O$_2$ N$_2$</td>
<td>12.5</td>
<td>3.81</td>
<td>52.78</td>
<td>400.3</td>
<td>4027</td>
<td>1.27(3)</td>
<td>2.98</td>
</tr>
<tr>
<td>(11.1)</td>
<td>(3.63)</td>
<td>(44.02)</td>
<td>(246.3)</td>
<td>(1790)</td>
<td>(912)</td>
<td>(2.86)</td>
<td></td>
</tr>
<tr>
<td>Ar O$_2$</td>
<td>12.4</td>
<td>3.76</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(11.2)</td>
<td>(3.69)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ar N$_2$</td>
<td>10.9</td>
<td>3.77</td>
<td>38.9</td>
<td>227</td>
<td>1608</td>
<td>2.05(3)</td>
<td>3.25</td>
</tr>
<tr>
<td>(10.6)</td>
<td>(3.72)</td>
<td>(39.4)</td>
<td>(237)</td>
<td>(1840)</td>
<td>(2.03(3))</td>
<td>(3.24)</td>
<td></td>
</tr>
<tr>
<td>O O$_2$</td>
<td>9.14</td>
<td>3.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1197</td>
<td>3.17</td>
</tr>
<tr>
<td>(9.23)</td>
<td>(3.38)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(997)</td>
<td>(4.02)</td>
<td></td>
</tr>
<tr>
<td>N N$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>843</td>
<td>3.23</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(891)</td>
<td>(2.83)</td>
<td></td>
</tr>
</tbody>
</table>

influence of the potential well (although the data is found with enough accuracy to allow treatment of the cross section at these temperatures). At energies above 3 eV there are also differences between the results of our method and the reference data. However, one should realized that these energies correspond with temperatures at which most plasmas will almost certainly be fully ionized — van der Waals interaction are no longer important but replaced by Coulomb collisions.

### 8.6.2 Neutral interactions

In Table 8.3 potential data is given for the interactions between the some main constituents of hot air namely oxygen atoms and molecules, nitrogen atoms and molecules and argon atoms.

Both data from literature and the results of the CTS approach are presented. The values for $A$ and $b$ found with our approach agree extremely well with the literature data. All calculated values of $b$ are within 2%, while the $A$ values are consistently within 40% of the experimental values.

As we have demonstrated with the noble gases, such accuracy is more than sufficient to reliably reproduce cross sections. In Figure 8.3 the reduced (1,1) collision integrals for the O$_2$-O$_2$ and O$_2$-N$_2$ interactions are shown with experimental data from Hirschfelder [15] and Cubley and Mason [12]. The works span several decades, the Hirschfelder results being found from diffusion data in the 1950's and the Cubley and Mason integrals were found from beam experiments in the mid '70's. Here we see that the collision integrals
Experimental and CTS values of the viscosities of two organic species. 

The CTS approach is by no means restricted to atomic or diatomic molecular interactions. Any molecule whose geometry is known can be treated. Our ability to determine the dipole polarizability for any molecule via Thole’s method permits this. The CTS approach can therefore be tested further by using the knowledge on transport properties of hydrocarbons. For these substances extensive measurements exist of the thermal conductivity and viscosity. Taking two species at random from the tabulations of Yaws [16], namely cyclohexane and tetramethyleneglycol we have applied the CTS relations to find their viscosities. This can be found easily from the collision integral for a binary mixture

$$\eta(T) = \frac{5k_bT}{8\Omega^{(2,2)}(T)} \tag{8.22}$$

The potential parameters were constructed as prescribed: the dipole polarizabilities were found using Thole’s method (the atomic values taken from Patil’s tables) and the higher order values were found from the scaling rules from equation (8.18).

The well-depth parameters were found using Cambi’s empirical rules and the Born Mayer parameters were recovered using the algorithm from Tang and Toennies. Since the bound nature of the interactions can not be ignored as before, since the characteristic temperatures for cyclohexane and tetramethyleneglycol are 850 K and 2185 K respectively, the BM potential is insufficient. However, all the parameters are available to use the T&T potential. To spare us the calculation of the triple integral in equation (8.2) the potentials were fitted to a Lennard Jones (m,6) potential. The index m was found to be 6.6 and 9 for cyclohexane and tetramethyleneglycol respectively and the collision integral was found from interpolating within existing tabulations [17]. In figure 8.2 the difference between the CTS approach and the reference values from Yaws is no more than 5%.
Figure 8.3: Comparison of reduced collision integrals for $N_2 - N_2$ and $O_2 - O_2$ interactions calculated here with two other sources. The Hirschfelder data was determined from the inversion of mobility data while the collision integrals from Cubley and Mason are found from the potential parameters they determined from beam measurements.

Figure 8.4: Collision integrals for the $N_2$ and $N^+$ interaction. The repulsive integral is shown by the solid line, the literature 'true' value by the dashed. In both cases the CTS approach faithfully reproduces the temperature dependence of the integral.

### 8.6.3 Neutral - ion interactions

While we have concentrated on the interaction of neutral species up to now, ion-neutral collisions can be treated just as easily. Such interactions usually have an appreciable characteristic temperature, in the case of $N_2 - N^+$ it is 1680 K, and the entire potential and not just the repulsive part has to be taken into account. Here we have made use of the 'supplementary' data, $r_m$ and $\epsilon_m$, to determine the collision integrals. In this case a Lennard-Jones potential was used and the collision integral data was found from the tables of Mason [17]. In figure 8.4 the reduced collision integrals for diffusion and viscosity for the interaction of $N_2$ and $N^+$ are shown along with literature data from Stallcop et al [18]. The accuracy and temperature dependence of the calculated values demonstrate
that while we are generally interested in the Born-Mayer parameters, the interaction data found via the various empirical approaches can serve a useful purpose themselves.

8.7 Conclusions

Since the scientific and industrial interest in plasmas containing exotic species will continue to outstrip efforts to either reliably measure or calculate these properties we have decided to assemble such empirical relations that exist to facilitate the accurate calculation of potential parameters for repulsive interactions that are characterized by exponential potential functions.

In this article we have assembled the works of Patil, Cambi and Thole, who have provided respectively tabulations of atomic hyperpolarizabilities from helium to uranium, accurate empirical means for the determination of the potential well parameters and a reliable method to calculate molecular dipole polarizabilities. We have made our own contribution in the form of a power law scaling that relates high order polarizabilities to the dipole value.

The Tang and Tonnies potential, their algorithm to determine the Born-Mayer parameters from the attractive part of the potential and the methods described to find these allow one can generate sufficiently high quality data to abandon the standard parameterized potentials. In this article we have outlined how to use each of the empirical techniques, demonstrated their accuracy and finally compared literature values for the potential parameters, cross sections and collision integrals.

The effectiveness of the CTS approach has been demonstrated, which not only results in reliable, high quality cross section data for atomic and molecular repulsive interactions but also provides accurate parameters for van der Waals potentials. We feel that we have amply demonstrated the approach which can be used with confidence to determine cross sections for previously unknown interactions.

Appendix A — dispersion coefficients

The dispersion coefficients can be written in terms of the polarizabilities of the interacting pair and the effective number of outer shell electrons[9].

The Slater-Kirkwood formula for the $C_6$ dispersion coefficient is

$$C_6^{AB} = 15.7 \frac{\alpha_A \alpha_B}{\left(\frac{\alpha_A}{N_{eff}^A}\right)^{1/2} + \left(\frac{\alpha_B}{N_{eff}^B}\right)^{1/2}} \left[\text{eV} \cdot \text{Å}^6\right]$$

where the interacting atoms have dipole polarizabilities $\alpha_A$, $\alpha_B$ and numbers of effective electrons $N_{eff}^A$ and $N_{eff}^B$. Koutselos and Mason provided formulas for higher-order two-body dispersion coefficients using the same effective numbers of electrons. The dipole-quadrupole coefficient $C_8$ is given by

$$C_8^{AB} = 3.75 \frac{\alpha_A \alpha_B^2}{\left(\frac{\alpha_A}{N_{eff}^A}\right)^{1/2} + \left(\frac{(\alpha_B^2/9N_{eff}^B)}{\alpha_1^2}\right)^{1/4}}$$
\[
+ 3.75 \frac{\alpha_2^A \alpha_1^B}{(\alpha_1^B/N_{eff}^B)^{1/2} + \left[(\alpha_2^A)^2/9N_{eff}^A\alpha_1^A\right]^{1/4}} \text{[eVÅ]}
\]

where \(\alpha_2^A\) and \(\alpha_2^B\) are the quadrupole polarizabilities of the species. The \(C_{10}\) coefficient is given by

\[
C_{10}^{AB} = \frac{\alpha_1^A \alpha_3^B}{(\alpha_1^A/N_{eff}^A)^{1/2} + 0.365 \left[(\alpha_3^B)^4/9N_{eff}^B\alpha_B(\alpha_2^B)^2\right]^{1/4}} + 17.5 \frac{\alpha_2^A \alpha_3^B}{\left[(\alpha_2^A)^2/9N_{eff}^A\alpha_A\right]^{1/4} + \left[(\alpha_3^B)^2/9N_{eff}^B\alpha_B\right]^{1/4}} \text{[eVÅ]}
\]

where \(\alpha_3^A\) and \(\alpha_3^B\) are the octupole polarizabilities of the species.

References


A set of interaction potentials is given which can be used to determine the transport properties of LTE plasma mixtures. These have been chosen since all necessary fundamental data can be generated or are required to determine the composition. The goal is to provide a standardized and automatic procedure for arbitrary plasma mixtures. Charged particle interactions are described by a shielded Coulomb potential, heavy particle interactions are treated with an exponential repulsive or Lennard-Jones potential. Electron neutral collisions are treated with a polarization model and resonant charge transfer is also taken into account. The transport properties found for three well known plasmas - 3 species argon, molecular oxygen and 11 species air - demonstrate that this regularized procedure is not only far superior to a hard spheres approach but also provides a reliable approximation to the accepted reference data.
Chapter 9: Influence of model potentials ...

9.1 Introduction

Accurate knowledge of transport properties is paramount to understanding plasma phenomena and the exploitation of plasma based applications. To be specific one requires information on the viscosity and electrical and thermal conductivities. However, these are particularly difficult to measure under plasma conditions and even if experimental techniques were effective the enormous variety of the plasma state remains a problem. Since the freedom in choosing the chemical composition of a plasma is in effect limitless and as transport properties of any particular plasma depend on the contribution of the binary interactions between all of the particles present, a broad range of conditions would have to be considered. Therefore, we must resort to theoretical approaches in most cases. Fortunately, there are several analytical transport property formulae available of varying levels of sophistication. However, all these transport property formulae require the same basic input, namely a set of collision integral (CI) between all species. These provide the volumetric rates for momentum transfer that determine diffusion or viscosity.

In our group the plasma simulation platform, PLASIMO, has been developed [1, 2, 3]. It provides an integrated environment for the construction and execution of plasma models. PLASIMO has been designed in such a way that the mathematical description of a particular mechanism is divorced from any physico-chemical details. Using a object oriented approach in C++, code re-use is optimized.

PLASIMO has been used to treat many different plasma applications. Models for DC, inductive and microwave power coupling have been constructed and we have experience with several chemistries, such as plasmas in argon [4, 5], mercury [6, 7], hydrogen [8], sodium-iodine [9] and sulfur [10, 11]. Its modular structure and design makes PLASIMO ideal for investigating existing configurations and simulating new applications. However, the lack of fundamental data on elementary interactions, which is a widespread problem, is a serious handicap to the credibility of plasma models. Specifically, it has been found that exclusive use of the hard sphere interaction can lead to non-realistic results. As such an alternative approach is required and that is the principal motivation for this work.

The goal of this chapter is to establish standard interaction models that describe all possible elastic interactions that occur in a plasma. The superset of these interactions can be used to determine the transport properties of LTE plasmas irrespective of their chemical composition. This superset of collision integrals and the means to determine all necessary data results in what we call an automatic procedure — once the plasma composition is specified the transport properties follow.

This is achieved by the classification of all possible interactions and prescribing a priori the means to calculate the CIs. The latter is the most important as the approach must be able to construct the CI for any interaction based solely on the properties of the collision partners. In making the interaction classification we assume the influence of inelastic processes are negligible and we confine ourselves to elastic collisions. Denoting charged particles c and neutrals n (which includes atoms a, and molecules m) leads to the following interactions: c-c, c-n and n-n. The first class, interactions between charged particles, is well understood. Cross sections follow from classical mechanics and the only property required from the collision partners is their charge numbers.

The next grouping, c-n, is subdivided into e-n and i-n. The electron neutral interaction, e-n, can be treated with the classical Langevin model [12]. This solely depends on the
9.1 Introduction

electron charge and the dipole polarizability of the neutral. However, if accuracy is an important issue we need to know the position and strength of the Ramsauer minimum. Therefore, accurate treatment of these collisions is possible only if existing literature covers the interaction or if one has access to experimental or theoretical methods. Although such a case-by-case treatment of interactions is facilitated by PLASIMO, we will confine ourselves to the study of the influence of using simple models for use in the automatic procedure.

Two possibilities arise when treating the interaction of ions and neutrals, i-n. There are collisions where charge transfer takes place and those in which the partners retain their identity. In the first case only the resonant process is considered. The collision partners must have the same matching internal energies so that the interaction is essentially elastic, i.e. the collision between an atom and its parent ion. This is a complex process that can be treated with a classical model which requires only the ionization of the neutral to determine the cross section. The other type of i-n collision can be described by a van der Waals (v/dW) potential. Thus belongs in a certain sense to the final category, n-n interactions. In chapter 8 it was shown that despite the large variety of interactions the generic approach according to Tang and Toennies [14, 15] can be used to great effect. Moreover, we established a means by which all parameters required by the T&T-v/dW potential can be described based solely on the properties of individual collision partners. However, due to the mathematical complexity of using the T&T potential in the CI calculation, we chose to distinguish between two extremes: deep and shallow potentials. The relation between the well depth, $\epsilon_m$, and thermal kinetic energy, $k_B T$, determines the separation between these extremes. Since LTE plasmas usually have high temperatures above 1000 K while above 15000 K are often fully ionized the division between shallow, $\epsilon_m/k_B T \ll 1$, and deep potentials, $\epsilon_m/k_B T \gg 1$, is straightforward. The only deep potentials treated are those between species that form stable association products. However, these association reactions and the corresponding well depths are included in the composition calculation. All the other v/dW interactions are treated with an exponential repulsive function, the so-called Born-Mayer potential.

Finally we should mention that although we primarily have LTE plasmas in mind we can also use the insights of this study to non-LTE conditions; that is conditions for which temperature of the electrons $T_e$ and heavy particle $T_h$ differ from each other while the degree of ionization and dissociation does not obey the distribution laws of Saha and Guldberg-Waage. Basically this means that for the interactions between heavy particles the temperature should be replaced by $T_h$ whereas in the interaction in which an electron is involved the temperature must be replaced by $T_e$. However, one should also realize that under non-LTE conditions the reactive part of heat conductivity can no longer be expressed simply. Instead we have to solve the energy equation of electrons and heavy particles separately. The reactive heat transport has then to be incorporated in the heavy particle energy balance as far as the non-equilibrium state of the association/dissociation balance is concerned.

This chapter is laid out as follows: in section 9.2 basic definitions are presented. Section 9.3 details which model potential is used for each of the four types of elastic collision that can take place in an LTE plasma. In section 9.5, the viscosity, thermal conductivity and electrical conductivities of the three reference plasmas are found with the automatic approach. The results are compared to accepted literature values and those
using hard sphere model exclusively. Finally, conclusions are presented in section 9.6.

9.2 Collision integrals

The kinetic motion of particles in a gas or plasma leads to collisions which are ruled by the impact parameter, the relative velocity of the species and the nature of the force; i.e. the shape of the interaction potential. These determine the magnitude of the deflection caused by the collision. In their turn, the deflections determine the material properties of the gas. For any type of interaction the collision integral is the essential quantity that determines transport property; it is given by

\[
\Omega^{(l,s)}(T) = \left( \frac{k_B T}{2\pi \mu} \right)^{1/2} \int_0^\infty e^{-\gamma^2} \gamma^{2s+3} Q^{(l)}(g) d\gamma \quad [\text{m}^3 \text{s}^{-1}]
\]

(9.1)

where \(\gamma^2 = \mu g^2 / 2k_B T\). The \(l\)th moment collision cross section \(Q\) is given

\[
Q^{(l)} = 2\pi \int_0^\infty (1 - \cos^l \chi) \beta d\beta \quad [\text{m}^2]
\]

(9.2)

where \(\beta\) is the impact parameter. Setting \(l = 1\) yields the diffusion cross section while \(l = 2\) defines the so-called viscosity cross section. The scattering angle is found from

\[
\chi = \pi - \int_{r_0}^\infty \frac{\beta dr}{r^2 \left[ 1 - \frac{r^2}{r_0^2} \frac{2V(r)}{\mu g^2} \right]^{1/2}}
\]

(9.3)

where \(r_0\) is the distance of closest approach. It can be found by setting the denominator equal to zero. All that is needed further to determine the scattering angle \(\chi\) is the interaction potential \(V(r)\).

The interaction potential \(V(r)\) is the basic quantity that determines the cross section which on its turn leads to the collision integral. There are several situations that can arise when the interaction between a particular pair of particles has to be considered. In the most favorable and thus less laborious case, the collision integral itself is available so that nothing further has to be done. This is for instance the case for the interaction between nitrogen and oxygen neutral/ion pairs where Stallcop et al [16] have provided polynomial coefficients for the collision collision integrals.

Somewhat less convenient is the situation in which not the CI but the cross section is known; this only demands for the computation of the integral in equation (9.1). The situation is more difficult when only potential data can be found. It is then required to evaluate the integrals (9.2) and (9.3). However, in the most general case we do not even know the potential. It is the main objective of this study to come to a general procedure in constructing the potential so that based on the properties of collision partners default transport properties can be computed automatically.

9.3 Interactions

This section is devoted to the classification of elastic collisions and to establish which appropriate model potentials are available. More specifically the aim is to determine
procedures that can be used for the construction of model potentials for which the structure parameters only depend on the properties of the collision partners. We follow the classification announced in the introduction and divide the interactions in following main classes: c-c; c-n and n-n. We start with the first class, the interactions between charged particles or Coulomb collisions, after that the charged neutral interactions (c-n) will be dealt with; these will be divided in e-n and i-n collisions. Finally attention will be paid to the Tang and Toennies (T&T) model potential of the van der Waals interaction (i-n and n-n).

### 9.3.1 Coulomb

Treating collisions between charged species is a straightforward task that can be done classically using the Coulomb potential. The divergent nature of the cross section in the binary encounter approximation is overcome by using a screened potential

\[
V(r) = \pm \left[ \phi_0/(r/\rho) \right] e^{-r/\rho}
\]

where \( \rho \) is the Debye length and \( \phi_0 \) is a positive constant. Highly accurate tabulations for the collision integrals are available from Mason et al for repulsive as well as attractive collisions [17]. Resuming we may state that the treatment of Coulomb collisions is straightforward and basically only determined by the charge number of the interacting particle. As a consequence the material properties of fully ionized plasmas can be treated almost exactly.

### 9.3.2 Electron-Neutral

In contrast to the Coulomb collisions we cannot treat electron-neutral interactions in a generic way. There is no classical potential that can be used since one cannot anticipate on the presence, the position or magnitude of the Ramsauer minimum. One possible way to treat them in a general way is to use the polarizability model of Langevin. In that case the potential between the species is an inverse repulsive given by

\[
V(r) = -\frac{\hat{e}^2 \alpha_1}{2r^4}
\]

where \( \hat{e} = e^2/4\pi\varepsilon_0 \) and \( \alpha_1 \) the dipole polarizability of the neutral particle. The collision integral is an analytical expression and temperature independent. It reads

\[
\Omega_{eN}^{(l,s)} = \pi \sqrt{\frac{\hat{e} \alpha_1}{\pi \mu}} \Gamma \left( s + \frac{1}{2} \right) A_4^l
\]

where \( \Gamma \) is the gamma function and \( A_4^l \) a constant [18]. In conclusion we can treat electron neutral collisions in a generic way by using the Langevin cross-section which only needs the dipole polarizability of the heavy particle. The advantage is that the collision integral is analytical and straightforward. The disadvantage is that the result is not very accurate. If accuracy is wanted we have to treat the interaction on a case-to-case basis.
9.3.3 Neutral-Neutral/Neutral-Ion

This last group encompasses the interactions between heavy particles. Since there is a large variety in heavy particles, molecules, atoms and (molecular) ions, several type of interactions are possible.

In the literature several well-established model potentials are used frequently. In many cases adjustment parameters that can be chosen are employed such that shape and magnitude can be adjusted to experimental results. However, in our search towards a direct relation between the properties of the collision partner and the CI it was found that the most universal approach is that given by Tang and Toennies [14, 15]:

\[ V(r) = Ae^{-br} - \sum_{n \geq 3} f_{2n}(r) \frac{C_{2n}}{r^{2n}} \]  

(9.7)

This is clearly an addition of an repulsive branch with exponential behaviour and a attractive part given as a series expansion. The first term, the exponential repulsive (ER) part is known as the Born-Mayer (BM) potential; \( A \) and \( b \) are the so-called Born-Mayer parameters. The coefficients \( C_{2n} \) in the attractive part are the dispersion coefficients. The summation in principle extends towards infinity but in practice it is found to be limited to \( n = 18 \). Moreover, only \( C_6, C_8 \) and \( C_{10} \) are relevant as the coefficients of higher order can be found by means of a recursion relation [19]. The factors \( f_{2n} \) are damping functions. They only depend on the BM range parameter \( b \) and serve to switch of the dispersion part of the potential for small inter-nuclear separations. In this way the close encounters are determined the repulsive BM part solely. The competition between the ER and the attractive ‘dispersion’ part form the potential whose most important features are the well position \( r_m \) and well depth \( \epsilon_m \). The T&T potential describes van der Waals interactions to a very high degree of accuracy and we have shown that all its parameters can be deduced from the properties of the colliding particles [13].

Apart from the (hyper) polarizabilities of the individual species the number of effective electrons plays an important role as well. However, there is an important disadvantage associated to the use of the T&T potential in its general form as given in equation (9.7). Due to the presence of a minimum it is difficult to determine the corresponding collision integrals. A way out of this unfavorable situation is to classify the potentials according to the potential depth \( \epsilon_m \). In the case of \( \epsilon_m/kT \ll 1 \) we confine ourselves to the ER given by

\[ V(r) = Ae^{-br} \]  

(9.8)

In the opposite situation \( \epsilon_m/kT \gg 1 \) we choose to use the Lennard Jones (LJ) model instead. This is given by

\[ V(r) = 4\epsilon_m \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]  

(9.9)

where \( \epsilon_m \) is the potential well depth and \( \sigma \) the internuclear separation which is related to the position of the potential minimum by means of \( r_m = 2^{1/6}\sigma \). The LJ model gives a good description of the potential well but for close encounters the \( 1/r^{12} \) is often found to be too repulsive.

In both cases we can use the procedure as described in [13] so that the BM parameters and those for the LJ potential, \( \sigma \) and \( \epsilon_m \), can be deduced from atomic parameters. The
principal advantages of using these potentials is that we can all the required parameters can be obtained from the set of properties of the collision partners and that the collision integrals have been tabulated for a wide range of temperatures [20, 21]. Thus the triple integral (9.1) does not have to be performed and the appropriate lookup tables are included in PLASIMO.

In conclusion, apart from the resonant charge transfer we can describe the vast class of interactions between heavy particles with the Tang and Tonnies model potential. However, this expression is not easy to handle mathematically so we distinguish two limiting cases: the deep \((\epsilon_m/kT \gg 1)\) and shallow \((\epsilon_m/kT \ll 1)\) potentials. For both cases suitable analytical expressions or tabulations of the corresponding integrals are available.

**Charge Transfer**

This is a special case of ion-neutral interactions. We have the reaction equation \(X^+ + X \leftrightarrow X + X^+\), expressing that an electron is exchanged between identical particles. It is an elastic collision since there is no net change in internal energy and known as resonant charge transfer. The cross section for the process is in many cases larger than that of the corresponding van der Waals like process in which both particles preserve their identity. While it is a complex quantum mechanical process we can use for the resonant charge transfer process the model of Rapp and Francis [22] for which only the ionization energy of the neutral species is required.

**9.3.4 Multi-channel collisions**

A final remark has to be made on multi-channel interactions. For instance the collision of two ground state oxygen atoms can proceed along any one of 18 potentials [23], some of which are attractive-repulsive and others purely repulsive. Ideally, one would determine the statistical weighted average of these single potentials

\[
\left< \Omega^{\ell,s}(T) \right> = \left( \sum_i g_i \right)^{-1} \sum_i g_i \Omega^{\ell,s}_i(T) \tag{9.10}
\]

where \(i\) ranges over the attractive-repulsive and purely repulsive potentials and \(g\) is the electronic degeneracy of the state. However, we cannot treat this situation in a universal manner. Such a multitude of potentials chiefly arise between species that form a chemically bound molecule. In this case we use a one potential approach using the LJ model and set the well depth to the dissociation energy of the molecule. The latter is required in any case needed for the composition calculation.

**9.3.5 Hard sphere**

In literature it is often found that the hard sphere description is selected if insight into potentials is lacking. Although we definitely do not follow this approach we will use it here to highlight our procedure. In the composition examples given in section 9.5 we will show that the hard sphere approach often leads to significant deviations from reference data.
Chapter 9: Influence of model potentials ...

The main advantage of the hard sphere potential is that the collision integral is a straightforward function of temperature [18]

\[
\Omega_{HS}^{(l,s)}(T) = \frac{\pi}{2} (s + 1)! \left[ 1 - \frac{1}{2} \frac{1 + (-1)^l}{1 + l} \right] \sqrt{\frac{k_B T}{2\pi \mu}} \sigma^2 \tag{9.11}
\]

For all interactions we can use the collision diameter \(\sigma\) where the species radii are found from the LJ model and the equation (8.8). For the special case of electron-neutral interactions the neutral radius is used.

9.4 Automatic calculation

As reported in the introduction one of our goals is the automatic calculation of the transport properties of LTE plasmas. Here we highlight the issues surrounding this and address the data requirements of the various models presented in the previous sections.

In order to simulate an LTE plasma one needs to specify the composition and chemical reactions. Individual species information is required. For atoms this means the ionization energy and for molecules the dissociation energy, vibrational constant(s) and its structure. An automatic approach to the transport property calculation of such a mixture cannot rely on external sources of information so we must use what is known — various properties of individual species.

In c-c collisions all that is needed is the charge numbers of the interacting pair, which are trivial parts of the composition specification. For e-n collisions the dipole polarizability of the neutral species is required to use (9.6). If an atom is involved the value is taken from Patil's tables [24]. If the neutral species is a molecule the semi-empirical approach of Thole is used [25]. Here the structure of the molecule and the polarizabilities of the constituent atoms are needed. The latter are again found from Patil and the former is already present in the composition specification to determine the rotational constants of the molecule.

Collisions between species which form association products that appear in the composition are treated with the Lennard-Jones potential. The potential well and position are again taken from the composition specification.

Table 9.1: A list of possible interactions and potentials used for the ‘automatic’ calculation.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>c - c</td>
<td>Coulomb</td>
<td>charge number from composition</td>
</tr>
<tr>
<td>e - n</td>
<td>Langevin</td>
<td>polarizability from Patil[24]/Thole[25]</td>
</tr>
<tr>
<td>n - n (bound)</td>
<td>Lennard-Jones</td>
<td>binding energy from composition</td>
</tr>
<tr>
<td>n - n (unbound)</td>
<td>Exponential Repulsive</td>
<td>Born-Mayer parameters from [13]</td>
</tr>
<tr>
<td>n - i (parent ion)</td>
<td>Rapp-Francis</td>
<td>ionization energy from composition</td>
</tr>
<tr>
<td>n - i (unlike-bound)</td>
<td>Lennard-Jones</td>
<td>potential well parameters from [13]</td>
</tr>
<tr>
<td>n - i (unlike-unbound)</td>
<td>Exponential Repulsive</td>
<td>Born-Mayer parameters from [13]</td>
</tr>
</tbody>
</table>
There are two ways of treating species that form molecules that do not appear in the composition: the potential well depth is calculated from Cambi [26], which requires only the dipole polarizabilities of the interacting pair. In the case where $k_B T/\epsilon_m \ll 1$ the Lennard-Jones potential is employed. If $k_B T/\epsilon_m \gg 1$ the interaction is treated as being purely repulsive. The Born-Mayer parameters for repulsive interactions are found from the Tang and Toennies potential (9.7) using their algorithm [15]. The dispersion coefficients, $C_6$, $C_8$ and $C_{10}$, for which analytical expressions are available [27], require the dipole, quadrupole and octupole polarizabilities of each collision partner. Patil’s tables again provide the data for atoms and when molecules are involved a scaling law can be applied [28] to find the higher order values from the dipole, which are found from Thole’s approach. Finally, resonant charge transfer, calculated from the Rapp and Francis model [22], requires the ionization potential of the neutral species only.

This fixed set of interactions and the required potential data and collision integral lookup tables are included in PLASIMO and form the basis of the automatic approach. A quick summary of the interactions is given in table 9.1.

9.5 Case studies

Now that the interactions have been classified, the model potentials constructed and the collision integrals determined, we will undertake three case studies showing how the various interactions will contribute in the transport properties of the plasma as a whole. Several composition procedures will be discussed which leads to the material properties like the electrical and heat conductivity and the viscosity of the medium. Reference data for argon and oxygen are taken from [29] and from [30] for the 11 species air.

9.5.1 Argon

In figure 9.1(a) the composition of argon at a fixed pressure of 1 bar is shown. The gas is neutral until $10^4$ K when ionization starts to take place. The ionization transition temperature, that is the temperature at which the atom and ion densities are equal, occurs at 15 kK above which the gas is fully ionized. In figures 9.2(a), (c) and (e) the viscosity thermal and electrical conductivity as found from the automatic approach are shown with the literature values.

First considering the viscosity and thermal conductivity, the deviation from the literature value is never more than 20%, save at 12.5 kK in the viscosity. While we treat the collision of an argon atom and ion as proceeding along one potential curve, in reality there are 8 possible potentials. Taking the statistical weighted average of these as in (9.10) one finds a more repulsive interaction and a hence a larger viscosity. The peak in the thermal conductivity at 15 kK is due to ionization and the magnitude of the peak is determined by the resonant charge exchange cross section. In this case the model of Rapp and Francis provides a fine result. At temperatures where the gas is fully ionized, Coulomb interactions dominate and there is no difference between the automatic approach and the reference values.

The polarization model used for the electron-neutral interaction provides a reasonable value for the electrical conductivity above 5000 K, being within 40% of the reference
Figure 9.1: The composition of a 3 species argon, (a); molecular oxygen, (b); and an 11 species air plasma, (c).
Figure 9.2: Figures (a), (c) and (e) show the viscosity, thermal and electrical conductivity of a three species argon mixture. In each case solid lines are the literature values from Murphy [29]. Figures (b), (d) and (f) show the relative deviation of the various approaches from the literature value. Note that the hard sphere approach is in all cases far from reality. HS = Hard Sphere, AA = Automatic Approach.
Chapter 9: Influence of model potentials

Figure 9.3: Figures (a), (c) and (e) show the viscosity, thermal and electrical conductivity of a molecular oxygen plasma. In each case the solid line is the literature value from Murphy [29]. Figures (b), (d) and (f) show the relative deviation of the various approaches from the literature value. Note again that the hard sphere approach is in all cases far from reality. HS = Hard Sphere, AA = Automatic Approach.
Figure 9.4: Figures (a), (c) and (e) show the viscosity, thermal and electrical conductivity of an 11 species air plasma. In each case the solid line is the literature value[30]. Figures (b), (d) and (f) show the relative deviation of the various approaches from the literature value. HS = Hard Sphere, AA = Automatic Approach.
value. However, the temperature independent nature of the collision integral conflicts with the actual behaviour of the interaction. The Ramsauer minimum occurs at 1500 K above which the cross section steadily increases. The polarization model clearly provides a value that is too low around 7000 K and too high below 5000 K. In order to solve this problem one should simply make use of existing literature data for the cross section which in this case is given by Devoto [31]. This is easily added to PLASIMO, but beyond this study. As regards the hard sphere model, we can state that it is substantially less accurate at all temperatures for each of the properties. As one might expect from a temperature independent cross section, there is only one temperature at which it actually reproduces the interaction and for argon this seems to be at \(10^4\) K. For the thermal conductivity and viscosity the difference with the reference value is as much as 100%.

### 9.5.2 Oxygen

While argon presents the challenge of giving a good description of low temperature atomic and high temperature ionizing gas components, oxygen provides an additional challenge. At low temperatures the oxygen atoms are associated so there is a molecular and dissociating component to the material properties. The plasma composition at a fixed pressure of 1 bar is shown as function of temperature in figure 9.1(b). Up to 2500 K the gas is almost entirely molecular. The dissociation transition temperature, that is the temperature at which the molecule and atom densities are equal occurs at 3500 K. In figures 9.3(a), (c) and (e) the viscosity, thermal and electrical conductivities are shown which were found using the automatic approaches together with the reference data.

The viscosity found with the automatic approach is slightly less accurate than was the case for argon. Up to \(10^4\) K the agreement with the literature value is reasonable, to within 25%. The fact that an oxygen atom and ion can interact along 20 different potentials [23] has quite some affect on the transport properties at the ionization transition temperature. Our one potential approach provides a too low viscosity which is reflected also in the thermal conductivity. While the peak at the dissociation transition temperature is well reproduced, demonstrating the effectiveness of the one potential approach for the \(\text{O}_2\)-\(\text{O}\) interaction, the enhancement in the conductivity at the ionization transition temperature is less than the reference value.

The use of the polarization model for the electron neutral interaction results in a reasonable value for the electrical conductivity over a slightly larger temperature range than was found in argon. This is due to the Ramsauer minimum in oxygen being more or less temperature independent up to \(10^4\) K with a value close to the hard sphere cross section. Again the hard sphere approach is substantially less reliable for determining the viscosity and thermal conductivity than our automatic approach.

### 9.5.3 11 species Air

The next step in the scale of increasing difficulty, is that of a mixture of different chemically reacting species. An 11 species air plasma provides such a challenge. In figure 9.1(c) the composition is shown as a function of temperature for a constant pressure of 1 bar. Now there is not only molecular oxygen but also nitrogen. Since the latter dissociates at a higher temperature it will behave as a buffer during the dissociation of \(\text{O}_2\). Due to the
large number of interactions and its proven lack of efficacy we no longer consider the hard
sphere approach. (The density of nitrogen monoxide is too low to be seen in figure 9.1(c)
and is ignored in the transport calculations.)

The viscosity, thermal conductivity and electrical conductivity are shown figures 9.4(a),
(c) and (e) in respectively. There are three peaks in the thermal conductivity now at 3500
K, 7500 K and 15000 K due to the dissociation of O$_2$ and N$_2$ and the ionization of O and
N. The automatic approach is as accurate for this mixture as for argon and oxygen.

However, there is a marked deviation in the viscosity calculation. For the oxygen
plasma at the ionization transition temperature our use of a single potential approach
9.3.3 had its consequences. The calculated viscosities are deviates 75% from the literature
value. This time there are not only O-O$^+$ and N-N$^+$ collisions, both of which can follow
many potentials but the attractive component of the potentials cannot be ignored. The
electrical conductivity is deviates 40% from the literature value above 5000 K.

**9.6 Conclusions**

PLASIMO is a multi-faceted program for the simulation of plasma applications. While it
can be used to investigate the influence of complex phenomena it is ultimately restricted
due to the general lack of interaction data, as are other comparable programs, to plasmas
for which such data is available. This is a widespread problem that will become more
apparent as interest in novel plasmas increases. However, in contrast to the ever increasing
affordability of computing power, experimental facilities are few and cannot be relied upon
to provide required data on elementary interactions.

One aspect of this problem are the cross sections for elastic scattering of various neutral
and charged particles. These are crucial to the simulation of the momentum and energy
balances of LTE plasmas. This paper embraces the results of two previous works that
permit the accurate determination of interparticle potential functions for a wide range of
interactions, based purely on properties of the colliding species. Such an approach is ideal
for the automatic determination cross sections and hence transport properties.

Five temperature regions can be identified in which the transport properties are de-
termined by different types of collision. There are the neutral regions on either side of
the dissociation transition temperature where the symmetric interaction of the species
is important, for instance in molecular oxygen the O$_2$-O$_2$ collision is dominant. At the
dissociation temperature itself the non-symmetric interaction of the molecule and disso-
ciation products play a determining role. Again taking molecular oxygen, the reactive
component of the thermal conductivity is determined by the O$_2$-O interaction. Around
the ionization transition temperature ion neutral collisions are crucial, particularly so
when resonant charge transfer comes into play. Finally, once the temperature is high
enough and the gas is fully ionized Coulomb interactions are dominant and the transport
properties can be found exactly.

In the first four regions we have shown that the thermal conductivity can be found
to within 20% of the reference values for the three test-case plasmas. The viscosity is
less successful, giving deviations of 75%. For electron neutral collisions we have used a
polarizability model which has been shown to be accurate to within 40%.
Appendix A — transport property formulae

While there are several methods available for each of the transport properties, work by others in this field over the last few decades has lead to a more or less standardized use of the available transport property formulae.

The section gives an overview of the various transport property formulae needed to compute the viscosity, thermal and electrical conductivities. The fundamental ingredient in all of these is the collision integral, discussed in section 9.2

A-1.1 Viscosity

The contribution of electrons to viscosity is negligible and as such the total viscosity can be separated

\[ \eta = \eta_h + \eta_e \approx \eta_h \]  

(A.1)

An accepted reliable means to determine the viscosity of a plasma mixture is the Wilke approximation [32, 33]

\begin{align*}
\eta_{\text{mix}} &= \sum_i \frac{x_i^2}{\eta_i} + 1.385 \sum_{k \neq i} x_i x_k \frac{N_{kT}}{p} \\
&= \sum_i \frac{x_i^2}{\eta_i} + 1.385 \sum_{k \neq i} x_i x_k \frac{N_{kT}}{p} \\
&= \sum_i \frac{x_i^2}{\eta_i} + 1.385 \sum_{k \neq i} x_i x_k \frac{N_{kT}}{p}
\end{align*}

(A.2)

where \( x_i \) is the molar fraction and \( \eta_i \) is the viscosity of the \( i \)th species:

\[ \eta = \frac{5k_B T}{8\Omega_{(2,2)}(T)} \]  

(A.3)

Higher order approximations provide little more than a 1% improvement on (A.2).

A-1.2 Thermal Conductivity

The total thermal conductivity can be written as the sum of the several contributions: the translational \( \lambda_t \), the internal \( \lambda_i \), the electronic \( \lambda_e \) and the reactive \( \lambda_r \):

\[ \lambda = \lambda_t + \lambda_i + \lambda_r + \lambda_e \]  

(A.4)

Translational component

The second order translational contribution is given by Muckenfuss and Curtis [34]

\[ \lambda_t = 4 \sum_{i=1}^{\mu} \frac{L_{ij} x_i}{x_j} \]  

(A.5)

The \( L_{ii} \) terms are

\[ L_{ii} = -\frac{4x_i^2}{\lambda_{ii}} - \sum_{k=1}^{\mu} \frac{2x_i x_j \frac{15}{2} m_i^2 + \frac{25}{4} m_i^2 - 3m_i^2 B_{ik} + 4m_i m_k A_{ik}^*}{\lambda_{ij} A_{ik}^* (m_i + m_k)^2} \]  

(A.6)
Here $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$, the ratio between the reduced collision integrals for viscosity and diffusion. The parameter $B^*$ is more complex

$$B^* = \frac{5\Omega^{(1,2)*} - 2\Omega^{(1,1)*}}{\Omega^{(1,1)*}}$$

The off diagonal coefficients, $L_{ij}$, are given by

$$L_{ij} = \frac{2x_ix_j}{k_{ij}} \frac{m_im_j}{(m_i + m_k)^2} A_{ij}^* \left( \frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right)$$

The binary thermal conductivities, $\lambda_{ij}$, are given by

$$\lambda_{ij} = \frac{75}{64}\frac{k_B^2 T}{\mu\Omega^{(2,2)}}$$

The internal contribution can be calculated from the Eucken-like expression from Yos [35]

$$\lambda_i = \sum_s \frac{x_sC_p}{\sum_{j\neq e}(D_{sj})}$$

where $C_p$ is the specific heat of species $s$.

**Reactive contribution**

In a mixture of gases a chemical reaction increases the thermal conductivity. This can be understood by considering the dissociation of a molecule, $A_2 \rightarrow 2A$ which requires a certain amount of energy. In an LTE situation where the system is exposed to a temperature gradient a stationary state will be reached where the molecules diffuse to higher temperature regions where their density is low. They subsequently dissociate by absorbing heat and the atoms so produced then diffuse to the lower temperature regions where they recombine and release the dissociation energy. This is an enhanced chemical heat conductivity. It can only be described analytically under LTE and we use the relations of Butler and Brokaw [36, 37]. Vanden Abeele[41] showed that these relations, originally developed for dissociation balances, can be used equally for ionizing gases.

All reactions that occur in a plasma can be seen as a sequence of $\nu$ independent chemical reactions. Involving $\mu$ species these can be expressed as

$$\sum_{k=1}^{\mu} R_{ik}X^k = 0 \quad i = 1, 2, \ldots \nu$$

where $X^k$ is the $k^{th}$ species and $R_{ik}$ the stoichiometric coefficient of the species $k$ in reaction $i$. Note that even if a species does not take part in any reaction it is still included but its stoichiometric coefficient is zero. In this way the influence of buffer gases and their suppression of reactive peaks in included. The reactive thermal conductivity, $\lambda_r$, is then

$$\lambda_r = \frac{1}{RT^2} \begin{vmatrix} A_{11} & \cdots & A_{1\nu} & \Delta H_1 \\ \vdots & \ddots & \vdots & \vdots \\ A_{\nu1} & \cdots & A_{\nu\nu} & \Delta H_\nu \\ \Delta H_1 & \cdots & \Delta H_\nu & 0 \end{vmatrix}$$

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where $\Delta H_i$ is the enthalpy released in reaction $i$, in kJ mol$^{-1}$. The $A_{ij}$ factors are given by

$$A_{ij} = A_{ji} = \sum_{k=1}^{n-1} \sum_{l=k+1}^{n} \left( \frac{RT}{D_{kl}P} \right) x_k x_l \left( \frac{R_{ik}}{x_k} - \frac{R_{jl}}{x_l} \right) \left( \frac{R_{jk}}{x_k} - \frac{R_{il}}{x_l} \right)$$  

(A.13)

where $R$ is the gas constant. Here $D_{kl}$ is the binary diffusion coefficient between species $k$ and $l$

$$D_{kl} = \frac{3}{16} \frac{k_B T^2}{p m_{kl} \Omega_{kl}^{(1,1)}(T)}$$  

(A.14)

where $p$ and $m_{kl}$ are the pressure and reduced mass of the $kl$ system.

**Electronic contribution**

Devoto's third order expression is used to find the electronic contribution [38]

$$\lambda_e = \frac{75 n_e^2 k_B}{8} \left( \frac{2\pi k_B T}{m_e} \right)^{1/2} \frac{1}{q^{11} - (q^{12})^2 / q^{22}}$$  

(A.15)

The $q$ terms are combinations of collision integrals for electron interactions with all other species and we refer the reader to Devoto for more information.

**A-1.3 Electrical Conductivity**

The second order expression from Devoto for the electrical conductivity is given as [38]

$$\sigma_e = \frac{3 n_e^2 q_e^2}{2k_B T} \left( \frac{2\pi k_B T}{m_e} \right)^{1/2} \frac{1}{q^{00} - (q^{01})^2 / q^{11}}$$  

(A.16)

Again the $q$ terms are combinations of collision integrals.

**A-1.4 Some comments**

All transport formulae are the highest order approximations that are widely used throughout the literature [39, 40, 41]. While we have demonstrated in chapter 8 that the accuracy with which n-n and i-n interactions can be found is high, the same cannot be said for e-n interactions. Here we will discuss some implications of this inaccuracy.

The electronic contribution to the thermal conductivity is only significant when the plasma is substantially ionized. In that case Coulomb collisions will dominate the thermal conductivity and it will be found to a high degree of accuracy. Electrons have no influence on the viscosity and they are ignored in the calculations. However, the electrical conductivity, whose magnitude at low ionization degree will be important for applications using partially ionized gases, is entirely determined by e-n interaction. So any inaccuracy in the e-n interaction will manifest itself. One may wonder why we have chosen to use the highest order relation to determine the electrical conductivity and not just some simple mixing rule. Since the input data may not be of the highest quality the resulting transport property may well reflect this. In PLASIMO the above transport property formulae are implemented and using the most sophisticated model allows individual interactions to be
treated on a case-by-case basis. Thus we may have a situation in which some interactions are well known and others not. Using the ‘best’ approach possible provides the most freedom to improve results if literature data is found and will expose the influence of using a standardized set of collision integrals. The latter case is ideal for testing the robustness of the overall automatic approach.

References


[11] Chapter 4 of this thesis


[13] Chapter 8 of this thesis


[28] *Chapter 7 of this thesis*


CHAPTER 10

General conclusions

This thesis is primarily devoted to a scientific description of the high pressure sulfur plasma. The principal use of this plasma is for lighting purposes. The lamp features a high efficacy and a quasi-continuous distribution that matches the eye sensitivity curve very well.

The main goal of this study is to understand the energy balance from an LTE perspective and verify the resultant picture of the lamp through experiments. A general lack of fundamental data is a large bottleneck to the study of novel plasmas, molecular ones in particular. Therefore, an additional goal of this study is to determine important parameters needed to understand radiation from diatomic molecules and potential parameters needed for the determination of the transport properties of LTE plasma mixtures, all the while concentrating on generality and completeness. The conclusions drawn from this work are listed below:

- More than 99% of the light generated by the high pressure sulfur lamp is molecular in origin and is produced by the $S_2$.

  *Chapters 2 and 4*

- The quantity and distribution of power in the spectrum from the plasma produced by the radiative decay of the vibrational levels in the $B$ state of $S_2$ to the ground $X$ state can by and large be explained with an LTE view of the plasma. There is a discrepancy between reality and the model in the sense that the lamp produces more red and near infra red than can be explained by the LTE model.

  *Chapters 2 and 4*

- The short wavelength behaviour of the spectrum is determined solely by absorption in a thin layer of $S_3$ formed at the inner wall of the bulb.

  *Chapter 4*
• Using spectral lines found in the near infra-red in the spectrum of the lamp, attributable to atomic sulfur, a temperature characteristic of the centre of the bulb has been found. The value of 4100 K determined agrees very well with those found from the LTE modelling of the discharge.

Chapter 3

• The central temperature is ca. 4100 K and the profile is flat. This reveals that the lamp is operating close to the dissociation transition temperature of diatomic sulfur which implies that the heat capacity and heat conductivity of the bulk part of the lamp is very large.

Chapter 4

• The observed slow decay of the spectrum when power is removed confirms the very large heat capacity of the plasma, for which the presence of molecules and dissociation reactions are responsible.

Chapter 5

• The magnitude of the decay and response of the molecular spectrum as a function of wavelength can be reproduced well by an LTE model of the power interruption experiment. Thus, the decay of the lamp during power interruption can be described by the decrease of only one parameter; the temperature. There are deviations; namely the atomic lines decay slower whereas the red part of the molecular spectrum decays faster than according to that of the temperature. Non-LTE considerations that are required to repair the long wavelength deficit found from the LTE simulations are very likely related to the red and near infra red excess of the lamp.

Chapter 5

• Large inelastic losses incurred by electrons in the excitation of vibrational levels in the $B$ state from the ground $X$ prevents any significant difference between electron and heavy particle temperatures.

Chapter 5

• Since the valence electrons in atoms are highly localized the dipole moment operator between two atoms is dominated by these. Using this fact the transition dipole moment (ETDM) for a molecular absorption in one species can be found from that in an isovalent molecule for which the ETDM is well known. The resultant scaling rule is applicable to asymptotically allowed and forbidden transitions.

Chapter 6
A simple power scaling law can be found between the dipole, quadrupole and octupole polarizabilities of atoms. Applying this scaling to molecules and using the model potential of Tang and Toennies the cross sections for van der Waals potentials can be found with the same accuracy as provided by experiment.

Chapters 7 and 8

A new standard set of potentials and collision integrals is proposed. From these the transport properties of LTE plasma mixtures can be found in a general way with a high degree of confidence. All that is required is information needed to specify the plasma composition and the number of valence electrons in each of the particles in the mixture.

Chapters 9
The central topic of this thesis is the high pressure sulfur plasma lamp which is maintained by microwaves. Due to the large densities and the natural ability of the sulfur molecule to radiate strongly, the plasma produces a spectrum which is very favourable for lighting applications. Conversion of electrical energy to visible light is efficient and sulfur is less environmentally damaging than mercury, a common lamp filling. Of particular interest is the manner in which the spectrum is produced — it is entirely molecular in origin. Understanding the sulfur lamp is the first step towards greater insight into molecular plasmas as light sources.

A subsidiary topic is that of fundamental data and the general lack of it. When one wishes to study molecular plasmas in which radiation plays a role there are at the very least three pieces of information required: knowledge on how a molecule radiates, conducts electricity and transports heat. Therefore any means to determine such data is a great asset to the main subject of this thesis and to the plasma community as a whole.

The apparatus required to ignite and maintain a high pressure sulfur discharge must constitute one of the more unusual plasma lamps ever. The bulb is simply a hollow quartz ball that contains several milligrams of sulfur powder and some argon gas. This is placed inside a resonant cavity that is fixed on top of a magnetron, similar to those found in microwave ovens. Furthermore, the bulb is rotated to achieve optimal vapour pressures. Since the only commercial lamp to use sulfur, the Solar 1000, was such a niche product, only the plasma medium is of interest.

The agreement of our LTE models with the observed spectra and reproduction of operational trends coupled with measurement of the central temperatures and response of the spectra to power removal strongly indicates that the system is indeed close to LTE. The picture of the sulfur lamp that emerges is of a molecular plasma where the radiating species density is uniform save at the wall where absorption in a heavier polymer is responsible for the position of the spectral maximum. The temperature is uniform throughout, typically around 4100 K, depending on the pressure and input power. A temperature gradient is only supported towards the wall. S_2 and S^+_2 are the dominant neutral and ion species and the radiation produced by the \( B^3\Sigma_u^- \rightarrow X^3\Sigma_g^- \) transition certainly produces light in the quantities observed. However, it is only when S_3 is included in the composition and UV absorption in it is treated that the short wavelength behaviour of the spectrum and the
position of the spectral maximum can be explained. Indeed only a very thin layer of the polymer, less than a millimeter, is required.

In short, the performance of the sulfur lamp both in the form and efficiency of the spectral output can be explained quite well with an LTE approach. Even the time dependent decay of the spectrum can be reproduced with an LTE model. The only discrepancy between model and experiment is in the description of the spectrum above 800 nm. Since the \( B^3\Sigma_u^- \rightarrow X^3\Sigma_g^- \) transition cannot produce any more radiation in LTE than displayed by the simulations a non-LTE process was suspected. The rapid decay of the spectrum in this range observed in the power interruption experiments indicates that the top of the vibrational state distribution function over the \( B \) state is ruled by a slightly lower excitation temperature than the rest of the system.

Considering fundamental data, scaling laws have proved highly useful. The electronic transition dipole moment for a molecular absorption in one species can be found by scaling that from another similar species. The scaling takes into account the differing spatial extent and energy schemes of the target and reference molecular transitions. With such a tool radiative transitions can be treated without recourse to quantum-chemical calculations.

A scaling law for molecular polarizabilities on the other hand, determined from a scaling observed in atomic values, provides sufficient species data to determine cross sections for elastic collisions for van der Waals potentials. The accuracy of the approach means that collisions between arbitrary atoms, ions and molecules can be found within experimental accuracy. This reliability means that transport coefficients for plasma mixtures can be found in a generic and reliable manner.
Het hoofdonderwerp van dit proefschrift is de hogedruk zwavellamp, die wordt gevoed door microgolven. Door de hoge dichtheid en de natuurlijke eigenschap van het zwavelmolecuul om sterk te stralen, produceert het plasma een spectrum dat zeer voordelig is voor verlichtingstoepassingen. Verder is de omzetting van elektrische energie naar licht efficiënt en is zwavel minder schadelijk voor het milieu dan kwik, wat vaak als lampvulling wordt gebruikt. Bijzonder interessant is de manier waarop het spectrum wordt geproduceerd — het is volledig moleculair van oorsprong. Het begrijpen van de zwavellamp is de eerste stap op weg naar een beter inzicht in moleculaire plasmas als een lichtbron.

Een bijzonderwerp is dat van fundamentele data, of het gebrek daaraan. Wanneer men moleculaire plasmas wil bestuderen, waarin straling een rol speelt, dan zijn er op zijn minst drie gegevens nodig: kennis over hoe een molecuul straalt, over hoe het electriciteit geleidt en over hoe het warmte geleidt. Daarom is een manier om deze gegevens te verkrijgen van groot belang voor het hoofdonderwerp van dit proefschrift en voor de plasmafysica in het algemeen.

De apparatuur die nodig is een hogedruk zwavelontlading te ontsteken en te onderhouden vormt een van de meer ongebruikelijke plasmalampen. De ballon is eenvoudigweg een holle bal van kwarts die gevuld is met een paar milligram zwavelpoeder en wat argongas. Deze wordt geplaatst in een resonante trilholte die aan een magnetron, zoals die in een magnetronoven, bevestigd is. Verder wordt de ballon geroteerd om een optimale dampdruk te verkrijgen. De enige commerziële zwavellamp, de Solar 1000, is zo’n nicheproduct dat alleen het plasmamedium van belang is.

De overeenkomst met onze LTE-modellen met de waargenomen spectra, de reproductie van operationele trends, de metingen van de centrale temperatuur en de respons van de spectra op een onderbreking van het vermogen doen sterk vermoeden dat het systeem inderdaad dichtbij LTE is. Het beeld van de zwavellamp dat ontstaat is van dat van een molecuul plasma waar de dichtheid van de stralende deeltjessoort uniform is, behalve bij de wand, waar absorptie in een zwaarder polymeer verantwoordelijk is voor de positie van het spectrale maximum. De temperatuur is uniform door het gehele plasma, typisch rond 4100 K, afhankelijk van de druk en het vermogen. Er is alleen een temperatuurgradiënt bij de wand. $S_2$ en $S^+_2$ zijn de dominante neutraal- en ionsoorten, en de $B^3Σ_u^- → X^3Σ_g^-$-overgang produceert zeker zoveel licht als waargenomen wordt. Echter, pas wanneer $S_3$
wordt meegenomen in de samenstelling en de UV-absorptie erin wordt behandeld kan het
gedrag van het spectrum voor korte golflengten en de positie van het spectrale maximum
worden verklaard. Slechts een dunne laag polymeer, minder dan een millimeter dik, is
voldoende.

Samengevat kan zowel de vorm van het spectrum als de efficiency van de zwavellamp
verklaard worden in een LTE-beschrijving. Zelfs het tijdsafhankelijke verval van het spec-
trum kan worden gereproduced in een LTE model. De enige discrepantie tussen model
en experiment ligt in de beschrijving van het spectrum boven de 800 nm. Omdat de
\[ B^3\Sigma_u^- \rightarrow X^3\Sigma_g^- \] -overgang niet nog meer straling kan produceren in LTE dan door de sim-
ulaties wordt voorspeld wordt een non-LTE proces verondersteld. Het snelle verval van het
spectrum dat in dit gebied is waargenomen in de vermogensonderbrekingsexperimenten
geeft aan dat de bovenkant van de distributiefunctie over de vibrationele toestanden van
de \( B \)-toestand wordt bepaald door een iets lagere excitatietemperatuur dan de rest van
het systeem.

Voor het verkrijgen van fundamentele data hebben schalingswetten hun nut bewezen.
Het dipoolmoment voor de electronische absorptie-overgang van een deeltje kan gevonden
worden door dat van een ander deeltje te schalen. De schaling houdt rekening met
verschillen tussen de ruimtelijke grootte en het energieschema van het onderzoeksdeeltje
en het referentiedeeltje. Met een dergelijk gereedschap kunnen stralingsovergangen wor-
den behandeld zonder quantumchemische berekeningen. Verder geeft een schalingswet
voor moleculaire polarizeerbaarheden, bepaald aan de hand van een schaling die wordt
waargenomen in atomaire waarden, voldende gegevens over deeltjes om botsingsdoorsne-
den voor Van der Waals-potentiaal te vinden. De nauwkeurigheid van deze aanpak
betekent dat interacties tussen willekeurige atomen, ionen en moleculen bepaald kunnen
worden binnen de experimentele nauwkeurigheid. Deze betrouwbaarheid betekent dat de
transportcoëfficiënten van plasmamengsels gevonden kunnen worden op een algemene en
betrouwbare manier.
Acknowledgements

A thesis is never solely the result of individual effort, particularly so when one is a ‘buitenlander’. First and foremost I must thank Joost van der Mullen for his sometimes enormous efforts on my behalf, encouragement and supervision. As important as an individual project is, a positive and friendly environment in which to work is essential. I would like to thank the following persons in particular for their inestimable contribution to my life and work over the last 7 years (in chronological order): Jan van Dijk, Apocalypse, Ger Janssen, Jeroen Jonkers, Harm van der Heijden, Marco van de Sande, Carole Maurice, Bart Hartgers, Kurt Garloff, Bart Broks, Michiel van den Donker, Iain Houston and Mark Bowden.

Colin Johnston, January 2003

About the author

Colin Johnston was born in county Dublin, Ireland, on the 21st of September 1975. From 1992 to 1996 he studied physics at University College Dublin. After graduating with a Bachelor of Science degree (first class) he began a masters course in technological design at the Stan Ackermans Institute, Eindhoven, in 1997. After completion of the masters in 1999 he worked until 2003 as a doctoral student at the Eindhoven University of Technology in the Equilibrium and Transport in Plasmas group.

Colophon

This thesis was typeset using \LaTeX\ which is based on Donald Knuth’s \TeX\ program. All graphs were produced with Grace\textsuperscript{c}, a 2D plotting tool for the X Window System which is a superior tool for the production of publication quality figures. Contour plots were made using gnuplot\textsuperscript{d} together with Grace. The chapter headings are the Sonny predefined style provided by the FncyChap package written by Ulf A. Lindgren\textsuperscript{e}.

The cover image is a photo of a hollow quartz bulb used in the sulfur lamp. It contains nothing more than a few milligrams of sulfur powder and some argon gas. When rotated in a high power microwave field the discharge produced radiates up to 70% of the input power in the visible part of the electromagnetic spectrum.

\textsuperscript{a}http://www.latex.org
\textsuperscript{b}http://www.tex.org
\textsuperscript{c}http://plasma-gate.weizmann.ac.il/Grace/
\textsuperscript{d}http://www.gnuplot.info
\textsuperscript{e}http://www.ctan.org
Stellingen, behorende bij het proefschrift

Transport and equilibrium in molecular plasmas
the sulfur lamp

Colin William Johnston
1. The operation of the high pressure sulfur lamp can be described to a great extent via LTE.

*Chapters 4 and 5 of this thesis*

2. The short wavelength behaviour and pressure shift in the spectrum are due to absorption in a thin layer of thiozone \((S_3)\) at the bulb wall.

*Chapter 4 of this thesis*

3. The hard sphere description of molecular interactions is no longer the last resort.

*Chapter 8 of this thesis*

4. Despite the trend towards fully quantitative descriptions of physical phenomena, empirical scaling laws remain important tools.

5. Reliance on national stereotypes perpetuates the prejudice of previous generations.

6. In international politics one’s enemies do not necessarily hold opposing beliefs but are rather those who can or will not purchase one’s friendship.

8. The costly access to the judiciary prevents the public truly holding government to account.

9. The most strongly held beliefs are usually someone else’s.

10. The liberalization of public monopolies leads to private ones.