Positron cross sections 
and transport in water

A thesis submitted by

Wade Tattersall BSc(Hons)

in December 2016

for the degree of Doctor of Philosophy

in the Research School of Physics and Engineering

Australian National University

© Copyright WADE TATTERSALL, 2016.
All Rights Reserved
Sources Declaration

I declare that this thesis is my own work and has not been previously submitted in any form for any other degree or diploma at any university or other institute of tertiary education. Information derived from the published and unpublished work of others has been acknowledged in the text and a list of references is given.

_________________________    __________________________
(Author)                     (Date)
Acknowledgements

I am indebted to many people for support and assistance over the course of my PhD studies. I would like to give particular acknowledgement to the people listed below.

I will forever be grateful to my supervisor, Prof. Ronald White, for his unfailing patience and enthusiasm. The opportunities and support that he has offered me over the years have been invaluable.

I would especially like to thank Prof. Stephen Buckman, whose faith in my abilities allowed this JCU/ANU collaboration to exist and continue. His support of my studies, despite the thousands of kilometres that separated us, was always appreciated. Before his retirement, Prof. Robert Robson was also an inspiration, always willing to lend a hand with any intractable problems. Prof. Ian Whittingham, while not my supervisor, has nevertheless been a source of many philosophical discussions about the nature of what it is that we do.

The experimental portion of this thesis was largely facilitated by my academic advisor A/Prof. James Sullivan, and I would like to thank him as well as the students and post-docs who worked with me on the two experiments. Particular thanks are due to Dr. Joshua Machacek, who was invaluable in the preparation of chapter 2, as well as Dr. Luca Chiari, Dr. Casten Makochekanwa and Dr. Daniel Slaughter, who also worked with me closely on the two experiments and figuratively took this theoretician under their experimental wings.

The majority of this thesis, however, is based on Monte Carlo simulations of transport, and in this area, Dr. Daniel Cocks and Dr. Gregory Boyle were my closest colleagues; the reader will note that the majority of my comparisons are with Dr. Boyle’s Boltzmann equation results. Meanwhile, it was Dr. Cocks who helped develop the liquid structure aspects of the simulations, with tireless advice on numerical, computational and broader physical aspects of the problem.

I offer my thanks to my friend Melanie Sutton for her kindness and optimism.

An incredible amount of support, both academic and otherwise, was offered to me by my parents, Glenda and Malcolm Tattersall, and my sister, Katherine Tattersall.

Lastly, I wish to thank the The Centre for Antimatter-Matter Studies, an Australian Research Council Centre of Excellence, as well as James Cook University and the Australian National University for their financial support.
A detailed understanding of the behaviour of positrons and electrons as they pass through liquids is critical for a number of applications, from positron emission tomography and ion therapy to cosmic ray detectors and materials characterisation. In particular, transport in liquid water is vital for medical applications because of its similarity to human tissue, and is an area of continued research. This thesis presents newly measured experimental cross sections for positrons in water as well as several Monte Carlo simulation techniques aimed at improving our models of positron and electron transport. In particular, special efforts have been made to model the effects of elastic coherent scattering, which arise due to the position and velocity correlations between molecules in liquids and other dense media.

The experimental scattering results include the first measurements of integral and differential elastic positron cross sections for water vapour, as well as detailed grand total and positronium formation cross sections for the same. Performed on the positron beamline apparatus at the Australian National University, this transmission experiment passed a high-resolution beam of positrons through a scattering cell containing water vapour. The parallel component of the energy of the positrons after scattering was analysed to determine the ratio between the scattered and unscattered portions of the beam, from which absolute total cross sections were calculated. The experiment further utilised a differentiated magnetic field to separate elastic scattering from the other scattering processes, and to distinguish between scattering angles in order to measure angle-differential cross sections.

An original Monte Carlo track-structure simulation code has been written which aims to precisely model the transport behaviour of electrons and positrons in dilute gases, dense gases and liquids. This simulation incorporates several new features to improve its ability to model systems with high particle loss rates, varying electric fields and fully-differential ionisation interactions. Each feature has been rigorously tested against benchmark systems from the literature and, where necessary, against Boltzmann equation solutions of new benchmark systems. The simulation has also been applied to model elements of the positron trapping apparatus which is a critical component of the positron scattering experiment.

The simulation’s validity has been extended beyond dilute gases by including a treatment of the coherent elastic scattering that is caused by the structure of dense media. Following the theories of Van Hove, Cohen and Lekner, either a static or dynamic structure factor can be combined with gas-phase cross sections to form a modified scattering cross section that partially accounts for the temporal and spatial correlations of nearby molecules.

The benchmarked Monte Carlo simulation techniques are then used to calculate transport profiles for positrons in liquid water, using the measured water cross sections. These profiles are estimates of the spatial distributions of positronium formation and energy deposition,
from the positrons’ emission until their first positronium formation event. Comparisons between simulations employing different cross section sets demonstrate the importance of a complete and accurate set of scattering cross sections for positrons in water.
List of Publications

Lead author


Co-author


<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.2 Collision moments</td>
<td>46</td>
</tr>
<tr>
<td>3.5.3 Time/collision distributions</td>
<td>46</td>
</tr>
<tr>
<td>3.5.4 Collision type evolution</td>
<td>47</td>
</tr>
<tr>
<td>3.5.5 Full track</td>
<td>47</td>
</tr>
<tr>
<td>3.5.6 Final properties</td>
<td>47</td>
</tr>
<tr>
<td>3.5.7 Cut point counts</td>
<td>48</td>
</tr>
<tr>
<td>3.6 Transport coefficients</td>
<td>48</td>
</tr>
<tr>
<td>3.7 Steady-state quantities</td>
<td>50</td>
</tr>
<tr>
<td>3.7.1 Spatially varying</td>
<td>50</td>
</tr>
<tr>
<td>3.7.2 Random time offset sampling technique</td>
<td>51</td>
</tr>
<tr>
<td>3.7.3 Spatial volume scaling</td>
<td>51</td>
</tr>
<tr>
<td>3.7.4 Hydrodynamic regime</td>
<td>53</td>
</tr>
<tr>
<td>3.7.5 Statistical uncertainty</td>
<td>55</td>
</tr>
<tr>
<td>3.8 Benchmarks</td>
<td>58</td>
</tr>
<tr>
<td>3.8.1 Reid’s ramp model</td>
<td>58</td>
</tr>
<tr>
<td>3.8.2 Ionisation energy-sharing models</td>
<td>61</td>
</tr>
<tr>
<td>3.8.3 Attachment model</td>
<td>66</td>
</tr>
<tr>
<td>3.8.4 Other benchmarks</td>
<td>67</td>
</tr>
<tr>
<td>4 Trap simulations</td>
<td>69</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>69</td>
</tr>
<tr>
<td>4.2 Simulation procedure</td>
<td>70</td>
</tr>
<tr>
<td>4.3 Simulation parameters</td>
<td>70</td>
</tr>
<tr>
<td>4.4 Results</td>
<td>71</td>
</tr>
<tr>
<td>4.4.1 Effect of trapping gas density</td>
<td>72</td>
</tr>
<tr>
<td>4.4.2 Effect of initial positron energy distribution</td>
<td>73</td>
</tr>
<tr>
<td>4.4.3 Effect of dump ramp profile</td>
<td>74</td>
</tr>
<tr>
<td>4.4.4 Other variables</td>
<td>75</td>
</tr>
<tr>
<td>4.5 Conclusion</td>
<td>76</td>
</tr>
<tr>
<td>5 Monte Carlo with structure</td>
<td>77</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>77</td>
</tr>
<tr>
<td>5.2 Background and previous models</td>
<td>78</td>
</tr>
<tr>
<td>5.3 Static structure factor</td>
<td>80</td>
</tr>
<tr>
<td>5.3.1 Derivation from Cohen and Lekner transfer rates</td>
<td>80</td>
</tr>
<tr>
<td>5.3.2 Sampling coherent scattering in Monte Carlo simulations</td>
<td>82</td>
</tr>
<tr>
<td>5.3.3 Percus-Yevick model</td>
<td>85</td>
</tr>
<tr>
<td>5.3.4 Step model spatial benchmark</td>
<td>90</td>
</tr>
<tr>
<td>5.3.5 Liquid argon</td>
<td>92</td>
</tr>
<tr>
<td>5.4 Dynamic structure factor</td>
<td>95</td>
</tr>
<tr>
<td>5.4.1 Background</td>
<td>95</td>
</tr>
<tr>
<td>5.4.2 Properties of the dynamic structure factor</td>
<td>96</td>
</tr>
<tr>
<td>5.4.3 Defining the ensemble cross section</td>
<td>97</td>
</tr>
<tr>
<td>5.4.4 Sampling the ensemble cross section</td>
<td>98</td>
</tr>
<tr>
<td>5.4.5 Evaluating the integrals</td>
<td>99</td>
</tr>
<tr>
<td>5.4.6 Ideal thermal gas benchmark</td>
<td>99</td>
</tr>
<tr>
<td>5.4.7 Thermal Percus-Yevick structure benchmark</td>
<td>102</td>
</tr>
<tr>
<td>5.4.8 Conclusions and future work</td>
<td>104</td>
</tr>
</tbody>
</table>
6 Spatial simulations of water

6.1 Introduction .................................................. 105
6.2 Cross sections for positrons in water ............................... 107
  6.2.1 Integral cross-section sets ................................... 107
  6.2.2 Differential cross sections ................................... 110
  6.2.3 Ionisation energy sharing ................................... 110
6.3 Inclusion of coherent elastic scattering in liquid water ........... 112
6.4 Definition of energy deposition .................................... 113
6.5 Simulation parameters .......................................... 115
6.6 Results .................................................................... 116
  6.6.1 The standard simulation ........................................ 116
  6.6.2 Effect of anisotropic scattering ................................ 119
  6.6.3 Effect of ionisation energy sharing ............................ 120
  6.6.4 Impact of coherent elastic scattering from correlated water molecules in the liquid phase .................................. 124
6.7 Concluding remarks ...................................................... 126

7 Conclusion .................................................................. 128

7.1 Summary ..................................................................... 128
7.2 Recommendations for future work ................................. 129

A Code style .................................................................. 146

B Measurement data .................................................... 149
List of Figures

2.1 Render of the beamline used in these measurements, with cut-aways of the relevant sections. From left to right, the four sections (visually delimited by the vacuum pump junctions), are the source stage, the buffer gas trap, the scattering cell, and the retarding potential analyser. The channel plate detector was fitted to the right end of the beamline. This image depicts a CCD camera at that position, but at the time of the experiment, it was replaced with a channel plate electron multiplier. See the text for a brief discussion of each section. ........................................... 14

2.2 RPA 2 data recorded for positron scattering from H$_2$O at a beam energy of 45 eV (orange circles, $M = 5$ only), compared with a Monte Carlo simulation of the same system (blue curve) using the state-of-the-art cross sections listed in chapter 6. The ranges of energy losses applicable to each of the processes are also shown: the labelled ranges correspond to the largest cross sections, while the unlabelled ranges represent the remaining electronic excitation processes. Vibrational and rotational excitations are too small to be distinguished from the elastic range at this scale. Positronium formation manifests as the difference between the detection rate at 0 eV and 1 on the vertical axis. On the right, a higher ratio of magnetic fields can be seen to compress the parallel energy range of scattered positrons. ........................................... 21

2.3 Positron impact H$_2$O GTCS data compared with the literature for experimental GTCS and theoretical ECS results. None of the experimental data are complete total cross sections, as they do not account for positrons scattered in the forward direction. ........................................... 25

2.4 GTCS measured in Experiment 1, with and without an adjustment to account for forward scattering. The adjusted results of Kimura et al. [10] are shown for comparison. ........................................... 26

2.5 Ps formation measured in each of the ANU experiments, compared with the results of Murtagh et al. [11] and the theory of Hervieux et al. [12]. ........................................... 27

2.6 Elastic cross sections, both measured and estimated total, from Experiment 2. Theoretical comparisons are with Baluja et al.’s R-Matrix calculations [13] and García’s IAM-SCAR calculations [2]. Also shown is the synthetic elastic cross section first used in Banković et al. [14]. ........................................... 28

2.7 Measured total inelastic cross section, compared with theoretical positron impact ionisation cross sections from Hervieux et al. [12]. Also shown is an ionisation cross section from Tóth et al. [15], the sum of the excitation cross sections used by Banković et al. [14], and the latter two cross sections summed together. ........................................... 31

2.8 Measured differential quasi-elastic folded cross sections for H$_2$O at 1 eV, 2 eV, 3 eV and 5 eV. Where available, folded R-Matrix [13] and IAM-SCAR [2] theoretical cross sections are shown for comparison. ........................................... 32
2.9 Measured differential quasi-elastic folded cross sections for $\text{H}_2\text{O}$ at 8 eV, 10 eV, 15 eV and 20 eV, measured with the magnetic field ratio set to $M = 5$. Where available, folded R-Matrix [13] and IAM-SCAR [2] theoretical cross sections are shown for comparison. ................................. 33

3.1 Flowchart showing an overview of the simulation procedure. ............ 36
3.2 Flowchart showing scattering procedure. .................................. 38
3.3 Example of analysed data from the “Full Track” output, taken from [7]. See that reference for simulation details. ................................. 48
3.4 Time evolution of a single pulse, where each curve represents a successive time slice. Dashed lines denote slices using the time-offset sampling technique described in section 3.7.2, while solid curves are instantaneous measurements. 52
3.5 The spatial profile of the mean energy of positrons in water, using the liquid water simulation parameters from chapter 6, section 6.5, but varying the number of time slices and the time-offset sampling behaviour as discussed in section 3.7.2. ................................. 52
3.6 Histograms of samples of the particle-average energy at successive times, before and after hydrodynamic equilibrium is reached. A normal distribution is fitted to the latter for comparison. ................................. 54
3.7 Sensitivity test for mean energy and its uncertainty, comparing different time samples and numbers of particles. Inset: zoomed-in view of the same data, showing short-range fluctuations. ................................. 58
3.8 Estimated autocorrelation for each of the models shown in figure 3.7. See that figure for the legend. Each successive autocorrelation has been offset by 1 for clarity. ................................. 59
3.9 Thermalisation of the mean energy versus time for $E/n_0 = 24\ \text{Td}$ for the Reid’s ramp model, defined in equation (3.14). Inset: comparison of mean and standard error of the present results (red, and light red respectively), with the results of each of the alternative studies. ................................. 60

4.1 Comparison between experiment and simulation (a) pulse time profiles and (b) energy cutoffs. All simulation parameters are equal to those known for the experiment. Total gas pressure is 1.1 mTorr, ramping profile is logarithmic, starting at $-4\ \text{V}$ and increasing to 62 V. The final potential wall is set to 61 V. Positrons are initially thermalised to 300 K. There is presently no convenient way to synchronise the experiment output with the trapping cycle, so the time between the start of the dumping phase and the start of the pulse is unknown. In figure (a), the time of the peak of the experimental pulse has been arbitrarily set to be the same as that of the simulated pulse. Figure (b) does not suffer from this problem. ................................. 72
4.2 Comparison between different gas pressures for (a) pulse time profiles and (b) energy cutoffs. Total gas pressures are $1\times$, $100\times$, $200\times$ those used in the experiment. All other parameters are as in figure 4.1. ................................. 73
4.3 Comparison between the pulses produced with different initial temperatures for (a) pulse time profiles and (b) energy cutoffs. In each case, the temperature is that of the Boltzmann distribution of velocities of the positrons before the dumping begins. All other parameters are as in figure 4.1. ................................. 74
4.4 Ramp functions for the dumping electrode for the three cases compared in section 4.4.3. ................................. 75
4.5 Comparison between the results of different ramping functions for (a) pulse time profiles and (b) energy cutoffs. Ramping functions are as described in section 4.4.3, no gas was included, and all other parameters are as in figure 4.1. 75
5.1 Flowchart detailing how electric fields and coherent elastic scattering are implemented in the present code. This figure was originally published in [3], but applies to all static structure simulations. .................................................. 83
5.2 Schematic diagram of the various elastic cross-sections used in simulating a Percus-Yevick liquid (φ = 0.4). All quantities are given relative to the elastic cross-section for a single particle. Note that the $\sigma_{\text{tot}} \geq \sigma_{\text{sp}}$. ............................................. 84
5.3 Angle integrated Percus-Yevick structure factors, from equations (5.6) and (5.5), as a function of collision energy and volume fraction. ................................. 86
5.4 Mean energy $\bar{\epsilon}$, drift velocity $W$, and diffusion coefficients $D_L$ and $D_T$ for Percus-Yevick model simulations, as a function of reduced electric field $E/n_0$ and Percus-Yevick packing ratio $\phi$. Error bars are not visible at this scale. Circles (and for $D_T$, diamonds) are the present Monte Carlo results, and lines are Boltzmann equation solutions by White and Robson [16]. .................................................. 87
5.5 Ratio of diffusion coefficients as a function of reduced electric field strength $E/n_0$ and packing ratio $\phi$. Note that the ratio for $\phi \sim 0$ is 0.5 as required. . 88
5.6 Mean energy $\bar{\epsilon}$ and longitudinal diffusion $D_L$ percentage difference for each Monte Carlo model versus the Boltzmann equation (BE) model, for the Percus-Yevick structure factor at $\phi = 0.4$. ................................. 89
5.7 Spatial variation of the average energy (A) and velocity (B) under steady state Townsend conditions for the step model described in section 5.3.4 for various Percus-Yevick volume fractions $\Phi$. The dashed lines are results of the present Monte Carlo simulation, while the solid lines are solutions of a Boltzmann equation. Reproduced with permission from [9]. ................................. 91
5.8 Differential cross sections for electrons in argon from [17], with and without a screening correction. The cross sections are symmetric about the horizontal axis, since the choice of $\psi$ is isotropic in a liquid with no preferred molecular alignment. .................................................. 93
5.9 Static structure factor for liquid argon, integrated as per equation 5.9. The dilute gas structure is independent of the cross sections, as $\Gamma(\epsilon) = S(\Delta k) = 1$. The other three cross sections are the two anisotropic cross sections shown in figure 5.8, and an arbitrary isotropic cross section: $\Gamma(\epsilon)$ is independent of $\sigma_{el}(\epsilon)$ if the latter has no $\chi$ dependence (it reduces to equation (5.5)). . 94
5.10 Single-slice time snapshots of the spatial distribution of the number of electrons at three successive times, $t^* = 1, 10, 100$, for simulations with no structure factor or screening correction ("gas"), with a structure factor but no screening correction ("gas-coh"), and with both a structure factor and screening correction (liquid-coh). Time and space measures are scaled as per equation (5.7). Note that the three curves in the first snapshot coincide. . 96
5.11 Hard sphere total elastic cross section, with and without the inclusion of thermal effects via the ideal gas structure factor. The energy distribution of the neutrals is shown for comparison. .................................................. 101
5.12 Mean energy at hydrodynamic equilibrium $\epsilon$, as a function of reduced electric field $E/n_0$, for thermal Dilute Gas Hard Sphere and Maxwell models. The solid lines represent Boltzmann equation solutions by Boyle (unpublished), which also include solutions for $T = 0$ (straight lines). The uncertainty in the Monte Carlo results is not visible at this scale. .................................................. 102
5.13 Mean energy at hydrodynamic equilibrium $\epsilon$, as a function of reduced electric field $E/n_0$, for thermal Dilute Gas Hard Sphere and Percus-Yevick models. The solid lines represent Boltzmann equation solutions by Boyle (unpublished), including the $T = 0$ cases (darker lines). ................................. 103
6.1 The set of integral cross sections used in the present simulations. This is the set referred to in previous works [7, 14, 18], except that the elastic cross section is that shown in chapter 2, and all triplet excited states have been removed. Details are provided in the text. Uncertainties in the data are given in the original sources, but cannot be included in the present simulations. 107

6.2 Comparison of the integral elastic and grand total cross sections that are available for positrons in gas-phase H$_2$O. The Set B elastic cross section is used in the present simulations. See text for more details. . . . . . . . . . . 108

6.3 Comparison between the two available theoretical elastic differential cross sections: IAM-SCAR [2] and R-Matrix [13]. Experimental values [2] are plotted as circles, using the same colour scale. The dashed white lines denote the energies for which the DCSs have been explicitly calculated, while intermediate values use a linear interpolation. The angular resolution of the theoretical DCSs is 1°. . . . . . . . . . . . . . . . . . . . . . . . 111

6.4 Ionisation energy sharing distributions for positrons in water. Each line corresponds to one of the energy sharing ratios that can be sampled by the Monte Carlo simulation. For the H$_2$ and H$_2$O models, each line represents an energy-sharing ratio sampled with equal probability for any ionisation event with an initial positron energy of 60 eV. . . . . . . . . . . . . . . . . . . . . . . . 113

6.5 Angle-integrated static structure factor for liquid water, derived from the static structure measured by Badyal _et al._ [19] and calculated using equation (5.9). The lines correspond to calculations for both of the theoretical differential elastic cross section sets discussed in section 6.2.2, as well as for isotropic scattering. . . . . . . . . . . . . . . . . . . . . . . . 114

6.6 Steady-state linear density of positrons as a function of the radial distance from the source, using the standard simulation parameters. This is normalised to an emission rate of 1 Hz. As the lifetime of the positrons is very small, so too is the resulting density. . . . . . . . . . . . . . . . . . . . . . . . 117

6.7 Stacked line chart showing spatial profiles of the rate of energy deposition for the standard simulation parameters. Note that “Ionisation e-” represents the initial energy of the emitted electrons, while all other depositions are at the locations of the interaction events. Total energy deposition is included in parentheses in the figure legend. Energy deposition due to elastic and vibrational excitation collisions is not visible at this scale. . . . . . . . . . . 118

6.8 Stacked line chart showing the spatial profiles of the rates of collisions for each type of interaction, for the standard simulation parameters. Total collision rates (integrated over all distances) are shown in parentheses in the legend. . . . . . . . . . . . . . . . . . . . . . . . 119

6.9 Comparison of the fraction of positrons that undergo positronium formation at least once, for each of the variations of the standard parameters. The standard parameter set is red, while green represents variation in the ionisation energy sharing behaviour and cyan represents variants of the anisotropy for scattering events. The fraction reported here is not representative of the total Ps annihilation rate that would be obtained in experimental conditions, as it neglects break-up of the Ps atom. . . . . . . . . . . . . . . . . . . . . . . . 120

6.10 Steady-state positron number distributions, as a function of positron energy and distance from source. This is measured over an energy space of equal divisions, such that $\rho(r) = \int \rho(r, \epsilon) \, d\epsilon$ gives the total number of positrons as shown in figure 6.6. The simulations use the standard parameters listed in section 6.6.1, except that different differential cross sections, as listed in section 6.2.2, are used for both elastic and inelastic scattering. . . . . . . . . . . 121
6.11 Positronium formation rate as a function of the radial distance from the source. The results are presented for the different cross-section anisotropies. 122

6.12 Steady-state positron number distributions, similar to figure 6.10. The variants employ different distributions of post-collision energy sharing in ionisation events, as described in section 6.2.3. 122

6.13 Steady-state number distributions of the secondary electrons emitted in ionisation events, as a function of initial electron energy and distance from source. Note that this only includes electrons when they are first emitted. The simulations use the standard parameters listed in section 6.6.1, but with variations of the post-collision energy sharing in ionisation events according to the models listed in section 6.2.3. A precise definition of $N_I(r, \epsilon_{e^-})$ is given in section 3.7.3. 123

6.14 The rate of ionisation events for positrons in H$_2$O, as a function of the distance from the positron source. The effects of several ionisation energy sharing models are compared. 124

6.15 Spatial distribution of the positronium formation rate for each of the ionisation models. 125

6.16 Steady-state positron number distributions, similar to figure 6.10, but comparing the correlated (liquid) and uncorrelated (gas-like, but with liquid density) systems. 125
1 Introduction

1.1 Motivation and aims

An understanding of how electrons and positrons travel through their surroundings is critically important in many modern scientific applications. From photoelectric solar power to particle detectors, electron transport through gases, liquids and solids is ubiquitous in modern life. Positrons, while less common, are used in several medical applications as well as materials science characterisation techniques, in both cases exploiting their ability to annihilate with electrons and produce gamma rays that can be detected to establish their former position and thus provide information about their environment. For all of these applications, interpretation of the results require an accurate understanding of the behaviour of the particles as they travel through the medium, including how quickly they travel (mobility), how much they disperse while doing so (diffusion), and where and how much energy is deposited into the medium (dosimetry).

To fully develop these technologies, it is desirable to develop transport models that can predict their behaviour \textit{a priori}, and in doing so, explore a much larger parameter space than empirical experiments could hope to achieve. In practice, predicting the full collision dynamics of even a single electron or positron with a single water molecule from first principles is already impractical. One compromise is to treat the transport of electrons and positrons as classical Newtonian motion interrupted by instantaneous, binary collision events. With this approximation, it is possible to study these collision events in isolation, which is a large part of the motivation behind scattering theory and experimentation as a field of study. Some types of collision events may be theoretically derived from quantum mechanical scattering theory, while others are so far only known empirically through experiment. In general, they are quantified as cross sections, analogous to a classical cross
sectional area, and measure the probability of an electron or positron interacting with a target atom or molecule.

Meanwhile, while the Newtonian motion of the particle between collisions is elementary, the emergent behaviours when combined with collision events are often complex and difficult to compute directly. Monte Carlo simulations are often used to model the transport of particles as they diffuse through a material. Compared to direct solutions of the Boltzmann equation [20], they offer significant advantages in flexibility, particularly for unusual geometries or interfaces. This thesis presents an original Monte Carlo simulation which employs a number of features that have previously not been reported in the literature. This simulation code can be used to predict arbitrary macroscopic properties of a broad variety of charged-particle transport systems, provided that sufficient, accurate cross section data are available.

1.2 Electron and positron scattering processes

When an electron or positron interacts with a single atom or molecule, a number of interactions are possible [21], depending on the energy of the event and the initial state of the molecule. In general, positron and electron collision processes can be classified as one of the following:

\[
\begin{align*}
\text{e}^\pm + \text{AB}(\nu, J) & \rightarrow \text{e}^\pm + \text{AB} & \text{Elastic} \\
& \rightarrow \text{e}^\pm + \text{AB} (\nu', J') & \text{Rotational excitation} \\
& \rightarrow \text{e}^\pm + \text{AB} (\nu, J) & \text{Vibrational excitation} \\
& \rightarrow \text{e}^\pm + \text{A} + \text{B} & \text{Dissociation} \\
& \rightarrow \text{e}^\pm + \text{AB}^* & \text{Electronic excitation} \\
& \rightarrow \text{e}^\pm + \text{AB}^+ + \text{e}^- & \text{Direct ionisation} \\
\text{e}^- (\uparrow) + \text{AB} & \rightarrow \text{AB}^- & \text{Electron capture ionisation} \\
& \rightarrow \text{e}^- (\downarrow) + \text{AB}^* & \text{Spin exchange} \\
\text{e}^+ + \text{AB} & \rightarrow 2\gamma + \text{AB}^+ & \text{Annihilation} \\
& \rightarrow \text{Ps} + \text{AB}^+ & \text{Positronium formation}
\end{align*}
\]

In the above, e\(^+\), e\(^-\) and e\(\pm\) represent positrons, electrons and either particle, respectively. AB represents a molecular scattering target, \(\nu\) and \(J\) represents the vibrational and rotational states of AB (omitted when they are unchanged), \(\uparrow\) and \(\downarrow\) represent spin, and \(\ast\) indicates an electronically excited state.

Most of the above classifications are easily defined. Elastic collisions are distinguished by being the only interaction type that does not affect the internal state of the target molecule. Rotational and vibrational excitations (collectively known as ro-vibrational excitation, present only for molecules) change the corresponding quantum numbers in the molecule, adding or removing energy to the bonds between the component atoms. Dissociation breaks the molecule up into multiple separate components. Electronic excitation occurs when the electrons bound to an atom or molecule are given enough energy to enter a higher energy orbital. Direct ionisation occurs when the incoming positron or electron knocks off one of
the target’s electrons, which is ejected separately. For incoming electrons, it is also possible to have electron capture (negative ion formation), where the incoming electron becomes bound to the target, although this requires a third body to conserve momentum. Incoming electrons may also exchange with an electron that is bound to the molecule, a process which may also involve a spin exchange and a small exchange of energy. Finally, it is worth noting that if the target is initially in an excited state (electronic or ro-vibrational), there can be a “de-excitation” event, where the molecule returns to a lower energy state and the excess energy is returned to the positron or electron. The rate of excitation and de-excitation events must satisfy the principle of detailed balance [22], which states that the rates of excitation and de-excitation must be balanced in a system at thermal equilibrium.

Positron scattering in matter has two additional channels [23]. For most applications, the most interesting interaction occurs when an incoming positron strips an electron from the target and immediately forms a weakly bound state called positronium (Ps). This exotic atom comes in two varieties. The singlet state, where the positron and electron have anti-parallel spins, is called para-positronium (p-Ps). It has a short lifetime of $1.244 \times 10^{-10}$ s in a vacuum, and self-annihilates into an even number of gamma rays, usually two rays that have an energy of 511 keV each. The gamma rays must propagate in (nearly) opposite directions so that total momentum is conserved. This means that it is possible to determine the location of the event by detecting each gamma ray, and tracing them back to the site of the event. This property is exploited for positron emission tomography, discussed below. The triplet state, where the positron and the electron have parallel spins, is known as ortho-positronium (o-Ps). This has a lifetime of $1.42 \times 10^{-7}$ s in a vacuum, and its dominant decay path is into three gamma rays. As with para-positronium, the energy of the resultant gamma rays is equal to the sum of the mass and binding energies of the positronium.

Positronium of either variety has a binding energy of $6.8 \text{ eV}$, which means that it can occur even when the incoming positron is too slow to ionise the molecule directly. Consequently, the threshold energy for positronium formation is equal to that of direct ionisation minus $6.8 \text{ eV}$. The positronium may continue to interact with the medium, including all of the usual processes such as elastic and excitation collisions, as well as additional processes such as Ps dissociation (Ps → $e^+ + e^-$) or Ps spin conversion (o-Ps ↔ p-Ps).

Finally, direct annihilation between a positron and a bound or free electron can occur, but only at very low energies (on the order of $\{\text{meV}\}$), and even then, the cross section is very low. Nevertheless, if a positron reaches an energy below the threshold of positronium formation, it will eventually undergo direct annihilation which, like positronium, results in an ionised molecule as well as two or more gamma rays.

Most of these interactions can occur for atomic targets as well; the exceptions are ro-vibrational excitation and dissociation interactions.
1.3 Applications

1.3.1 Positron emission tomography

Positron emission tomography (PET) is a functional medical imaging technique that has been adopted in hospitals around the world, where it is a non-invasive diagnostic tool for humans and animals [24]. In this procedure, a short-lived positron-emitting isotope is chemically bound to a biologically-significant substance and injected into the patient. The eventual annihilation of the positrons can be tracked in real-time by gamma ray detectors, which can be used to show the distribution and uptake of the substance throughout the body. It therefore provides a uniquely functional, rather than structural, view of the target.

Most biological substrates and drugs can be modified to serve as a radioactive tracer. Such compounds are formed by replacing an atom in the original molecule with an unstable positron emitting radioisotope. Common radioisotopes include $^{18}$F, $^{13}$N, $^{82}$Rb and $^{15}$O, although others are also used. The most common biological target is glucose, which is transformed into fluorodeoxyglucose (FDG) when fluorine-18 is substituted in the place of one of the hydroxyl groups in the glucose molecule. The tagged compound continuously emits positrons and neutrinos through $\beta^+$ decay, at a rate commensurate with the half-life of the radioisotope. Each emitted positron then scatters repeatedly off molecules in the medium until it loses enough energy to undergo positronium formation or direct annihilation. The gamma rays emitted from such an event are detected by scintillators and photo-multiplier tubes in the scanning device, and image reconstruction software can use this information to identify the most common positron annihilation sites.

Due to the variety of biologically active substances which can be traced and the general utility of being able to trace the diffusion and accumulation of a substance throughout the body, there are many medical applications:

- In oncology, FDG can be used to locate cancer tumours, which consume more glucose than most other parts of the body. This is the most common clinical use for PET.

- In neurology, the radioactive tracer can be $^{15}$O that is delivered to areas of high blood flow in the brain, which is believed to correlate with brain activity. More recently, other radiopharmaceuticals such as $[^{18}$F]FDDNP [25] have been used to visualise amyloid plaques in Alzheimer’s patients.

- Some forms of vascular disease such as atherosclerosis can be imaged with $^{18}$FDG, $^{82}$Rb (used as a potassium analogue), $^{15}$O water or $^{13}$N ammonia [26].

- Infectious diseases cause an inflammatory response that can be imaged with FDG or more specific tracers such as $^{18}$F–fluorodeoxyxosorbitol, which accumulates only in gram-negative bacteria [27].

The PET apparatus includes a circular detector ring which registers the arrival of pairs of annihilation gamma rays. As the photons are approximately colinear with the annihilation site, the location of the pair of detection points localises the emission site to lie along the
line connecting them. Detection events must come in pairs – those that do not arrive as a pair within a specified timing window are ignored. Mathematical algorithms combined with statistical image reconstruction routines are used to automatically generate annihilation density images of cross sectional planar cuts of the target.

The choice of radionuclide is often constrained by supply. The half-life of $^{18}\text{F}$ is 109.771 min, which is long enough that it can be produced off-site and shipped to hospitals that require it. In some cases such as $^{68}\text{Ga}$ and $^{82}\text{Rb}$, the isotope may be produced by decay of a relatively long-lived parent isotope ($^{68}\text{Ge}$ and $^{82}\text{Sr}$, respectively). In such cases, the parent isotope can be produced at a proton accelerator and transported in a “generator capsule” to the hospital, where the child isotope is chemically separated from its parent and used as a tracer. Other radionuclides with short half-lives (for example $^{15}\text{O}$ with a half-life of 122.24 s) must be produced on-site in a cyclotron. In addition, the radionuclides must be chemically attached to their target molecule, and it is difficult to safely work with highly radioactive material. In recent years, small cyclotrons and automated chemical laboratories have sometimes been installed alongside new PET scanners.

As in most imaging techniques, it is always desirable in PET to have a finer resolution and enhanced contrast. Because it is the annihilation sites of positrons and positronium atoms that are detected, the resolution of the images depends partly on the distance between the annihilation site and the emission site, which is called the penetration range and depends primarily on the type of radioisotope. In general, the types of radioisotopes that may be used are limited by the ability of the isotopes to bind to the molecules of interest. One approach to this problem is to design organic molecules that act as cages around the radionuclide and that can be connected to the target molecule. There has been speculation that such a molecule would also enhance positronium formation locality, as the positron forms positronium and self-annihilates within the cage [28]. Another approach, which does not require any modification to the operation of PET itself, is to employ models of penetration distance within various forms of tissue, which can better estimate the location of the radionuclide by combining the annihilation locations with the expected types of tissue within the regions [29]. It is towards this latter approach that the techniques in this thesis may be directed, as one of the aims of this thesis is to be able to model the penetration of positrons in non-gaseous models, such as liquid water.

In many radiation based clinical applications, a critical limitation is the risk of radiation-induced cancer. Ionising radiation can modify the chemistry of biological matter which can lead to cell death, chromosome damage or the formation of cancerous tumours. A large body of medical physics practice and research is dedicated to radiation safety, in which the radiation exposure of both patients and practitioners is minimised. Radiation damage is a critical issue for PET. The positrons that are emitted from, for example, $^{18}\text{F}$, have average energies of about 250 keV. As they travel through the human tissue, they may also ionise many molecules, releasing showers of electrons.

As human tissue consists largely of water, the ionisation of water is particularly important. The ionised forms of $\text{H}_2\text{O}$ are unstable and may dissociate into further free radicals which may interfere with biological processes either directly or via subsequent damage to chromosomes.
or DNA. The ejected electrons, of which there are approximately $10^5$ per MeV of positron energy, are typically produced with energies of less than 20 eV. Electrons below 20 eV undergo a strong dissociative attachment process with DNA, and are known to cause single- and double-strand breaks [30]. As such, a model that can predict precisely where and in what manner the positron’s energy is deposited is of great interest from a patient dosimetry perspective. Some limited estimates of energy deposition in liquid water due to low energy positrons are given in chapter 6.

It must be emphasised that while Monte Carlo methods such as those presented in this thesis can model the processes involved with PET, these methods are ill-suited to directly reconstructing the parameters of the system from the measured outputs. Clinical PET image reconstruction includes positron transport modelling only as a ‘Point Spread Function’ [31], which can be used to improve the detail of images using spatial diffusion and positronium formation profiles previously obtained with Monte Carlo or other methods.

1.3.2 Time projection chamber particle detectors

High-energy particle detectors are useful in a number of fundamental physics research areas, including cosmology and nuclear physics. One type of particle detector called a Time Projection Chamber uses liquid-phase noble gases, as first proposed by Alvarez in 1968 [32]. Incoming ionising radiation can excite electrons in the medium, bringing them into the conduction band where they can be readily transported by an applied electric field. For this purpose, liquid argon (LAr) and liquid xenon (LXe) in particular are very effective: they are quite dense compared to gas-phase detectors, so incoming radiation is more likely to interact. At the same time, as noble gases, their low electro-negativity means that the ionised electrons are unlikely to recombine with other atoms in the medium. This results in a high mobility and low diffusion. Finally, argon in particular is relatively inexpensive, making large detectors practical. As part of the DUNES experiment, which aims to detect neutrino scattering events, plans are under way to construct four detectors with a fiducial mass of $1 \times 10^4$ kg of LAr at 92 atm in each [33]. While the incoming cosmic rays have energies far higher than can be modelled with the techniques presented in this thesis, the subsequent ionised electrons are emitted with an energy of approximately 20 eV, and experience electric field strengths of approximately 500 V cm$^{-1}$ (a reduced field strength of $2.4 \times 10^{-3}$ Td). This is an excellent fit for the techniques in this thesis. In addition, as an electron slows to match the thermal energies of the liquid, a dynamic structure factor approach as outlined in chapter 5 can precisely model the thermalisation of the electrons in the liquid.

1.4 Swarm scattering theories and experiments

Many systems, including those described above, can be accurately modelled in the “swarm approximation”, where the charged particles are essentially independent and their interaction with the medium, including external fields, can be expressed in terms of cross sections. To this end, it is necessary to develop a set of models which can describe the behaviour of
1.4.1 Definition and implications of the swarm scattering approximation

The “swarm limit” describes systems that consist of an ensemble of charged particles (“swarm particles”) that are interacting with a background medium of neutral atoms or molecules in either gaseous or condensed phase. In addition, the swarm limit assumes that:

1. mutual interactions between the swarm particles are negligible,
2. the background medium is not disturbed by the swarm particles, and
3. there are no intrinsic space-charge electric fields (although an externally-supplied electric and/or magnetic field is often present, which is weak enough so as not to affect the neutrals).

The second condition requires some elaboration: one definition [34] is that the distribution of molecular translational and internal states of the neutrals is unchanged by the interactions, or in other words, that there are so many neutrals, and so few of them are affected by the scattering that the disturbances to the medium as a whole are statistically insignificant. This further implies that swarm particles cannot affect each other indirectly via the neutrals.

Under these conditions, it is apparent that the behaviour of the ensemble is wholly determined by three distinct effects:

1. the collisions between the swarm particles and the neutrals, governed by scattering cross sections,
2. acceleration of the swarm particles via externally-applied electromagnetic fields
3. static properties of the background medium, including the velocity distribution function and structural correlations.

A comprehensive review of swarm theories and experiments is given by Kumar et al [35].

1.4.2 Boltzmann equation models

The first methods used to model swarm systems were solutions of the Boltzmann equation of continuity, that is

\[ \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) = -J(f(\mathbf{r}, \mathbf{v}, t)), \quad (1.1) \]

where \( f(\mathbf{r}, \mathbf{v}, t) \) is the phase-space distribution function and \( \mathbf{a} \) refers to the acceleration from external forces applied to the system. The distribution function represents the positions and velocities of all of the swarm particles at all times and from this quantity all macroscopic quantities can be calculated. The Boltzmann equation is essentially an equation of continuity for a 7-dimensional fluid, where the left-hand side represents the collisionless free flight of the swarm particles, and the right-hand side, \(-J\), accounts for
all particle-neutral interaction effects. Calculating macroscopic quantities for a swarm system thus consists of three steps [20]: specification of $J$ in terms of all of the interaction cross sections (including corrections for structure and temperature), solving the resulting partial-differential equation for $f(r, v, t)$, and finally integrating over the relevant parts of $f(r, v, t)$ to obtain the desired quantity. In most cases, the required integration must be performed numerically.

Boltzmann solutions and Monte Carlo simulations are in some ways complementary. While accurate steady-state transport coefficients are often readily accessible in Boltzmann equations, Monte Carlo simulations are more effective with complex geometries, equal mass-ratios, and transient spatial behaviours.

1.4.3 Swarm experiments

The cross sections for use in swarm scattering models are difficult to calculate ab initio, and are largely limited to either high energies, using the first Born approximation, or simple atomic species. Measurements of cross sections may be obtained either directly through single-scattering experiments, or indirectly through drift-tube swarm experiments. The former are discussed in section 1.5. Swarm experiments indirectly probe cross sections by measuring the steady-state transport coefficients of electrons in a gas, and with the aid of Boltzmann transport calculations, the cross sections can be inferred. This works well for atomic targets at low energies, because there are no rotational or vibrational excitations so that there are only a few open interaction channels. When too many types of interaction are possible, the degeneracy of the solutions makes it difficult to estimate even total cross sections.

Petrović and co-workers [36] have recently compiled a comprehensive review of swarm experiments and simulations. There have been few swarm experiments conducted in recent years, as they have largely been superseded by transmission and crossed-beam experiments. Modern swarm experiments are largely used as a means to ensure the self-consistency of particle, momentum and energy balance in the compiled cross-section sets [37].

1.5 Low energy positron scattering experiments

Briefly, the first positron scattering experiments were performed by Deutsch in 1951, in which positrons emitted from $^{22}\text{Na}$ were released into dense gases and the resulting gamma rays were detected. These early experiments provided evidence for positronium and were also the first estimates of annihilation rates. Further experiments by Paul and Saint-Pierre and later Smith and Paul in the 1960s and 1970s probed annihilation rates in gases. A comprehensive reference for these early experiments can be found in the review by Griffith and Heyland [38].

However, measurements capable of distinguishing specific atomic physics processes required a beam of positrons with a far smaller distribution of energies, and the initial solution to this problem was to use a positron moderator, analogous to the neutron moderators in high-energy nuclear physics. Several generations of moderators were tried,
CHAPTER 1. INTRODUCTION

W. Tattersall

with particular success found in single crystal tungsten [39], which is still used in some experiments [40], particularly for electrostatic beamlines. However, the most efficient moderators known at the present time are frozen noble gas moderators [41] such as the solid neon moderator that is presently used at the University of California San Diego (UCSD) [42] and the Australian National University (ANU) [43] beamlines.

Nevertheless, even with these moderators, the energy resolution of the beam remained $\geq 0.5$ eV. A major advance in positron scattering experiments came in the form of positron accumulator cooling traps, developed in the early 1990s by Surko at UCSD [44]. This device confines the positrons within magnetic and electric fields while they efficiently thermalise with $N_2$ and $CF_4$ gases. This enables the collection and efficient cooling of positrons to form pulsed beams with a considerably smaller energy spread, potentially as low as the temperature of the gases. Chapter 4 of this thesis describes and partially models the positron trap. Surko et al [45] have published a comprehensive review of positron experiments and theories prior to 2005.

There are now several research groups with positron beamlines measuring cross sections for a variety of atoms and molecules. Studies have ranged from the noble atomic gases to small molecules such as the trap gases $N_2$ and $CF_4$ [46], and the DNA precursors pyrimidine [47] and uracil [48]. Most importantly for this thesis, early measurements of positrons in water at [49] have been followed by a more precise and detailed series of measurements at ANU [2,5], which is the subject of chapter 2.

1.6 Monte Carlo methods for charged particle transport

1.6.1 Existing models

Monte Carlo methods are computational algorithms that can be used to predict the macroscopic behaviour for any system for which the microscopic behaviour is probabilistically known. The first Monte Carlo methods were aimed at integral geometry problems, with an early example being Buffon’s needle problem [50]. The first published applications of Monte Carlo methods for particle scattering were during the Manhattan Project, where Stanislaw Ulam and John von Neumann programmed the ENIAC computer to calculate penetration depths for energetic neutrons [51] as part of efforts to weaponise nuclear fission. Monte Carlo methods soon proved beneficial for many of the projects at the Manhattan Project, and later at Los Alamos.

The prototypical Monte Carlo model for swarm transport is perhaps that of Skullerud [52], who in the late 1960s developed Monte Carlo models of drift-tube experiments, employing a “null-collision” method which made it computationally feasible to simulate electron transport in electric fields. The progress in swarm simulations since then has been largely incremental and the fundamental algorithms have changed very little, although as the available computational power has dramatically increased, much more precise simulations are now available that can output higher resolution results.

There are several established codes for electron and positron swarm simulation. The EPOTRAN code [53] is directly targeted at medical dosimetry, simulating both positrons
and electrons in gas phase water using a mean free path simulation model. Their simulation energies range from 10 keV down to 7.4 eV, using theoretical cross sections calculated from a partial-wave expansion in the Born approximation. An alternative approach is taken with the LEPTS code [54,55], in which theoretical cross sections and experimentally measured energy loss spectra are combined to model the transfer of energy and momenta with positrons in liquid water. The LEPTS code has recently been incorporated into the GEANT4 general-purpose particle simulation package, extending the range of ability of GEANT4 to lower energies. Several studies by Emfietzoglou [56,57] and co-workers have included empirically measured dielectric functions to estimate the range of energy transfers possible due to inelastic scattering for electrons in liquid water. A similar approach is taken by Dingfelder et al. [58] as part of the PARTRAC and NOREC codes. Compared to the simulations in this thesis, the most similar study of positron (and electron) transport in gaseous water was recently performed by Petrović and co-workers [18], using a code that has been systematically benchmarked under highly non-equilibrium swarm experiment conditions [59]. A number of other relatively high-energy Monte Carlo simulations are described and compared in a review by Champion et al [60].

Research in Monte Carlo methods for swarm transport has been quite fragmented. In general, most research groups have developed their own codes, in many cases taking advantage of their own calculated or measured cross sections (which are often unpublished). The notable exception is the GEANT4 code, which began development at CERN in 1998 and has since been actively maintained and improved. Initially designed for very high energy particle modelling, it has been extended in recent years to low-energy systems with extension packages such as GEANT4-DNA [61].

1.6.2 General track-structure swarm simulations

While Monte Carlo swarm simulation techniques are the subject of chapter 3, a broad outline is given here. Virtual swarm particles are created by sampling at (pseudo-)random from initial velocity and position distributions. Each particle is then tracked as it passes through matter, interacting through binary collisions with virtual neutrals that are sampled from their own distributions. The interaction mechanics and frequency are governed by cross sections and selected by appropriate random sampling, while the motion of the swarm particles between collisions is deterministic, and governed by the equations of motion in electromagnetic fields. At various intervals, the state of the particle is recorded and stored for later analysis.

As additional particles are simulated, the uncertainty on the measurements is reduced, inversely scaling with the square root of the number of particles. Because each swarm particle is entirely independent, particles can be simulated sequentially, potentially as separate executions of the program running on different cores or even computers. As such, swarm Monte Carlo simulations are often used as an example of an ‘embarrassingly parallel’ [62] problem in computer science.

It is interesting to note that Monte Carlo simulations can be viewed [63,64] as “numerical solvers” of the Boltzmann equation, where the left-hand side of equation (1.1) is handled by
the Newtonian updates to the particle’s motion, the right-hand side is represented by the collision method, and $f(r, v, t)$ is estimated by the properties of the simulated particles. As additional particles are simulated, the central limit theorem ensures that the estimated value of $f(r, v, t)$ converges on the true value. The specific variation-reduction techniques employed by Monte Carlo methods to optimise the calculation can then be interpreted as types of ‘importance sampling’ that enhance the convergence rate.

The Monte Carlo simulation described in this thesis is loosely based on a code by White [65], and on my own honours project [66], although none of the original code now remains. The physics features include support for angle-differential cross sections, fully-differential ionisation cross sections, time- and space-dependent DC electric fields, non-conservative collision variance reduction [67], dynamic [68] and static [69] structure, and both spherical and plane-parallel geometries. It is targeted at low energy transport, with no attempt to include relativistic effects. The software features include an unusual code-generation architecture, which supports very flexible input and output definitions. The simulation kernel is portable, with no dependencies on external libraries, and can be run as batch jobs on a computer cluster or on independent computers.

1.7 Structure of the thesis

In chapter 2, interactions for positrons in water vapour are measured with a transmission experiment. In chapter 3, a Monte Carlo simulation technique is proposed that can use single molecule interaction cross sections to stochastically simulate the scattering system to yield the required information. The techniques are benchmarked on several highly non-equilibrium swarm systems. Simulations of the dumping behaviour of positrons in a Surko trap are presented in chapter 4. In chapter 5, the simulation described in chapter 3 is extended to the liquid phase, taking into account collective mode excitations for elastic collisions, using either a static or dynamic structure factor. Chapter 6 discusses a Monte Carlo simulation that employs the cross sections of chapter 2 along with the techniques of chapters 3 and 5, resulting in spatial distributions of the behaviour of positrons in liquid water.
2

Measurements of cross sections for positrons in water vapour

This chapter consists primarily of material that has been previously published in the following journal articles:


For the former article, I contributed to running the experiment and performed the total cross section adjustments. For the latter article, I ran the majority of the experiment and performed nearly all of the analysis. There is also some previously unpublished work in this chapter, including additional estimates of the total cross sections and more detail about the estimation technique, as well as further comparisons with the existing literature.

2.1 Introduction

As the aim is to use liquid water as an analogue for human tissue in PET simulations, an accurate set of cross sections for positron interactions with water ($\text{H}_2\text{O}$) is required. Cross
sections of electrons in water are well-studied [70], but there is a dearth of information on positron scattering. In 2009, measurements of cross sections for positron scattering in water vapour were performed using the positron beamline at the Australian National University (ANU). As part of this thesis, measurements were made of grand total and positronium formation cross sections for positrons in water vapour (and formic acid, which shall not be discussed here). Further studies were conducted in 2011 [2], in which a more elaborate experimental technique was used to determine angle-dependent differential quasi-elastic cross sections, as well as total quasi-elastic and total inelastic cross sections.

The latter experiment was the first time that differential cross sections had been measured for positron scattering in water. While these measurements are not sufficiently comprehensive to use in transport models in and of themselves, they can be used to inform theoretical predictions of differential cross sections such as those by Baluja et al. [13] and Garcia et al. (published as part of [2]), which in turn can allow transport models to accurately predict the spread of the positrons in the medium. In previous models, these angular effects have either been ignored (assuming isotropic scattering, for example in [14]), or based on untested theoretical data (for example in [71]). The second ANU experiment was also the first time that integrated elastic and inelastic cross sections had been measured as distinct quantities. These are likewise very important quantities for positron transport. Measuring the integrated elastic cross section directly is more precise than integrating the differential elastic cross sections and can be used directly in transport models, while the total inelastic cross section serves as an upper bound for theories of inelastic scattering at low energy. As such, these new measurements have the potential to improve the quality of the input data to both Boltzmann and Monte Carlo models of positron transport in water.

2.2 Experimental apparatus

The experimental apparatus and techniques that are used for this work have been described in detail previously in articles involving studies of both room temperature gas-phase [43,72] targets, and targets that are both liquid and gaseous at STP [5]. In particular, a comprehensive description of the experiment design is given by Gilbert et al. in [73] and a detailed description of the present apparatus is given by Sullivan et al. in [43]. However, for the benefit of readers who are unfamiliar with the experiment, here is a brief outline.

The beamline, shown in figure 2.1, consists of five major components, all connected with air-tight seals and kept under high vacuum by a series of turbo-molecular pumps. Electromagnetic coils around each component, usually set to 0.053 T (530 G), are used to radially confine the positrons. The components are as follows:

1. A sealed sample of $^{22}$Na that emits positrons through $\beta^+$ decay, encased within a frozen neon moderator.

2. A buffer gas trap, which accumulates and preferentially cools positrons, before producing pulses with a small energy distribution.
3. The scattering cell, which contains the target gas or vapour. A small retarding potential analyser lies immediately before it, which serves primarily to reject positrons that have scattered from background gases escaping from the trap.

4. A second retarding potential analyser that allows only positrons with a sufficient, tunable, energy to pass through.

5. The detector, which uses a double micro-channel plate electron multiplier to count positron impacts.

The sodium-22 ($^{22}\text{Na}$) source emits positrons with a distribution of energies of up to $\sim 540\text{ keV}$, with a peak at $\sim 240\text{ keV}$. It has a decay half-life of 2.6 years, so it must be replaced regularly, typically every 3-4 years. When the source was purchased it had an initial activity of $\sim 50\text{ mCi}$, but by the time the first experiment began, it had decayed to an activity of $\sim 25\text{ mCi}$. By the time of the second experiment, the source had been replaced, and it had an activity of $\sim 30\text{ mCi}$. The source is placed within a heavily shielded vacuum chamber, where it is cooled to 7 K by a closed-cycle liquid helium cryostat. High purity neon gas is admitted into the chamber, where it freezes around the source. The positrons are moderated by the frozen neon \cite{41}, and while many positrons are lost to annihilation, those that remain have a narrower distribution of kinetic energies. The rate of positrons leaving the moderator is on the order of $8 \times 10^5$ positrons per second, with an energy spread of approximately 1.5 eV. A combination of electric and magnetic fields guide the positrons into the buffer gas trap chamber.
The operation of the buffer gas trap is described in detail in several articles [74,75], and it is the subject of the Monte Carlo simulations described in chapter 4. Briefly, the buffer gas trap is used to further reduce the energy spread of the positrons down to near-thermal levels, as well as to form the beam into a series of pulses. It is filled with a mixture of N\textsubscript{2} and CF\textsubscript{4} gases, which are chosen because of their desirable inelastic cross sections and their small positronium formation cross section. As the positrons pass through the trap, they initially collide with N\textsubscript{2} molecules. The trap’s potential, relative to the source and moderator, is set such that the positron’s energy is greater than 8.4 eV but less than 8.8 eV, which in N\textsubscript{2} correspond to the thresholds for a\textsuperscript{1}Π excitation and positronium formation, respectively. This allows positrons to lose energy rapidly through excitation interactions, while reducing the chance of them forming positronium and being removed from the beam. Once the positrons have reached a low enough energy, they may interact with the CF\textsubscript{4} molecules through vibrational excitations, one of which has a threshold of 0.159 eV. A series of electrodes confine the positrons within the trap while they thermalise. Pulses of positrons are then formed by ramping up the potential in the second-to-last electrode, allowing the positrons to spill over the potential barrier of the final electrode. The entire procedure is approximately 10% efficient\textsuperscript{1}. For both of the experiments described here, the trap was configured to produce a pulsed positron beam of energy width $\sim$ 60 meV, with a repetition rate of 100 Hz and up to 1000 positrons per pulse.

These positrons subsequently pass down the beamline, through a retarding potential analyser (RPA 1), a configurable ring electrode that can selectively reflect those positrons that have insufficient kinetic energy from their axial velocity. This ideally rejects all positrons that have scattered with the trap gases that have diffused out of the trap. The remaining positrons proceed down the beamline and into the scattering cell. For the first experiment, the cell was 200 mm in length, while the latter used a 100 mm cell. In both cases, the pressure of the water vapour within the cell is maintained by the combination of vacuum pumps on either side of the cell and a needle valve on the inlet from the sample. A capacitance manometer (MKS Baratron Model: 690A01TRA) measures the pressure, which is automatically recorded by the control software. The pressure throughout the majority of the measurements was about 0.22 mTorr, chosen so that around 10% of the positrons could be expected to scatter within the cell. The scattering cell, gas lines and water sample are all held at a temperature of 23 °C; the low pressure inside the cell means the sample is in its vapour form at that temperature. The scattering cell is itself an electrode that can be tuned to an electric potential which is cycled throughout the course of the experiment. As the sum of potential and kinetic energy is conserved, this allows the measurement of scattering events over a range of collision energies.

Positrons that pass through the scattering cell may then pass through a second retarding potential analyser (RPA 2). Positrons that have insufficient energy can be prevented from reaching the detector by the electric field gradient set up by the potential on RPA 2. By stepping through a range of such potentials, it is possible to measure a cumulative distribution of the number of positrons with a sufficient axial velocity to overcome the

\textsuperscript{1}S. Buckman, personal communication
potential barrier. The energy discrimination only applies to that component of the positrons’ velocity which is in the direction parallel to the beamline, so with this technique alone it is impossible to distinguish between low-energy positrons and positrons that have a large helical component to their velocity. However, the magnetic field in the RPA region can be adjusted independently, which exploits the adiabatic invariability of the magnetic moment to divert some fraction of the non-parallel velocity into the parallel direction, and thus distinguishes between losses due to a change of direction and losses due to internal excitations of the target molecules, as discussed in section 2.4.

Finally, the positrons strike the micro-channel plate electron multiplier. Two insulated plates are stacked together, each containing thousands of tiny holes (channels) that are angled slightly away from perpendicular to the beam, with the orientation of the two plates such that the holes do not align. When positrons strike the inside edge of a channel, they precipitate a cascade of electrons, effectively amplifying the signal by several orders of magnitude. The front face was biased to $-300\,\text{V}$ and the back to $\sim 1700\,\text{V}$, so chosen to provide the maximum gain. The resulting current pulse is fed through a transimpedance amplifier to produce a voltage pulse that is digitally measured and recorded. The absolute scattering cross sections may then be calculated using the Beer-Lambert attenuation law, as described in section 2.3.

The $\text{H}_2\text{O}$ sample was deionised, and after it was connected to the system, it was frozen with liquid nitrogen, using the low pressure pumps to extract any dissolved gases as the sample thawed. This was repeated several times before measurements began. The sample holder and tubing were also cleaned with an ultrasonic bath, and most elements of the beamline were heated and evacuated to remove any remaining contaminants.

### 2.3 Integrated and angle-differential scattering

For both integral and differential cross sections, it is assumed for the sake of analysis that each positron undergoes either a single collision, or no collisions at all. The pressure of the gas within the cell is set with this in mind, aiming for a collision frequency that will see approximately 10% of the positrons undergoing one collision. It is also assumed that all of the positron’s initial energy is due to the positron’s velocity in the direction parallel to the beamline. This can be approximated by ensuring that both the magnetic coils and the electrodes are concentric around the beam, in which case perpendicular components of the velocity will be at near-thermal levels.

The parallel component of the kinetic energy of a positron as it travels through the beamline can be manipulated by changing the electrostatic potential applied to each electrode. When the potential of an electrode is set higher than the potential of the source, the positrons lose energy as they enter the electrode, and indeed will be reflected at the entrance to the electrode if the potential difference is higher than the energy of the positrons. Conversely, a low potential increases the kinetic energy of the positrons. This allows the measurement of the scattering cross sections at multiple energies by changing the electrostatic potential of the scattering cell. It also allows the distribution of kinetic
energies of the positrons to be determined by scanning through a range of potential energies on RPA 2 and measuring the fraction of positrons that have sufficient energy to overcome the potential barrier.

From these transmitted intensities, it is possible to calculate sums of cross sections using the Beer-Lambert attenuation law [73]:

\[ \sigma = \frac{1}{n_0 l} \ln(H) \]  

(2.1)

where \( l \) is the path length that the positrons travel through the gas, \( n_0 \) is the number density of the molecules, and \( H \) is the ratio of transmitted to incident intensity. The resulting cross section, \( \sigma \), can be specifically identified based on the retardation potentials that were applied to obtain \( H \).

In figure 2.2, the orange circles represent a typical cutoff curve, obtained by measuring the relative count of impacts with the detector, while RPA 2 is set to successive cutoff potentials. As the analyser’s potential is increased, fewer of the positrons in the cell have sufficient energy to scale the potential barrier, so the analyser effectively filters out positrons with a low velocity in the direction parallel to the beam. When a positron scatters off a molecule, its parallel energy is modified by two distinct effects:

1. Some of the total kinetic energy is lost during the collision, due to excitation of the internal states of the target molecule. In the case of ionising collisions, energy is also shared with the product electron.

2. The direction of the positron’s velocity is changed through a scattering angle \( \chi \). This reduces the amount of velocity in the direction parallel to the beam, and redirects it into the perpendicular direction where the magnetic field forces it into a helical form.

In addition, each energy loss may be due to one of many different available collisions. This means that the data that is measured is potentially due to the sum of several cross sections, each integrated over a small energy distribution due to the beam’s energy and angular width, and further integrated over different sub-intervals of the possible scattering angles.

For the first experiment, the only fundamental measurements are of the grand total cross section \( \sigma_{\text{GTCS}} \) and the Ps formation cross section \( \sigma_{\text{Ps}} \). For this purpose, four intensities are measured:

**Incident beam intensity** \( (I_0) \) is measured with the RPA 2 potential set to allow through all positrons, and the scattering cell’s potential is set such that the energy of the positrons within the cell is below the positronium formation threshold. The positrons will still undergo scattering events with the medium, but regardless of their energy loss, they will inevitably reach the detector eventually. Direct annihilation interactions are the exception, but this cross section is known to be very small.

**Background intensity** \( (I_b) \) is measured by setting the potential of RPA 1 to a high value, causing all positrons to be reflected back into the moderator before they reach the scattering cell. The detector then measures the background signal, which is
typically very small compared to the other intensities, and largely due to electrical noise in the apparatus.

**Total Transmitted beam intensity** ($I_t$) is measured with the RPA 2 set to allow all positrons through, and the scattering cell’s potential set so that the kinetic energy of the positron in the cell is set to the energy of the measured cross section. If the energy is lower than the positronium formation threshold, $I_t = I_0$. Otherwise, this will be smaller than $I_0$, the difference being entirely due to positronium formation, which allows the calculation of this interaction cross section. This is sometimes denoted $I_{or}$, as in [76].

**Unscattered beam intensity** ($I_m$) is measured with RPA 2’s potential set to a value $V_m$ that is just below that of the beam, so that only those positrons with energy equal to the beam energy are allowed to pass. If the positron’s parallel energy is detectably lower than the incident beam energy, it is treated as though it has been scattered.

There is some degree of error inherent in choosing an appropriate value for $V_m$. If the potential is too high, low-energy unscattered positrons from the initial beam will not be detected, while if the potential is too low, positrons that have scattered without losing much energy and with a small scattering angle will be detected as part of the unscattered beam. In practice, the offset was set to 150 mV, which is approximately three standard deviations of the beam width. This is sufficiently far from the centre of the beam energy that there should be few unscattered positrons removed from the beam. In any case, the effect that $V_m$ has on the resulting cross section can be quantified and a correction factor can be estimated.

Given these intensities, the integrated cross sections can then be calculated using equation 2.1, with $H$ set according to the desired cross section. The ratio $H = I_T/I_0$ gives $\sigma_{Ps}$, while $H = I_m/I_0$ gives $\sigma_{GTCS}$. The ratio $H = I_m/I_T$ yields $\sigma_{GTCS} - \sigma_{Ps}$ directly, which is mathematically identical to measuring the two quantities separately, but is often reported at the same time.

Some fraction of the scattered positrons will be included in the nominally unscattered intensity $I_m$, which means that the measured intensity does not cover the entire angular range of a cross section. This is the “missing angle” effect which has been discussed at length in a number of articles and theses such as [5, 72, 76], and particularly [77]. It is possible to quantify exactly what the measured cross section represents when the value of $V_m$ is taken into consideration. Every cutoff potential corresponds to a distinct energy loss in the parallel component, which further corresponds with a pair of scattering angles for each possible collisional process. After a collision, the energy of the positron in the parallel component is given by

$$\varepsilon_\parallel = \varepsilon' (\cos \chi)^2,$$

where $\varepsilon'$ is the energy of the positron after the scattering event, and $\chi$ is the scattering angle. In this experiment, any positrons that are scattered through an angle of more than 90° will be reflected forwards again by the potential of RPA 1, so each measured intensity includes contributions from both the back-scattered and forward-scattered angles.
Consider a positron of incoming energy $\varepsilon$, interacting through a process $p$ that has a threshold $\Delta\varepsilon_p$. Each potential $V$ on the cutoff curve, which is set to allow positrons with a minimum parallel energy of $\varepsilon_{||}(V)$, can be mapped to a scattering angle for that process:

$$\chi(V, \Delta\varepsilon_p) = \cos^{-1}\left(\sqrt{\frac{\varepsilon_{||}(V)}{\varepsilon'}}\right) = \cos^{-1}\left(\sqrt{\frac{\varepsilon_{||}(V)}{\varepsilon - \Delta\varepsilon_p}}\right). \tag{2.2}$$

This is the case for every energetically available process, so that the ratio between two intensities measured at $V_1$ and $V_2$ can be used with the Beer-Lambert law to give a mixture of angular differential cross sections (DCS):

$$\sum_p \int \chi(V_2, p) \, \sigma_p(\varepsilon, \chi') \, d\chi' = \frac{1}{n_0 l} \ln\left(\frac{I(V_1)}{I(V_2)}\right), \tag{2.3}$$

where $p$ iterates over the available processes (other than Ps formation, which is a loss process and thus unaffected by angular considerations).

### 2.4 Magnetic field ratio effect

The magnetic moment of the positron within a magnetic field is given by [22]:

$$\mu = \frac{\varepsilon_{\perp}}{B},$$

where $\varepsilon_{\perp}$ is the energy of the positron in the directions perpendicular to the beam. Provided the magnetic field does not change too rapidly, this is an adiabatic constant. The apparatus has the capability to set a different $B$ field within the RPA 2 region from that within the scattering cell. If the magnetic field in RPA 2 is reduced, $\varepsilon_{\perp}$ in that region is reduced, and by conservation of energy, $\varepsilon_{||} = \varepsilon' - \varepsilon_{\perp}$ is increased. However, as the change in $B$ only affects the positron’s motion after it has already scattered, the change from $\varepsilon$ to $\varepsilon'$ due to the collision (from excitations, ionisation, or momentum transfer) is unaffected. This effect can be exploited to distinguish between energy transfer into the target due to the collision and energy that is no longer in the parallel component of the positron’s velocity due to scattering at an angle from a molecule.

The ratio of $B$ fields between the scattering cell and RPA 2 is denoted as $M$, which is the factor by which $\varepsilon_{\perp}$ is reduced within RPA 2. The remainder of what was previously $\varepsilon_{\perp}$ is added into $\varepsilon_{||}$. As the parallel and perpendicular components of the energy are both trigonometrically related to the total energy $\varepsilon'$, equation (2.2) can be rewritten as
\[ \chi (V, \Delta \varepsilon_p) = \sin^{-1} \left( \frac{M \varepsilon_{\perp}}{\varepsilon'} \right) \]
\[ = \sin^{-1} \left( \sqrt{\frac{M \varepsilon_{\perp}}{\varepsilon - \Delta \varepsilon_p}} \right) \]  \hspace{1cm} (2.4)
\[ = \sin^{-1} \left( \sqrt{M \left( 1 - \frac{\varepsilon_{||} (V)}{\varepsilon - \Delta \varepsilon_p} \right)} \right) . \]  \hspace{1cm} (2.5)

Energy is redirected from the perpendicular component of the positron’s velocity into the parallel component, and if the field ratio is high enough, the parallel energy of the detected positrons can be mapped to singular cross sections, with no overlap in most cases\(^2\). One of the earliest uses of this technique is shown in figure 1 of Sullivan et al. [78], where a ratio of \( M \sim 35 \) was used to clearly separate the contributions from vibrational excitations in \( \text{N}_2 \), yielding a cutoff curve that shows clear steps for each of the inelastic processes. For the water experiment, the ratio was set to \( M \sim 5 \), which is insufficient to separate the excitation processes in such detail. Nevertheless, this technique distinguishes between inelastic collisions and nearly all quasi-elastic collisions.

Figure 2.2 shows simulated cutoff curves for \( \text{H}_2\text{O} \), using the current state-of-the-art cross sections described in chapter 6. The ranges of energy losses applicable to each of the processes are also shown, illustrating the mapping between \( \chi \) and \( V \) for each \( p \) for both \( M = 1 \) and \( M = 5 \). This cutoff curve was measured experimentally, and is shown as orange circles on the \( M = 5 \) plot. Unfortunately, this does not agree particularly well with the simulated result, and is in fact more consistent with the \( M = 1 \) curve, which suggests that either the magnetic ratio is not in fact as high as intended, or that the simulation’s cross section set is incomplete or incorrect.

Note that in the case of ionisation, \( \Delta \varepsilon_p \) includes both the energy required to ionise the molecule as well as the kinetic energy retained by the electron ejected by the collision. As such, it is not possible to fully determine the scattering angle for ionisation events using this type of data, so another technique must be used such as a COLTRIMS experiment [79].

\[2\]The exceptions are rotational and vibrational excitations, where the threshold energy is smaller than the experiment's energy resolution, and ionisation, where the loss energy is variable due to the presence of the secondary electron.

2.5 Estimating the total cross section

Because this experiment cannot distinguish between forward-scattered and unscattered positrons, it is not possible to measure a complete total cross section. Equation 2.5 can be used to determine a critical angle, \( \chi_c \), below which positrons are detected as unscattered:

\[ \chi_c = \sin^{-1} \left( \sqrt{\frac{M V_m}{\varepsilon}} \right) , \]
Figure 2.2: RPA 2 data recorded for positron scattering from H$_2$O at a beam energy of 45 eV (orange circles, $M = 5$ only), compared with a Monte Carlo simulation of the same system (blue curve) using the state-of-the-art cross sections listed in chapter 6. The ranges of energy losses applicable to each of the processes are also shown: the labelled ranges correspond to the largest cross sections, while the unlabelled ranges represent the remaining electronic excitation processes. Vibrational and rotational excitations are too small to be distinguished from the elastic range at this scale. Positronium formation manifests as the difference between the detection rate at 0 eV and 1 on the vertical axis. On the right, a higher ratio of magnetic fields can be seen to compress the parallel energy range of scattered positrons.

where $V_m$ is the distance, in energy terms, from the centre of the beam to the cutoff potential at which $I_m$ is measured. This distance is set with the positron beam’s energy resolution in mind. For the first experiment, $V_m = 150$ meV, yielding the critical angles listed in the second column of table 2.1. Positrons that are scattered into an angle in the interval $[0, \chi_c]$ are not seen as scattered, so the total cross section for elastic scattering will be underestimated. In addition, for the present apparatus, positrons that are scattered in the backward direction, $(\pi / 2 < \chi < \pi)$ are subsequently reflected from the potential wall of the last electrode of the buffer gas trap, and will therefore pass through the cell once more. As the probability of them scattering in the cell the second time is still only $\sim 10\%$, they will likely arrive at RPA 2 with a velocity corresponding to an angle of $\pi - \chi$. As such, the experiment cannot discriminate between forward and backward scattering, so scattering events with angles in the interval $[\pi - \chi_c, \pi]$ are likewise undetected.

It can be seen that a larger $M$ increases the critical angle, as changes in the measured $\varepsilon|_{\parallel}$ are smaller for the same difference in angle. Consequently, a smaller angular fraction of the total cross section can be measured, in effect the same as if the energy width of the beam were multiplied by $M$. For this reason, measurements of the grand total cross section are better performed with $M = 1$. For the second experiment, some measurements were made with $M = 5$ and again $V_m = 150$ meV, yielding the critical angles listed in the fourth column of table 2.1.
For comparison with other experiments and theories, which measure different fractions of the total cross section, it is recommended [77, 80] that an estimate of the true total cross section be made, allowing comparisons to be made with the results of other experiments where the measured angle is different or with theories that propose a true total cross section. The estimation procedure is reasonably straightforward. Take for example the elastic cross section, in which case the unmeasured fraction $p_{el}$ of the cross section is given by:

$$p_{el} = \frac{\int_0^{\chi_c} \sigma_{el}(\chi) \sin \chi d\chi + \int_{\pi-\chi_c}^\pi \sigma_{el}(\chi) \sin \chi d\chi}{\int_0^\pi \sigma_{el}(\chi) \sin \chi d\chi},$$

where $\sigma_{el}(\chi)$ is the true differential elastic cross section. The true total cross section $\sigma_{el}$ is then

$$\sigma_{el} = \frac{\sigma'_{el}}{[1 - p_{el}]},$$

where $\sigma'_{el}$ is the measured elastic cross sections from experiment. As $\sigma_{el}(\chi)$ can not be measured by this experiment below $\chi_c$ (by the very definition of $\chi_c$), its value must be obtained from an alternative source, such as theory.

The true $\sigma_{GTCS}$ can also be estimated:

$$\sigma_{GTCS} = \sigma_{el} + \sigma_{Ps} + \sigma_{exc} + \ldots = \frac{\sigma'_{el}}{[1 - p_{el}]} + \frac{\sigma'_{Ps}}{[1 - p_{Ps}]} + \frac{\sigma'_{exc}}{[1 - p_{exc}]} + \ldots$$

However, as positronium formation removes positrons from the beam entirely, there is no critical scattering angle, so $p_{Ps} = 0$. Furthermore, there are no theoretical predictions for $\sigma_{exc}(\chi)$, and indeed the experiment does not separately yield $\sigma'_{exc}$ in any case. To a first approximation, the estimated $\sigma_{GTCS}$ can be obtained by applying the elastic correction to the measured value of $\sigma_{GTCS} - \sigma_{Ps}$, and afterwards adding the measured $\sigma_{Ps}$. Values of $\chi_c$ and estimates of $p_{el}$ are given in table 2.1, where the latter are calculated using Baluja’s differential elastic cross sections [13] shown in section 2.7.5.

### 2.6 Sources of uncertainty

The sources of uncertainty and how they have been accounted for are largely unchanged in these experiments, compared with similar previous experiments (e.g. [81, 82]).

Every measured intensity has an associated statistical uncertainty, since every measurement is subject to effectively random variation due to the energy width of the positron beam, the possibility of multiple scattering in the gas (exacerbated by a possibly changing path length from the first collision), the inherent noise of the multi-channel plate detector, and other effects. Repeated measurements were made, typically around 1500 scans, to obtain a Gaussian distribution of resulting intensities. Because all of these measurements are recorded separately, the distribution itself can be used to estimate the standard error of the intensities. This can then be propagated when calculating the resulting cross sections.
Table 2.1: Critical angles $\chi_c$ and the corresponding unmeasured percentage $p_{el}$ of the total elastic cross section, at several beam energies, for experiments at magnetic ratios of 1 and 5. Note that critical angles are expressed in degrees for legibility. As described in the text, the unmeasured percentage of the TECS is determined from the theoretical DCS of Baluja et al. [13], by calculating the proportions of the total elastic cross sections that lie below each of the critical angles.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$M = 1$</th>
<th>$M = 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\chi_c$ (°)</td>
<td>$p_{el}$ (%)</td>
</tr>
<tr>
<td>0.5</td>
<td>33</td>
<td>67.2</td>
</tr>
<tr>
<td>1</td>
<td>23</td>
<td>69.57</td>
</tr>
<tr>
<td>2.5</td>
<td>16</td>
<td>63.93</td>
</tr>
<tr>
<td>5.0</td>
<td>10</td>
<td>52.57</td>
</tr>
<tr>
<td>15.0</td>
<td>6</td>
<td>29.58</td>
</tr>
<tr>
<td>30.0</td>
<td>4</td>
<td>21.71</td>
</tr>
<tr>
<td>60.0</td>
<td>3</td>
<td>11.50</td>
</tr>
</tbody>
</table>

This effect is analogous to the uncertainty in the Monte Carlo simulations described in section 3.7.5 of chapter 3. For an in-depth treatment of the statistical uncertainty, please refer to the thesis of Machacek [76].

There are also systematic uncertainties that may bias the results in a non-statistical manner. The target density, $n_0$, is used in the Beer-Lambert law (equation 2.1) as a multiplier of the absolute magnitude of the scattering cross sections. In this experiment, the pressure of the target gas was measured using a capacitance manometer, which was found to suffer from a drifting zero value, perhaps due to variations in temperature. In practice, the zero of the pressure is measured both before and after the experiment, and interpolated to perform a background subtraction of the measured density during the experiment. There is also thermal transpiration at the interface of the manometer, because the measurement volume of the manometer is internally heated to 45°C, while the scattering cell is at a room temperature of 23°C. While the latter value was monitored via a thermocouple on the outside of the scattering cell, the internal heating was not checked and was assumed to be within the manufacturer's quoted tolerance of 0.1°C. A correction is applied [83], with the resulting pressure reduced by 4 – 5% from the values that were recorded.

After positrons leave the buffer gas trap, they may continue to scatter with trap gases that have diffused from the trap into the remainder of the beamline. This background scattering will modify the energy distribution of the positron beam before it enters the scattering cell. A background scattering test is performed prior to admitting the water vapour for the main experiment and can compensate for the modified energy distribution. In addition, a teflon collar surrounding the exterior of the cell (and the positive pressure inside the cell) prevents background gas from leaking into the region after the cell. For full details, please refer to the thesis of Machacek [76].

It is interesting to note that the path length of the positrons in the scattering cell does not depend on the strength of the magnetic field. Provided that the solenoids are concentric around the beam, the conservative magnetic force means that the speed of the positrons remains constant and provided that the magnetic field is (approximately)
Table 2.2: Simulated multiple-scattering rates for positrons in water vapour under scattering cell conditions. The first column is the number of scattering events that a positron undergoes before striking the detector, the second column is the fraction of positrons for which this count applies. As positrons that form positronium do not strike the (simulated) detector, these events are counted separately. Positron beam energy was initially at 45 eV, with an energy width of 0.06 meV.

<table>
<thead>
<tr>
<th>Collision count (not Ps)</th>
<th>% of positrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90.7</td>
</tr>
<tr>
<td>1</td>
<td>6.61</td>
</tr>
<tr>
<td>2</td>
<td>0.36</td>
</tr>
<tr>
<td>3+</td>
<td>0.07</td>
</tr>
<tr>
<td>Ps. formation</td>
<td>2.17</td>
</tr>
</tbody>
</table>

constant throughout the scattering cell, there is no energy transfer between the axial and perpendicular directions. As such, regardless of the strength of the field, the positron still crosses the cell in the same amount of time, travelling with the same speed, and must therefore cover the same distance. However, the perpendicular velocities of the positrons will be rotated by the field, causing the positrons to gyrate about the axis of the beamline and preventing them from being lost in collisions with the walls of the cell.

The density of the target gas is set such that it is expected that 1% of the positrons undergo more than one scattering event, such that the Beer-Lambert law no longer applies. This depends primarily on the path length of the positron after a single scattering event, which in turn depends solely on the ratio of perpendicular to parallel velocities, $\sqrt{1 + E_\perp/E_\parallel}$ (see [73]). Prior to a collision, this ratio is negligible, less than 1% for 1 eV positrons in this experiment, so the probability of a second scattering event remains low. However, when a positron scatters at a large angle, nearly all of its $E_\parallel$ may be transferred into $E_\perp$. Since the positrons must still travel through the same axial distance to exit the cell, the decreased $E_\parallel$ means an increased time within the cell and increased possibility of further scattering. In practice, this effect is not particularly significant in water, because the forward-peaked differential cross section renders a positron unlikely to scatter into a perpendicular direction.

A Monte Carlo simulation of 45 eV positrons in the scattering cell was performed using the cross sections listed in chapter 6, and the rates of multiple scattering events are shown in table 2.2.

2.7 Results and discussion

The first experiment provided measurements of the GTCS and Ps formation cross sections with a then-unprecedented energy resolution. The results are shown in figures 2.3 and 2.5. The second experiment provided measurements of the total elastic and total inelastic cross sections, where the magnetic field was reduced within RPA 2 in order to separate the elastic cross section from the inelastic cross sections. The results are shown in figures 2.6 and 2.7. Finally, the second experiment also produced differential elastic cross sections for several energies, which are given in figures 2.8 and 2.9. In all cases, the errors represent the
Figure 2.3: Positron impact H\textsubscript{2}O GTCS data compared with the literature for experimental GTCS and theoretical ECS results. None of the experimental data are complete total cross sections, as they do not account for positrons scattered in the forward direction.

What follows is a detailed comparison of the results of the two ANU experiments with those of similar experiments and theories. Most of the discussion and data are available in the articles that resulted from these experiments [2,5], but there is additionally an estimate of the total cross section, with a correction to compensate for forward-angle scattering, over the full energy range. In addition, several comparisons have been made with the alternative set of cross sections used by Banković et al. [14].

Tables of all of the ANU data are included in appendix B.

2.7.1 Grand total cross sections

In figure 2.3, the grand total cross sections obtained in both experiments are compared with the earlier experimental results of Zecca [84] and Beale [85], as well as with the theoretical predictions of Gianturco [86] and Baluja [13].

The GTCS measured in the first ANU experiment monotonically decreases with energy from 0.5 eV to the highest energy that was measured, 60 eV. This behaviour is likely due to either long-range polarization effects in the water molecule, or the permanent dipole of water at low energies. The results of the second experiment do not appear to agree with those of the first, however this is because only the measurable part of the GTCS is

![Graph showing cross section vs collision energy]
shown. As discussed in section 2.5, forward-scattered positrons are indistinguishable from unscattered positrons in this type of experiment. In the second experiment, this effect is exacerbated by the magnetic field ratio, which effectively reduces the energy resolution by a factor of $M = 5$. As such, a significantly larger fraction of the scattered positrons are treated as unscattered, and the measured part of the GTCS is considerably smaller, particularly at low energies.

The results of the first experiment are in good agreement with the results of Zecca et al. [49] at low energies, although they trend higher above $\sim 8$ eV, being up to 12% higher at their maximum energy point. As Zecca’s results have a broader energy resolution of about 0.3 eV, a larger range of scattering angles are seen as unscattered. This is also the likely reason for the disagreement with the results of Beale et al. [85]. At low energies, the present GTCS is smaller than both of the theoretically predicted TECSs, probably once again due to forward-scattering considerations, while at higher energies, there more scattering processes than just elastic, and the GTCS is correspondingly higher than the TECSs.

In figure 2.4, the GTCS data are once again presented, this time adjusted to account for those positrons that scatter into small angles, as discussed in section 2.5. This allows for comparison with the measurements of Kimura et al. [10], who made a similar correction to their own data, as well as with data from the second experiment, where the angular resolution was effectively poorer due to the modified magnetic field ratio. The quantitative and qualitative agreement with Kimura’s results is reasonable, and while the first experiment
agrees slightly better, the corrected results of both experiments are within 10% of Kimura’s results over the shared range. While both sets of data have been adjusted using the same differential cross sections, this adjustment is proportional to the measured partial cross section and therefore dependent on the accuracy of the measured data, so the agreement is quite promising. The GTCS measured in the second of the ANU experiments is in excellent agreement with the original measurements, once the different forward-scattering range is accounted for. In both cases, the correction was made using the elastic DCS of Baluja et al. [13].

2.7.2 Positronium formation cross sections

The positronium formation cross section, shown in figure 2.5, is a loss process, which makes it relatively easy to measure. It is unaffected by scattering angle considerations, since it removes the positron from the beam. As such, it is unsurprising that there is good agreement between the two experiments –the exception being at the highest energies, where the added complexity of the magnetic field ratio in the latter experiment appears to have caused excessive positron loss, most likely due to the magnetic field being imperfectly aligned with the beam. There is only one other water Ps formation experiment that has been conducted to date, that of Murtagh et al. in 2006 [11]. There is broad agreement at low energies, while there is disagreement by up to 70% at higher energies, well outside the quoted statistical uncertainty, although it is reasonable to expect a large amount of systematic error.
2.7.3 Total elastic cross sections

To distinguish elastic and inelastic scattering, a stronger magnetic field is set in the region of RPA 2, as described in section 2.4. With a field ratio of $M = 5$, elastically scattered positrons with initial energy $\varepsilon$ can lose a maximum energy of $\frac{1}{5} \varepsilon$ in the parallel direction, which distinguishes them from the lowest electronic excitation threshold of 7.49 eV. However, as the cutoff curve in figure 2.2 shows, this does not allow the distinction between the various inelastic processes to be measured, so the only intensities that were measured were at 0 eV, 35.85 eV and 44.85 eV on RPA 2, where the latter two values are determined by $\varepsilon - V_m$ and $\varepsilon - \frac{1}{5} \varepsilon - V_m$. This is sufficient to distinguish between elastic and inelastic processes, and offers a superior scan rate and therefore better statistics.

It was therefore possible to measure distinct elastic and inelastic cross sections (as well as positronium formation, as shown in the previous section). The measured elastic and inelastic cross sections are shown in figures 2.6 and 2.7 respectively, and the tabulated cross

---

**Figure 2.6**: Elastic cross sections, both measured and estimated total, from Experiment 2. Theoretical comparisons are with Baluja et al.’s R-Matrix calculations [13] and García’s IAM-SCAR calculations [2]. Also shown is the synthetic elastic cross section first used in Bankovič et al. [14].

A theoretical treatment by Hervieux et al. [12] uses an independent electron model and a continuum distorted-wave charge transfer, which agrees at high energies, but is significantly smaller at low energies. In this region, the Ps formation channel competes with the elastic channel as well as several inelastic channels, necessitating a two-centre expansion for accurate calculations.
section data are given in table B of appendix B. The results shown here are quasi-elastic total cross sections, which include vibrational and rotational excitations as well as elastic scattering.

The measured elastic cross section has been compared with several alternatives. Figure 2.6 shows the rotationally-averaged total elastic cross sections of Baluja et al. [13], calculated using the R-matrix formalism, as well as an independent atom model (IAM) calculation performed by García, the details of which are described in [2]. The elastic cross section measurements are indicated by the dense array of solid red circles, and they are seen to lie well below both the R-matrix calculation (solid line) and the IAM cross section (dashed line). However, it is notable that the measured elastic cross section is not the total elastic cross section. Rather, it is the integral of differential elastic cross sections over a limited range of scattering angles, as described in section 2.3, and as such it would be expected to be significantly lower than both of the theoretical results, which are integrated over all scattering angles.

An estimated total elastic cross section (TECS) has been constructed by scaling the measured value by a factor that accounts for the fraction of Baluja et al’s DCS that is within the critical angle for forward scattering, as described in section 2.5. While the DCS data was only available at a few energies, it has been interpolated across the whole energy range using spline interpolation. This may introduce some error, but it is necessary if the cross section is to be directly used in applications such as transport calculations. The resulting estimated TECS is considerably larger than the measured value, particularly at low energies, but it is in very good agreement with both of the theories at low energies. At higher energies, the results are notably smaller than theory, even though forward scattering is not so significant. This is perhaps not surprising, however, as the positronium formation process is difficult to compensate for in present theories.

The strong dipole polarisability of water ($\sim 10$ a.u.) and its large dipole moment ($\sim 1.85$ D) are expected to increase the elastic scattering cross section as the collision energy decreases, a prediction that is born out by these results. Other polar molecules have exhibited similar effects in recent studies [87,88]. This also explains the strong preference for small-angle scattering, and hence the inability to measure the total cross sections at low energies.

A further comparison has been made with a synthetic elastic cross section that was first used in Banković et al’s article on positron transport in water [14]. This cross section was developed by a collaboration of authors, including some who worked on the experiments described here. It was obtained by taking the adjusted $\sigma_{GTCS} - \sigma_{Ps}$ from the first experiment, and subtracting a number of theoretical cross sections for the various known excitation processes. The remainder is taken to be the elastic cross section. The estimated TECS from the second experiment is consistently lower than the synthetic cross section, particularly at higher energies, probably because it is difficult to account for all of the other processes that may contribute to the synthesised cross section.

---

3These data are not presented in this chapter, but can be found in the original article [5].
Note that all of the above elastic cross sections also implicitly include rotational excitations, which have thresholds smaller than the energy resolution of the experiment.

2.7.4 Total inelastic cross section

As the elastic cross section has been separated from all other scattering events, it is also possible to measure the total inelastic (excitation and ionisation) cross section (TICS). This is shown in figure 2.7, along with a continuum distorted wave calculation of the direct ionisation cross section by Hervieux et al. [12]. The measured inelastic cross section rises slowly across the energy range measured, starting at the $\tilde{A}^1B_1$ electronic state threshold of $\sim 7.4$ eV [89] and reaching a maximum of $\sim 4$ Å$^2$ at the highest measured energy of 60 eV. Unlike the case for elastic scattering, the present experiment is able to accurately measure the total of the electronic excitation processes, as even the smallest electronic excitation thresholds are orders of magnitude larger than the energy width of the beam, so it is easy to distinguish a positron that has scattered from one that has not. However, the possible energy losses for each of the electronic excitations largely overlap, as can be seen on figure 2.2, and it is therefore impossible to distinguish individual processes with $M = 5$. The ionisation process should in theory account for the majority of energy losses of more than 12.6 eV, however the measured cutoff curve suggests that contributions were not so clearly distinct, likely due to systematic errors in the experiment. As such, only the total inelastic is shown here.

The measured total inelastic cross section is larger than the ionisation cross section of Hervieux et al. From the 45 eV cutoff curve, it is apparent that the majority of the inelastic cross section is due to ionisation, and the sum of the known excitation cross sections for electrons is quite small, so this suggests that the calculated ionisation cross section may underestimate the true magnitude by a factor of as much as four.

An additional comparison has been made with the sum of the inelastic cross sections that were included in a set, currently considered to be state of the art, that was first used in Banković et al.’s study on positron transport in water [14]. This includes a set of vibrational excitation positron cross sections calculated by Nishimura et al. [90], several electronic excitation cross sections for electrons in water from Thorn et al. [91], and a positron ionisation cross section calculated by Tóth et al. [15]. A spline interpolation of Tóth et al.’s ionisation cross section is shown separately, and it is the dominant inelastic process at most energies. The sum of the cross sections is in surprisingly good agreement with the measured total inelastic cross section, with the present results being less than 0.5 Å$^2$ larger over most of the range.

2.7.5 Differential elastic cross sections

The differential quasi-elastic scattering cross sections that were measured are shown in figures 2.8 and 2.9, at energies ranging from 1 to 20 eV. In each case, the cross sections have been “folded” around 90°, so that forward and backward scattering are summed together. Comparisons are made with two theories: the R-Matrix calculations by Baluja et al. [13] and the Independent Atom Model with Screening-Corrected Additivity Rule (IAM-SCAR).
CHAPTER 2. MEASUREMENTS

Figure 2.7: Measured total inelastic cross section, compared with theoretical positron impact ionisation cross sections from Hervieux et al. [12]. Also shown is an ionisation cross section from Tóth et al. [15], the sum of the excitation cross sections used by Banković et al. [14], and the latter two cross sections summed together.

The lowest energy measurements are shown in figure 2.8. For these measurements, the magnetic field was kept constant between the scattering cell and the retarding potential analyser, as there are no electronic excitation processes that are active at such low energies. At all low energies, the agreement with the IAM-SCAR calculations is surprisingly good, and indeed unexpected given the approximations involved in the model. At all energies below 8 eV, the experimental DCS decreases monotonically with increasing scattering angle, with no evident features. The cross section also decreases rapidly with increasing collision energy, which is typical of a strong dipole scattering system [92]. Compared to the R-Matrix calculations, the present results are noticeably more forward-peaked. However, as established in section 2.7.3, the estimated total elastic cross sections are in good agreement with the R-Matrix calculations. This comparison is somewhat nuanced however, as the corrected measurement has been scaled in an effort to account for the unmeasured portion of the beam, and that scaling ratio is based on the equivalent portions of the R-Matrix calculations. As the present results appear to be more forward-peaked, it is likely that the unmeasured portion of the beam is a larger fraction of the whole than that predicted by the R-Matrix theory, and consequently, that the predicted total elastic cross section is underestimated at low energies.

At energies above 5 eV, the magnetic field ratio was modified to be $M = 5$, allowing...
W. Tattersall CHAPTER 2. MEASUREMENTS

Figure 2.8: Measured differential quasi-elastic folded cross sections for $\text{H}_2\text{O}$ at 1 eV, 2 eV, 3 eV and 5 eV. Where available, folded R-Matrix [13] and IAM-SCAR [2] theoretical cross sections are shown for comparison.

the distinction between inelastic electronic excitation and elastic scattering as discussed in section 2.4. As seen in figure 2.9, the measurements display the same overall behaviour of the cross section and an overall reduction in magnitude with increasing energy. The increased magnetic field ratio adds a noticeable level of noise to the measurements and it is difficult to compare them with the theories, although they appear to be mostly a little higher than either of the theories predict, particularly at lower angles.

2.8 Conclusions

In this chapter, measurements of positron scattering in water vapour have been presented, including the results of two separate experiments performed at the ANU positron beamline. While these measurements are not sufficiently detailed to be used directly in transport simulations, they do represent a distinct improvement on the previous knowledge of positron-water cross sections, and in some cases are the only measurements available. This informs theoretical models, and comparisons have been made with several such models.

Agreement with the theoretical models of elastic scattering is reasonably good. Provided the limited angular resolution of the experiment is accounted for, the total elastic cross section at low energies agrees with several theories and experiments to within experimental error. The positronium formation cross section measurements presented here agree with each other, and also broadly agree with the earlier measurements of Murtagh. Finally, the
differential elastic cross sections are the first ever to have been measured, and agree very well with the IAM-SCAR theoretical model.

It would be highly desirable to obtain further measurements of positron-water cross sections. A tighter beam-energy resolution would allow for more precise measurements, covering more of the available scattering angles, while an increased magnetic ratio would distinguish the electronic excitation cross sections. The former is the goal of the cold positron beamline experiment that at the time of writing is under development at UC San Diego, while the latter may be achieved with a more carefully aligned beam and better external magnetic shielding to prevent $E \times B$ forces. The development of the “reaction microscope” [93] will potentially allow measurements of the complete kinematics of ionisation events, recording fully differential cross sections. Finally, a stronger positron source could be used to quickly collect more statistically significant results.
Monte Carlo design and benchmark simulations

This chapter contains material previously published in the following journal articles:


I have obtained permission from the co-authors to republish parts of these articles here. All text and figures are my own.

3.1 Introduction

This chapter presents an original Monte Carlo simulation code developed over the course of the PhD. The code is a research platform for testing Monte Carlo transport ideas and implementations, and has evolved quite substantially as new features have been added to support additional transport processes and outputs. The physics features include support for
angle-differential cross sections, fully-differential ionisation cross sections, time- and space-dependent DC electric fields, non-conservative collision variance reduction [67], dynamic [68] and static [69] structure, and both spherical and plane-parallel geometries. The software features include an unusual code-generation architecture, which supports unusually flexible input and output definitions. The simulation kernel is portable, with no dependencies on external libraries, and can be run as batch jobs on a compute cluster or on independent computers. Technical features of the code are described in appendix A.

It is not unreasonable to question the value of writing an original code when other Monte Carlo simulations are available that are open source, and can do much of the work already. Part of the reason for the reinvention is historical: it has naturally evolved from an earlier code by White [65], and on my own honours project [66], although none of the original code now remains. Another reason is that as a single developer, there is a great deal of flexibility and simplicity in not having to integrate my work with those of other programmers – projects such as GEANT4 involve the work of literally hundreds of other programmers, and have many capabilities that have no relevance to the intended goals of this study, which only adds to the complexity of the code.

There are several features of Monte Carlo track-structure simulations that have not been reproduced in this work. Magnetic and AC electric fields are not included, although they were part of this code’s predecessor [65]. Geometry-dependent media are not included either, so all of the systems simulated have the same density and ratios of gases throughout the entire simulation space. There is no attempt to simulate high-energy particles, so there are no relativistic effects, and no need for condensed-history elastic collisions [94,95].

This chapter outlines the simulation procedure before breaking into more detail about the free flight and scattering procedures. Electric fields are discussed in section 3.3, including three alternative implementations. Non-conservative interactions and the relevant algorithmic optimisations are discussed in section 3.4. The possible outputs of the simulation and their applications are described in section 3.5, while section 3.6 describes how to calculate the traditional swarm transport coefficients from them. The steady-state and hydrodynamic regime is discussed in section 3.7, along with a discussion of correlated uncertainties in steady-state quantities. Some brief remarks on the architecture of the code are given in section A. The chapter concludes with a number of benchmark systems in section 3.8 which have been used to validate various features of the code.

3.2 Simulation procedure

The broad structure of the Monte Carlo charged particle transport code is shown as a flowchart in figure 3.1. Briefly, the code generates a virtual particle, and simulates its motion over a set period of time. During this time, it undergoes virtual events which modify its velocity. As each particle is simulated, its velocity and position (and potentially other variables) are recorded. This is repeated many times (typically between $10^5$ and $10^6$ particles), and the measured properties are combined, in most cases by accumulating as
arrays of data. Once every particle has been simulated, or the program is interrupted, the measured properties are written to a set of files and the program halts.

3.2.1 Free flight and the events model

The motion of the simulated particles can be described as a series of free flights, punctuated by instantaneous scattering events. The average time between scattering events is determined by the total collision frequency, given by:

\[ \nu(v) = n_0 \int f_0(v_0) |v - v_0| \sigma_T(|v - v_0|) d^3v_0, \]  

(3.1)

where \( n_0 \) is the density of neutral molecules, \( \sigma_T(g) \) is the total scattering cross section at a collision energy corresponding to a relative speed \( g = |v - v_0| \), and \( f_0(v_0) \) is the distribution of neutral molecule velocities. In nearly all of the simulations in this thesis, the neutral molecules are at zero temperature, so \( f_0(v_0) = \delta(v_0) \), and the above equation
reduces to
\[ \nu(v) = n_0 v \sigma_T(v). \] (3.2)

Even for non-zero gas temperatures, if the ratio of neutral mass to particle mass is high, \( v_0 \) is small relative to \( v \), and the same result is achieved. This is discussed in more detail below.

While the collision frequency represents the average rate of collisions over an extended period of time, the stochastic nature of the simulation means that the particles may encounter neutral molecules at any time. However, it is possible to calculate the probability that the time between collisions is greater than \( \tau \), which can be expressed as
\[ P(\tau) = \exp\left(-\int_0^\tau \nu(v(t)) \, dt\right). \] (3.3)

Since \( P(\tau) \) is a cumulative probability distribution, the inverse transform sampling procedure can be used to sample \( \tau \) by equating \( P(\tau) = R \), a variate selected from a uniform distribution from 0 to 1, and solving for \( \tau \). If the velocity of the particle does not change between collisions, as is the case in the absence of electric fields, this reduces to
\[ R = \exp[-\nu\tau] \]
\[ \tau = -\log(R) / \nu. \]

When electric fields are present, this procedure is modified as detailed in section 3.3.

3.2.2 Scattering procedure

The scattering subroutine encapsulates the quantum-mechanical features of the semi-classical transport simulation, and it is perhaps the best place to introduce new approximations to the physics of the real-world systems that are modelled. Largely self-contained, it takes as input a data structure containing the properties of the particle being simulated (position, velocity, statistical weight, and particle type) and returns an updated copy of the particle post-collision. Figure 3.2 shows a flowchart describing the principal features of the scattering subroutine.

Each collision is treated as an instantaneous and spatially local binary collision between a positron or electron (“particle”) and an atom or molecule from the scattering medium (“neutral”). In multi-component media, such as the trap simulations in chapter 4 where both \( \text{N}_2 \) and \( \text{CF}_4 \) gases are present, the first step of the scattering procedure is to determine which type of neutral is involved in the collision, the probability of which is simply given by the relative concentration of each type of neutral, multiplied by its grand total cross section. The choice of neutral then determines the set of available interaction channels, and also has implications for the energy and momentum transfer between the particle and the neutral, as these depend on the mass ratio of the swarm particle to the neutral.

In each collision, the particle can interact with the neutral through one of a number of discrete processes. Each process is characterised by its cross section, which describes how (relatively) frequently that type of scattering event occurs. Thus, selecting the scattering
process is done by sampling from a discrete distribution that is the magnitudes of the total (angle-integrated) cross section at the collision energy, using a standard cumulative inverse transform sampling technique. An example of discrete collision process sampling is shown in code listing 1, later in this chapter. One subtlety of this part of the procedure is the treatment of particle loss processes such as positronium formation: it is usually advantageous to exclude loss processes at this stage of the collision calculation, and account for it later using a statistical rescaling, as discussed in section 3.4.

In an elastic collision, the total kinetic energy is conserved for the particle and the neutral, so the relative speed does not change. For inelastic collisions, including excitation and de-excitation events, the total kinetic energy is reduced by the threshold energy of the process, after which the momentum and energy transfer proceed as per an elastic collision. This means that elastic and simple inelastic collisions can be treated similarly, with the threshold energy for elastic collisions at zero.
Neutral temperature

When a swarm particle collides with a neutral, the neutral may have some velocity due to the temperature of the background gas. In most systems, the temperature effects are largely irrelevant: at room temperature, the mean energy of $\frac{3}{2}k_B T \approx 40 \text{meV}$ is considerably lower than any electronic excitation levels, and for molecules, overlaps with the largely unknown ro-vibrational cross sections, so it is unusual for drift tube or similar experiments to probe behaviours at that energy level. For other systems with a small electric field, however, the mean particle energy often relaxes to be comparable to the thermal energy. A simple treatment of thermal neutrals is offered by Lin and Bardsley [96] and is implemented in the present code. Briefly, when the collision occurs, the neutral’s velocity is randomly sampled from a normal distribution:

$$v_0 = c_0 \bar{R}$$

$$c_0 = \sqrt{\frac{k_B T}{m_0}},$$

where $c_0$ is the average speed of the gas molecules (calculated only once, when the simulation begins) and $\bar{R}$ is a vector of random normal variates with zero mean and unit variance. Since $m_0$ is usually much larger than $m$ (e.g. a factor of $\sim 4000$ for electrons in molecular hydrogen), $c_0$ is much smaller than the speed of the swarm particles, even when the latter are at the same energy. Nevertheless, to be precise, it is the relative speed $g = |v - v_0|$ that determines the rate of collisions. This is introduced into the code when selecting the type of interaction, as above. For a mixture of gases, $c_0$ varies with the masses of each component gas, and the calculation of which component is collided with takes this into account by calculating the neutral velocity for each component and, from the resulting relative velocity, calculating a total collision frequency. The sum of these frequencies is rescaled to 1, and a particular component is selected in the usual manner.

However, this does introduce a subtle approximation, as noted by [97]. At the moment when a swarm particle collides with a neutral, the probability that it collides with a neutral of a particular velocity is not only a function of the the neutral velocity distribution function $f_0(v_0)$, but also depends on the cross section and relative velocity, as per equation (3.1). This has two consequences:

1. The total collision frequency is slightly modified, because the integration in equation (3.1) samples $\sigma_T(|v - v_0|)$, which is not necessarily symmetric when integrated over all possible $v_0$. As an extreme example, consider a swarm particle at rest: the collision frequency in a cold gas would be 0 by equation (3.2), but it is clear that the neutrals that are still in motion can initiate a collision.

2. When a collision does occur, the neutrals cannot be directly sampled from $f_0(v_0)$, because the collision frequency varies with $v_0$, so certain neutral velocities are preferentially selected, depending on the particle’s velocity and the energy dependence of the collision frequency. As an extreme example, $v_0 = v_0 \hat{v}$ with $v_0 > v$ must not be
sampled, because the particle could not catch up to the neutral. Even if \( v_0 < v \), a collision with \( v_0 = v \hat{v} \) is less likely than a collision with \( v_0 = -v \hat{v} \) if the collision frequency decreases with collision energy.

It must be emphasised that neither of these effects is very large for electron or positron scattering with atoms or molecules, because \( v_0 \) is typically much smaller than \( v \). However, for ion transport, which is the subject of [97], it must certainly be included.

This is quite difficult to include, however, as it necessarily makes sampling \( v_0 \) much more computationally expensive. An alternative implementation is discussed in section 5.4.6 of chapter 5, where a dynamic structure factor is used to enforce a thermal equilibrium without explicitly calculating the velocities of the neutrals.

**Scattering angle**

During a collision, the angle of scattering must be randomly selected from the probability distribution given by the differential cross section for the collision process at the energy of the collision, \( \sigma (\varepsilon, \chi) \). In general, the scattering angle \( \chi \) can be obtained as

\[
R_\chi \approx \frac{\int_0^\chi \sigma (\varepsilon, \chi') \sin \chi' d\chi'}{\int_0^{\pi} \sigma (\varepsilon, \chi') \sin \chi' d\chi'},
\]

where \( R_\chi \) is a number generated from a uniform random number distribution ranging from 0 to 1, and \( \chi \) forms the upper limit of the integral in the numerator. Since \( \sigma (\varepsilon, \chi) \) is not known analytically, the integrand in the numerator must be numerically integrated to various upper bounds until the result is sufficiently close to the given \( R_\chi \). The integration was performed using adaptive Gaussian quadrature, and a standard root-finding algorithm, Ridders’ method [98], was used to search for the required \( \chi \). This calculation is too computationally expensive to perform during a simulation in which tens of millions of collisions may occur, so it is instead calculated for an evenly-spaced mesh of values for \( R_\chi \) before the simulation starts. This means that selecting a scattering angle during the simulation becomes a constant-time operation, at the expense of limiting \( R_\chi \), and hence \( \chi \), to predefined values. Sensitivity tests have been performed to ensure that increasing the size of this probability mesh does not affect the results.

In a medium with no preferred molecular alignment, which is assumed to be the case here, the azimuthal coordinate \( \psi \) is arbitrary. For unaligned neutrals, axial symmetry implies that every azimuthal angle is equally likely, so the simulation’s scattering method selects a random azimuthal angle \( \psi = 2\pi R_\psi \), where \( R_\psi \) is another random variate from the same distribution as \( R_\chi \). To simulate a medium with preferred molecular alignment, such as a polar molecule in a strong magnetic field, one would ideally include a triply-differential cross-section, \( \sigma_{el} (\varepsilon, \chi, \psi) \), which would have no such symmetry; data for these are currently unavailable for most species however.

**Ionisation**

Ionisation events are three-body collisions, with a (secondary) electron being ejected from the neutral. This electron has a non-zero velocity and its kinetic energy must be taken
into consideration when calculating the post-collision energy of the transport particle. If a double-differential ionisation cross section is known, \( \sigma_I(\varepsilon, \chi, \varepsilon_e) \), where \( \varepsilon_e \) is the energy of the secondary electron, the energy of the scattered electron can be sampled with an inverse transform sampling technique in a manner analogous to the above sampling of \( \chi \). Ideally, a triply-differential cross section \( \sigma_I(\varepsilon, \chi, \varepsilon_e, \chi_e) \), could be used to determine the ejection angle \( \chi_e \) of the secondary electron as well, which would influence the outgoing velocity as well through conservation of momentum, but there is insufficient data for this for any species at this time. At present, momentum considerations for ionisation events are essentially ignored: the collision is treated as binary between the primary particle and the neutral, after the secondary particle’s energy is removed from the primary. In any case, the sampling may still be performed with inverse transform sampling, though admittedly the lookup tables become rather large.

If electrons are the swarm particle, then the ejected electrons are indistinguishable from the input electrons and therefore contribute to the swarm, increasing \( n \). The naive approach to Monte Carlo simulation is to add the additional electron to a stack, and simulate it in full. In practice, for high ionisation rates, the particle number can increase exponentially and it may become infeasible to finish the simulation for even a single initial electron. Instead, a statistical weighting technique can be employed, as discussed in subsection 3.4.

Post-interaction

Now that both the direction and magnitude of the relative velocity is known, the system can be transformed and rotated back into the lab frame, giving the post-collision velocity of the particle. The velocity of the particle is the only quantity that is changed; the position of the particle remains the same as the collision is treated as instantaneous. All information about the neutral is discarded, as the swarm limit assumes that there are no long-term effects on the medium.

3.3 Treatment of electric fields

While electric fields are mostly insignificant in PET applications, many benchmark systems include electric fields to simulate highly non-equilibrium conditions as an indirect means of probing cross sections at a range of collision energies. The first experiments in electron transport were drift-tube swarm experiments, where the strength of the electric field was altered across repeated measurements. Macroscopic quantities such as drift velocity were reported for each field strength. This lead to a series of benchmarks based on swarm experiments, such as [99] and [100]. While there are very few positron swarm experiments, this format has continued to be used for positron simulation benchmarks such as [34]. Electric fields are therefore a necessity for accurately benchmarking the Monte Carlo simulation code.

Electric fields present a particular challenge for Monte Carlo transport simulations. As the collision frequency \( \nu \) of a given charged particle is dependent on its energy \( \varepsilon \) (see equation 3.2), the time between collisions \( \tau \) can be altered by the change of energy of the
particle due to the electric field, even as it is undergoing the transport between collisions. Mathematically, the probability of a time between collisions greater than $\tau$ can be expressed as [52]

$$P(\tau) = \exp\left(-\int_0^\tau \nu(\varepsilon(t)) \, dt\right),$$

where the charged particle’s energy is time dependent due to the particle’s passage through an electric field. Explicitly performing this integral for every collision is computationally expensive, given that the changes in $\varepsilon$ will depend on the velocity at which the particle is travelling and, for non-uniform electric fields, the position of the charged particle as well. Note that performing this integral is common for non-uniform field simulations such as [101]. For uniform electric fields, several faster approaches are possible.

### 3.3.1 Null collision method

One popular approach uses the method of "null collisions" [52], where the collision frequency is calculated based on the maximum collision frequency $\nu_0$ that the particle is likely to be able to reach during its transport. Using this constant collision frequency, equation (3.4) can be solved by equating $P(\tau)$ with a uniformly distributed random number $R$ sampled on $(0,1]$, in which case

$$\tau = -\nu_0^{-1} \ln R.$$  \hspace{1cm} (3.5)

When the collision occurs, a second random number is generated which is used to account for this overestimation by allowing the charged particle to undergo "null" collisions, where no exchange of energy or momentum occurs. This procedure suffers from a requirement to "backtrack" if the assumed collision frequency is too low, where it must then make a second assumption with a higher collision frequency. It is therefore important to minimise the number of null collisions and backtracks to optimise the simulation speed, and more recent simulations [102] have done so by making modifications to the selected maximum collision frequency. The null collision method effectively amounts to a form of rejection method for sampling from $P(\tau)$, which means that potentially many random numbers are generated for each valid collision.

### 3.3.2 Piecewise integration method

An alternative approach is employed for most of the simulations in this thesis. The cross-sections are specified as a function of energy, but are assumed to be constant within energy bins of width $\delta\varepsilon$. These energy bins can be made arbitrarily small, so there is no loss of accuracy provided that one is careful to test that the results are independent of the bin width. However, this means that it is sufficient to recalculate $\tau$ only when the energy of the particle changes from one bin to another, so until this occurs, the collision frequency in equation (3.5) remains constant. The simulation is therefore designed so that particles can undergo two types of interactions: collisions with neutrals, and “field updates”. Collisions with neutral particles are described above, and are governed by $i$, the energy bin of the particle. The second type of interaction occurs when the energy bin is judged to have
changed due to the effect of the electric field. In such an interaction, the only parameter that changes is $i$, which either increases or decreases by one, triggering a recalculation of the time until the next neutral particle interaction. The time until the change, $t$, is determined by analysis of the particle’s current velocity and the (constant) acceleration that it is experiencing due to the electric field. This is given by the smallest real, positive solution to the following equation for the kinetic energy:

$$\frac{1}{2} m (v_0 + (a t))^2 = \varepsilon_i \pm \frac{1}{2} \delta \varepsilon.$$  \hfill (3.6)

Recalculating the time until collision $\tau$ does not require the use of another random number. Recalling equation (3.5), we now have additional terms for each change in energy bin:

$$\tau = t_0 + t_1 + \ldots + t_n$$

$$-\nu_n^{-1} \left[ \ln (R) - \nu_0 t_0 - \nu_1 t_1 - \ldots - \nu_{n-1} t_{n-1} \right],$$  \hfill (3.7)

where each $t_i$ is determined by the time required for the particle to change energy from one bin to the next and each $\nu_i$ represents the average collision frequency for the energy bin that contains the particle’s energy at the beginning of the particle’s free flight. This equation reduces to equation (3.5) in the case of constant $\nu_n$ or zero $t_i$. In practice, the simulation maintains a running measure of the remaining “collision probability” for each particle, which is the dimensionless quantity in square brackets in equation (3.7) that is divided by the current $\nu$ to calculate the time until next collision.

It is important to check that the energy resolution $\delta \varepsilon$ is sufficiently small. If $\delta \varepsilon$ is too large, the effective collision frequency will take the form of a series of steps, which can either over- or under-estimate the true collision frequency. The magnitude of the effect depends on the energy derivative of the total cross section, but does not directly depend on the strength of the electric field: while the collision frequency will change more rapidly if the energy is changed quickly, the mean collision frequency between field updates will always be the collision frequency corresponding to the centre of the energy bin. An excessively small $\delta \varepsilon$ increases the running-time of the simulation, but is otherwise unproblematic (save for cumulative rounding error, which has proven to be insignificant). In practice, the easiest way to compensate for this effect is to repeat the simulation with a smaller $\delta \varepsilon$ and see if the results change.

This procedure essentially solves the collision frequency integral, equation (3.4), in a piecewise manner, while ensuring that each piece is constant in time by exploiting the often implicit assumption that numerical cross sections are constant within each energy bin.

### 3.3.3 Potential cells method

It is possible to model electric fields as a ‘staircase’ of potential cells along the z-axis. In such a design, the swarm particles undergo no acceleration during free flight, but instead undergo a third type of collision, ‘wall’ collisions, whenever they collide with or pass over one of the edges of the cells.
In support of this is a capability to loop the potential space: that is, a pattern of potentials can be repeated indefinitely in both directions, allowing for an unbounded electric field. As such, a continuous electric field over all space can be implemented as a three potential cells, or two boundaries. When a particle passes the lower boundary, its position in potential space is moved. A field resolution parameter determines the size of the steps, while the width of the steps is defined by the ratio of the step size to the field strength. Compared to the above piecewise integration method, it is somewhat inefficient, so it is no longer used for continuous electric fields. It is however very effective for systems such as the Surko positron trap, where changes in potential are effectively discrete and inherently step-wise. In this thesis, the potential cells method is used solely for the simulations of the trap in chapter 4, and is discussed further there.

3.4 Non-conservative interactions

Positronium formation is a strong loss process, which presents a particular challenge for Monte Carlo simulations [67]. The naive approach is to simply stop simulating the positron whenever the Ps formation process is selected for a collision. This does provide accurate results, but sampling spatial properties at large distances from the source becomes very difficult, because only a small proportion of the initial positrons remain in the system for long enough to contribute to the statistics. A large body of work exists in the literature concerning ‘variance reduction’ techniques [103, 104], which are methods of ensuring that the particles that are simulated are the particles that have the most statistical significance, whilst still remaining representative of the system. The technique employed in the present work, which has previously been described in reference [7], allows the simulation to explore the probabilities of both loss and regular processes simultaneously.

Every time a particle undergoes a collision, the probability of it undergoing a loss process is excluded from the list of possible interaction types, forcing it to undergo another process. However, the particle is assigned a statistical weight, $w$, according to the probability that it has not been lost, and all summed statistics become a sum that is weighted by $w$. For positronium formation, this is conceptually equivalent to simulating “bundles” of identical positrons which shed positrons due to positronium formation as the simulation proceeds. The effect on statistical correlations is actually nil: while each bundle of particles is perfectly correlated, there are no fewer bundles being simulated than there would otherwise be single particles, so the statistical significance remains the same. All of the above applies equally well for the equivalent process of electron attachment.

A variant of the technique can be employed in the case of electron-impact ionisation, where an additional electron is added to the swarm with every ionisation event. This can lead to an exponential avalanche of electrons that can be difficult to simulate within a finite time-period. Instead of simulating every electron, the simulation picks one electron at random, after every ionisation event, and doubles its statistical weight. The electrons thus chosen are a representative sample of the swarm, for the same reasons that the positrons above remain representative of the positron swarm.
A recent article by Mirić et al. [67] suggests two alternative rescaling procedures intended for electrons in gases with very large attachment cross sections, which is a functionally similar problem to positron positronium formation and annihilation. One method involves generating new electrons, which are sampled from the distribution of existing electrons, whenever the total number of electrons exceeds an arbitrary preset range. The other method is to introduce a fictitious ionisation cross section that duplicates randomly selected electrons at a rate that matches the loss due to attachment. The present method is distinct from both methods of [67] and has the advantage of a simple implementation while maintaining exact statistical properties, which is evidenced by how it satisfies the benchmark attachment model described in section 3.8.3.

3.5 Simulation outputs

One of the principal motivations for performing realistic simulations of physical systems is that simulations can provide detailed predictions of physical quantities that cannot be measured experimentally. As the entire simulation runs in a constrained, monitored environment, it is possible to take virtual “measurements” of anything that occurs during the simulation. While developing these simulations, several general classes of measurement have proven to be interesting.

3.5.1 Time moments

Time moments are measurements that are performed at pre-determined times, where for each particle, particle properties are added to accumulators. The resulting output is a set of summed values for each sample time. The properties that are summed can be arbitrary expressions, and may be vectors or scalars. When non-conservative interaction types are available, and the variance reduction scheme described in (3.4) is in effect, the quantity that is added to the accumulator can be optionally pre-multiplied by the statistical weight of the particle.

The sums can be segregated spatially, depending on either the particle’s position along the z-axis of the simulation (plane parallel geometry), or the particle’s radial distance from the origin (spherical geometry). As the points are measured at specific times rather than positions, it is easy to extend this to arbitrary geometries—in particular, there is no need to predict vector/plane intersections. One other option is whether the results are segregated in time; while the samples are still taken at fixed times, they can all be accumulated into the same bin, which reduces the size of the output for properties that do not change with time.

In terms of the swarm particle distribution function, \( f(\mathbf{r}, \mathbf{v}, t) \), the accumulated variables are given by

\[
\bar{\psi}_{l,m} = 4\pi \int_{v} d^{3}v \int_{r_{i}}^{r_{i+1}} J(\mathbf{r}^{'}) \, dr^{' \phantom{w}} \psi(v) \, f\left(\mathbf{r}^{'}, \mathbf{v}, t_{m} + R_{t}\right),
\]

where \( \psi(v) \) is an arbitrary function of a particle’s properties, \( R_{t} \) is an optional per-particle anti-aliasing random variate described in section 3.7.2, \( t_{m} \) represents the time slices at
which the moments were recorded, the \( r_i \) are the boundaries of the spatial bins, and \( J (r) \) is the Jacobian determinant: 1 for plane-parallel slices or \( r^2 \) for spherical shells.

The sample times do not need to start at zero or even be linear, and logarithmic time meshes have proven useful in some cases since most processes slow down as the system relaxes. However, if the time bins are non-linear, care must be taken to weight them accordingly for averages over time. The same flexibility and caveats apply to the spatially segregated bins.

Some examples of time moments include an instantaneous particle count by adding 1 for every particle sampled, or the summed energy of the swarm obtained by adding the weighted energy of each particle. As an example of a vector variable, the centre of mass of the swarm can be obtained by adding the weighted mass of the particle multiplied by its position.

Time moments are used to calculate the macroscopic transport coefficients defined in section 3.6 and used throughout the thesis.

### 3.5.2 Collision moments

Every time a collision occurs, particle properties can be sampled and added to a separate set of accumulators. These collision moments differ from the above time moments because they are additionally weighted by the frequency of collisions. As they occur for every collision, there are additional data available, including the interaction type (elastic, ionisation, etc.), scattering angle, and energy transfer. The sums can again be separated spatially, and they can also be separated based on time. There are also “overflow” bins in case collisions occur at times or distances that are beyond the measured range.

### 3.5.3 Time/collision distributions

Each of the above outputs can be further refined by considering each measured property as a distribution rather than just a sum. For each property, a sampling mesh is specified, and every time the property is sampled, the particle’s weight is added to an accumulator selected with an arbitrary expression (usually the property in question), e.g. sampling the density distributed over energies. This adds another dimension to the output matrices which can make them inconveniently large, however being able to view the full distribution is often valuable.

In terms of the swarm particle distribution function, \( f (r, v, t) \), the value in each bin of a time distribution output is given by

\[
\bar{\psi}_{i,j,m} = 4\pi \int d^3v \int_{r_i}^{r_{i+1}} J (r') dr' \int_{y_j}^{y_{j+1}} dy \delta (y (r', v', t_m) - y') w \psi (v) f (r', v, t_m + R_t),
\]

so that \( \bar{\psi}_{i,j,m} \) is the sum of the sampled property \( \psi (v) \) for all particles within the \( i \)th radial shell or planar slice, and (optionally) the \( j \)th bin of the discriminant \( y(r, v, t) \), at each discrete time \( t_m \). The other type of result that is presented here are particle properties that are measured at pre-determined times. These distributions take the form
\[ \tilde{\psi}_{i,j,m} = 4\pi \int d^3v \int_{r_i}^{r_{i+1}} J(r') \, dr' \int_{t_{m+1}}^{t_{m+1}} dt' \int_{y_j}^{y_{j+1}} dy' \delta (y(r', v', t) - y') \times \]
\[ w\psi(v) \nu_{\text{tot}}(v) f_p(r', v, t'), \]  

(3.10)

where the arbitrary particle property \( \psi(v) \) is summed over all collisions that occur within the spherical shell \( r_i < r < r_{i+1} \). The dimensions of each of the forms of \( \tilde{\psi} \) is always the same as that of \( \psi \), but the magnitudes depend on the widths of the bins involved.

The discriminant \( y(r, v, t) \) allows for conditional measurements, e.g. \( \psi(v) = \Delta \epsilon(v) \) and \( y(r, v, t) = \epsilon(v) \) gives a distribution of the energy losses during collisions, as a function of positron energy and radial position, and time. In both cases, the statistical weight \( w \) is used to account for positronium formation, as discussed in section 3.4. These types of output (summed over all sample times) were used to produce the density plots in chapter 6.

### 3.5.4 Collision type evolution

It is often interesting to see how the types of collisions vary as the simulation progresses. This output is a result of samples during each collision, where the particle’s weight is added to accumulators indexed by the simulation time and the particle’s position. This is strictly a subset of the collision moments output, but it is convenient and slightly more efficient to implement these samples as a separate output. This output was used to produce figure 6.8 in chapter 6.

### 3.5.5 Full track

This is an exhaustive listing of every single collision, including the particle’s position and the time of the event, possibly including other quantities such as amount of energy transferred. This can be used to reconstruct particle track images such as the example in figure 3.3. However, it uses a great deal of disk memory -- several gigabytes for the track of a single particle in some cases -- and so the code also includes a filtering provision so that tracking is only performed under certain circumstances, such as only for inelastic collisions, or only when a particle’s energy is within a particular range. While it does make for visually interesting and intuitive figures, it must be emphasised that they may be misleading: while the particle tracks are representative, the small number of particles gives no indication of the variability of the results and it is quite possible that the next simulated positron might travel much further than any so far, or that it might annihilate on its first collision. In general, Monte Carlo results are only statistically significant when large numbers of particles are simulated.

### 3.5.6 Final properties

Serving, as a lightweight alternative to the full track output in some circumstances, this returns the properties of every particle, individually, at the very end of the simulation time. This can be used to precisely construct distributions of arbitrary properties without needing
Figure 3.3: Example of analysed data from the “Full Track” output, taken from [7]. See that reference for simulation details.

Table 3.1: Transport coefficients expressed as particle averages.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{\varepsilon}$</td>
<td>Mean energy</td>
<td>$\langle \varepsilon \rangle$</td>
</tr>
<tr>
<td>$W$</td>
<td>Drift velocity</td>
<td>Flux $\langle \mathbf{v} \rangle$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bulk $\frac{d}{dt} \langle \mathbf{r} \rangle$</td>
</tr>
<tr>
<td>$D_L$</td>
<td>Longitudinal diffusion coeff.</td>
<td>Flux $\langle r_z v_z \rangle - \langle r_z \rangle \langle v_z \rangle$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bulk $\frac{1}{2} \frac{d}{dt} (\langle r_z^2 \rangle - \langle r_z \rangle^2)$</td>
</tr>
<tr>
<td>$D_T$</td>
<td>Transverse diffusion coeff.</td>
<td>as $D_L$, averaged over $x, y$.</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Loss rate</td>
<td></td>
</tr>
</tbody>
</table>

...to know the expected range of the distribution \textit{a priori}. As it only records properties once for each particle, it has little effect on how long the simulation takes to run, but may be still be a prohibitively large output if many particles are simulated.

3.5.7 Cut point counts

A lightweight diagnostic output, this output maintains totals of several scalar variables which can be incremented at arbitrary points in the code. It is used to monitor problems that may occur if the system’s parameters are set to suboptimal values. These cut points are parsed from the code file, so the output arrays are automatically set to the necessary size, and any cut point can be referenced by a descriptive label. Some examples include counts of “hot” collisions where the particle’s energy is higher than the maximum for the supplied cross section set, and “field update” counts which keep track of how many times a particle’s energy is updated due to acceleration by the electric field.

3.6 Transport coefficients
In keeping with the swarm-experiment origins of transport modelling, most benchmarks express their results in terms of several macroscopic transport coefficients. These coefficients are well known in swarm and plasma modelling, and have been defined in a number of texts [20,105]. The transport coefficients used throughout this thesis are listed in table 3.1.

In this table, \( \langle x \rangle \) represents an average of the particle property \( x \), over all of the particles in the simulation, obtained by dividing the relevant accumulator of the time moments by the weighted number of particles that have been simulated. With the present Monte Carlo simulation these can be calculated at any measured point in time and/or slice/shell of space, provided that the appropriate summed properties have been included in the time or collision moments outputs, as defined in section 3.5. Note that every transport coefficient definition above can be decomposed into averages of properties that apply to single particles. In other studies [105,106], the bulk diffusion coefficient is defined as

\[
D = \frac{1}{2} \frac{d}{dt} \langle r^*r^* \rangle
\]

\[r^* = r - \langle r \rangle.\]

The two definitions can be shown to be equivalent, by recognising that \( \langle \ldots \rangle \) is an operator that is both idempotent and linear:

\[
\langle r^*r^* \rangle = \langle (r - \langle r \rangle)(r - \langle r \rangle) \rangle
\]

\[= \langle r^2 \rangle - \langle r \rangle^2.\]

A distinction must be made between ‘Flux’ and ‘Bulk’ quantities. Physically, the flux quantities describe averages of the particles in the swarm, while the bulk quantities describe the velocity and diffusion of the centre of mass [106]. When there are no non-conservative processes, these quantities are identical. However, in systems with selective non-conservative processes, the two quantities can differ significantly. It is the bulk quantities that define the macroscopic behaviour, and are measured in experiment. They can differ from flux properties by orders of magnitude and can exhibit qualitative differences, leading to phenomena such as attachment-induced non-differential conductivity (the Tagashira-Sakai-Sakamoto effect [107]).

The loss rate is an interesting quantity for simulations of positrons or positronium atoms, because spatial distributions of the loss rate indicate where direct annihilation is most likely to occur. It therefore corresponds to the expected emission points for the gamma rays that can be detected by experiment. It is calculated somewhat differently, using the collision moments output type to accumulate the amount of statistical weight that is lost in each collision.
3.7 Steady-state quantities

3.7.1 Spatially varying

In most of the systems considered in this thesis, a steady stream of incoming particles forms a steady-state equilibrium: particles are continually added by the source, and lost by leaving the boundaries of the system or through attachment processes. One may then wish to obtain the steady-state distribution of various properties with respect to the distance from the source. The distribution function for the continuously emitting source can be constructed [108] as a set of \( k \) pulses, each containing \( n_p \) particles per pulse:

\[
f(r, v, t) \approx n_p \left[ f_{p:1}(r, v, t) + f_{p:2}(r, v, t) + \ldots + f_{p:k}(r, v, t) \right],
\]

where \( f_{p:i}(r, v, t) \) is the distribution function normalised to one positron, released in the \( i \)-th pulse. To correspond to a continuous source of emission rate \( \alpha \), we choose \( n_p = \alpha \Delta t \), where \( \Delta t \) is the time between subsequent pulses. Since there are no time-varying parameters of the system, each pulse only differs by the time of its emission, that is:

\[
f(r, v, t) \approx \alpha \Delta t \left[ f_p(r, v, t) + f_p(r, v, t - \Delta t) + \ldots + f_p(r, v, t - k\Delta t) \right],
\]

where \( f_p(r, v, t) \) is the distribution function of a single pulse released at \( t = 0 \). In the limit of small \( \Delta t \), corresponding to summing many pulses, the continuous distribution is defined exactly, and this becomes an integral, where \( t_{\text{end}} = k\Delta t \):

\[
f(r, v, t) = \alpha \int_0^{t_{\text{end}}} f_p(r, v, t - t') \, dt'.
\]

By a change of variable, \( u = t - t' \) and noting that \( f_p(r, v, t < 0) = 0 \) by definition, we obtain:

\[
f(r, v, t) = \alpha \int_0^t f_p(r, v, u) \, du.
\]

Similarly, if the measurements are confined to a limited radial distance and minimum velocity, then for each \( r \) and \( v \), there exists a \( t = t_{lt} \) such that:

\[
f_p(r, v, t > t_{lt}) = 0,
\]

where all particles have either been annihilated, left the boundaries of the simulation, or reached a velocity below the cutoff threshold. Hence we can write

\[
f(r, v, t \leq t_{lt}) = f_{SS}(r, v) = \alpha \int_0^{t_{lt}} f_p(r, v, u) \, du,
\]

which can be obtained from the simulation, provided \( t_{lt} < t_{\text{end}} \). This condition can be trivially checked by the simulation to ensure that the steady-state has been reached.
3.7.2 Random time offset sampling technique

For properties which refer to the results of individual collision events, such as energy deposition or positronium formation, the accumulation occurs at each collision event and is therefore unaffected by timing considerations. In contrast, swarm properties, such as mean energy, are recorded at discrete times $t_i$ which ensures that all particles are sampled equally. In this case, the best estimate of the steady state particle distribution function $f_{SS}(r, v)$ is

$$f_{SS}(r, v) = \alpha \Delta t \sum_{i=0}^{k} f_p(r, v, t - i \Delta t),$$

which strongly depends on the granularity of $\Delta t$. A better approximation can be obtained by introducing an offset to each particle’s initial time variable, which is selected randomly from a uniform distribution $R_t = [-\frac{\Delta t}{2}, \frac{\Delta t}{2}]$. Thus, the sample nominally at time $t$ is actually an average of the property for a range of particles which have been undergoing transport for any times between $t - \frac{\Delta t}{2}$ and $t + \frac{\Delta t}{2}$. This reduces the dependence on $\Delta t$ whilst still ensuring that every particle is sampled at times that are distributed evenly over the length of the simulation.

To demonstrate the effect of this adjustment, two simulations have been performed with $k = 1000$ time slices, with and without the time offset adjustment. As this technique was first published as part of a liquid water simulations article [4], it uses the system parameters described in chapter 6, but the behaviour is general.

The first three time slices of the spatial density of the positrons are presented in figure 3.4, where the linear density distribution is given by $n_j(r_i) \approx n_{ij}/\Delta r$ and

$$n_{i,j} = \frac{4\pi}{n_p} \int_v \int_{r_i}^{r_{i+1}} f_p\left(r', v, t_j\right) r'^2 dr' d^3v.$$

The mean energy, analogous to $n_j(r_i)$, is integrated over time to give its steady-state value, $\epsilon_{SS}(r_i) = \sum_j \Delta t \epsilon_{j}(r_i)$, and is shown in figure 3.5. For $k = 1,000$, these distributions are shown with and without the time-offset included in the sampling procedure, and the accuracy can be judged by comparing to a case of $k = 10,000$ time slices. The time offset technique dramatically improves the convergence of the results, bringing the low resolution $k = 1000$ results into qualitative agreement with the high resolution $k = 10,000$ results.

3.7.3 Spatial volume scaling

For collision-specific outputs, such as ionisation energy deposition and positronium formation rates, samples are taken whenever a collision occurs and then assigned to sampling bins according to the radial distance of the positron from the positron source. Other outputs can be measured on a per-time basis but are similarly assigned spatial bins based on the radial position of the particle at that time. Since we are starting with a point source and simulating a spherically symmetric system, any volume-dependent properties such as radiation dosimetry have to be calculated using spherical shells for the volume. As an example let us consider the number of electrons per volume that are formed in ionisation...
Figure 3.4: Time evolution of a single pulse, where each curve represents a successive time slice. Dashed lines denote slices using the time-offset sampling technique described in section 3.7.2, while solid curves are instantaneous measurements.

Figure 3.5: The spatial profile of the mean energy of positrons in water, using the liquid water simulation parameters from chapter 6, section 6.5, but varying the number of time slices and the time-offset sampling behaviour as discussed in section 3.7.2.
events, which has a practical application in estimating the rate of DNA strand breaks due to ionising electrons. Whenever an ionisation event occurs, the statistical weight $w_i$ of the positron is added to an accumulator for the radial bin (spherical shell) corresponding to the positron’s current position. The accumulators can be used to form averages $N_{I,i} = \langle w_i \rangle$ where $i$ denotes the index of the radial bin and $\langle \cdots \rangle$ is an average over the particles simulated. The local density of ionisation events per positron per cubic meter is given by:

$$\rho_{I,i} = N_{I,i}/\Delta V_i,$$

where $\Delta V_i = \frac{4\pi}{3}(r_{i+1}^3 - r_i^3)$ is the volume of the shell. This can be generalised to a continuous density distribution $\rho_I(r)$, so that the total number of ionisation events inside a spherical volume of radius $R$ is given by $N_I = \int_0^R r^2 dr \int d\Omega \rho_I(r)$, where $\Omega$ integrates over all solid angles.

It is more useful to plot distributions as a function of radius only, scaling out the geometric $r^2$ dependence on shell volume. Hence, most results are shown using the distribution:

$$\bar{\rho}_{I,i} = N_{I,i}/(r_{i+1} - r_i),$$

such that the total number of ionisation events inside a spherical volume of radius $R$ is given by $N_I = \int_0^R dr \bar{\rho}_I(r)$. Note that $\rho_I(r) = \bar{\rho}_I(r)/4\pi r^2$. Analogous distributions can be formed for most other measurable quantities.

3.7.4 Hydrodynamic regime

In a drift-tube experiment, a source electrode emits a continuous flow of electrons which are accelerated to a collector electrode by a tuned electric field. The experiment is designed so that an equilibrium is reached in which the drift velocity and diffusion coefficients are uniform in space, when far enough from the starting electrode. In this volume, the system has evolved to a hydrodynamic regime and the hydrodynamic transport coefficients can be calculated with the above methods by averaging their values over the volume range in which they are constant.

However, it is more common to treat the equilibrium as being reached after a certain amount of time has passed for the particles. In a continuous source drift tube experiment, there can of course be no consideration of the age of a particle. It can be shown to be an equivalent problem however by reversing the arguments in section 3.7.1 to decompose the spatial average into a single pulse. Benchmarks such as Reid’s ramp (section 3.8.1) or Ness’ step model (3.8.2) can therefore be most easily represented in terms of an initial pulse and a time-dependent relaxation to the hydrodynamic regime. This in fact describes a simplified pulsed-Townsend experiment [109].

In a Monte Carlo simulation, determining when the system has reached a steady-state is not trivial. Individual collisions are stochastic in nature and do not precisely obey this balance, so the equilibrium state can only be obtained by studying the collective transport properties of the swarm as a whole. The collective swarm properties themselves
also fluctuate, but the system can be considered at equilibrium when the fluctuations of the quantity of interest are larger than any detectable trends.

Previous authors have taken different approaches to this problem. Skullerud’s early work on ion transport [110] does not discuss the equilibrium time, but does plot the diffusion coefficients as a function of time, so the starting time for the average quantities that he describes is probably based on a visual examination of the data. Similarly, Reid [111] chose somewhat arbitrarily to include the time samples from $\tau = 101$ to 200, saying only that the “the averages approached a limit quite quickly”. Nolan et al. [112] also decline to go into detail, however they use a variance reduction technique whereby after one electron has been simulated, subsequent electrons are released with the final energy of the previous electron, so that it is close to equilibrium already.

In this work, the equilibrium time has been determined in a similarly empirical manner. However, a test is performed on the resulting samples. Most distributions will converge asymptotically towards the equilibrium values. The system always has an inherent level of statistical noise as described below in section 3.7.5. If the distribution has converged to a constant value, the distribution of this noise will be an unbiased normal distribution. Figure 3.6 shows histograms of per-time mean energies for the 24 Td case of the Reid Ramp benchmark given in section 3.8.1, comparing the distribution of the entire run (including results prior to equilibrium) to a distribution of only those energies after the results have thermalised.
3.7.5 Statistical uncertainty

Theory

For equilibrium quantities, the goal is to estimate the mean value of properties of the electrons or positrons in the system, once the system has relaxed to an equilibrium state where such values are stationary. This can be achieved by recording the properties of a representative sample (subset) of the particles in the system, at several points in time. It is not possible to sample every particle in the system, as the model does not presuppose a limited supply of particles nor a finite time; Boltzmann equation solutions of the same system will leave both unspecified and implicitly calculate results in the limiting case of both infinite time and particle number. Furthermore, the time required to perform the Monte Carlo simulation scales linearly with both the number of particles sampled and the number of collisions that the particles undergo, so it is advantageous to minimise them.

The autocorrelation of the measurements informs us whether the measurements are sufficiently separated in time to be considered independent. Once the system has reached the hydrodynamic state, the distribution for a property such as mean energy becomes a strictly stationary process, which implies that the autocorrelation function $\rho(\tau)$ can be expressed as a function of the time difference between two measurements (denoted $\tau$), without reference to the absolute times involved. The estimate of the autocorrelation is calculated from the samples, $x = \{x_1, \ldots, x_n\}$, as:

$$\rho(\tau) = \frac{\sum_{i=1}^{n-h} (x_i - \bar{x})(x_{i+\tau} - \bar{x})}{\sum_{i=1}^{n} (x_i - \bar{x})^2},$$

where $\bar{x}$ is the mean of the samples. The denominator can be recognised as the summed variance of $x$. The autocorrelation can be further summarised with the Durbin-Watson statistic [113]:

$$d = \frac{\sum_{t=2}^{T} ((x_t - \bar{x}) - (x_{t+\tau} - \bar{x}))^2}{\sum_{t=1}^{T} (x_t - \bar{x})^2}.$$

This statistic is 2 for perfectly correlated data (e.g. $x = \text{const}$), and 0 for perfectly uncorrelated data. Negative values indicate a predominance of anti-correlation, where it is statistically more likely for corresponding samples to be on opposite sides of the mean than to be on the same side.

Mean and uncertainty

The sampled mean energy of the system, considered over the given temporal period, is simply the energy of each particle, at each time, divided by the number of particles. Even if the time samples are not independent, they are still representative of the energies of the simulated particles, and the electrons are still representative of the complete population, so that the mean of the sample remains an unbiased estimator of the mean of the population.

However, the uncertainty is somewhat harder to estimate when autocorrelation is significant. The Guide to the Expression of Uncertainty in Measurement [114] states that
type-A standard uncertainty can be defined as the square root of the unbiased estimator of the variance of the mean. Less formally, this is the square root of the variance of the means of all possible sets of samples that could be taken of the complete population. Provided that the samples are independent, it can be calculated as

$$u(x) = \sqrt{s^2(x)} = \sqrt{\frac{s^2}{n}},$$

(3.13)

where $s^2(x)$ is the (unbiased) estimator of the variance of the mean $x$, $s^2$ is the sample variance, and $n$ is the number of samples. However, sequential time samples from a Monte Carlo simulation can have significant autocorrelation, so that the samples are no longer independent and equation (3.13) drastically underestimates the uncertainty.

Based on the procedure outlined in Zięba [115], the uncertainty of the autocorrelated samples can be calculated directly. The autocorrelation factors, $\rho_k$ are used to compute the effective number of observations:

$$n_{\text{eff}} = \frac{n}{1 + 2 \sum_{k=1}^{n-1} \frac{n-k}{n} \rho_k}.$$

This quantity is an estimate of the number of independent samples that would give the same uncertainty as the present autocorrelated data. This is used to construct the sample variance for autocorrelated data, $s^2_a$, through a scaling factor:

$$s^2_a = Cs^2$$

with $C = \frac{n_{\text{eff}} (n - 1)}{n (n_{\text{eff}} - 1)}$,

which in turn leads to the estimator of the sample of the mean:

$$s^2_a(x) = \frac{s^2_a}{n_{\text{eff}}},$$

and finally, the type-A standard uncertainty (standard error) of

$$u_a = \sqrt{s^2_a(x)}.$$

**Benchmark**

Here, several examples of the uncertainty treatment are given. The base case is a Reid ramp model, discussed in section 3.8.1, with the following parameters:
Throughout this subsection, \( n \) is the number of time samples. This system has a well-known equilibrium mean energy of 0.41 eV and converges monotonically to that energy. The number of electrons is conserved, since there are no ionisation or attachment processes.

By modifying various measurement-related quantities, their impact on the autocorrelation and resulting uncertainty can be compared. Five variants have been tested. The \( t_{\text{end}}/10 \) simulation is run for a short period of time: since the number of time samples is held constant, the energy is sampled more frequently, but there is less time for the electrons to scatter between samples. The \( n \times 10 \) case uses ten times as many samples, over the same length of time, resulting in the same sampling rate as the previous variant, but for the same length of time as the base simulation. The last simulated variant is the \( N_{e-}/10 \) case, where fewer electrons are simulated, resulting in a statistically noisier sequence of samples. Two synthetic cases have also been constructed: the fully uncorrelated case, where samples are independently picked from a Gaussian distribution with the same parameters as a fit of the base case, and the “Sorted” case where results of the uncorrelated variant are sorted in ascending order, producing strong autocorrelation.

For each of the variants considered here, the mean energy samples are shown in figure 3.7. The inset sub-plot in that figure is a magnified view of a small range in the main plot, showing the changes in mean energy from one sample to the next. From the inset, it is clear that we can expect strong short-range autocorrelations, as the data consist of slowly varying trends. However, every simulation shows approximately the same sample mean, and the sample standard deviation is the same for all cases other than the \( N_{e-}/10 \) case.

The autocorrelations \( \rho_k \) are shown in figure 3.8, where they have been offset for clarity. Here we see that in all simulated cases, strong autocorrelations are restricted to time lags of less than about 1.6 ns. The longer range correlations are surprisingly strong, much more so than those of the purely uncorrelated case. The reasons for this are not clear. One would expect that if the long-range autocorrelations were due to the scattering rates or electric field acceleration rate of the electrons, the autocorrelations would strengthen with fewer electrons. However, this is not the case, as the \( N_{e-}/10 \) shows similar autocorrelations to
Figure 3.7: Sensitivity test for mean energy and its uncertainty, comparing different time samples and numbers of particles. Inset: zoomed-in view of the same data, showing short-range fluctuations.

Table 3.2: Table of uncertainty-related values for the simulation variants shown in figure 3.7.

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>$n \times 10$</th>
<th>$t_{\text{end}}/10$</th>
<th>$N_{\varepsilon}/10$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>9600</td>
<td>96000</td>
<td>6000</td>
<td>9600</td>
</tr>
<tr>
<td>$d$</td>
<td>0.00803</td>
<td>0.00058</td>
<td>0.00126</td>
<td>0.00688</td>
</tr>
<tr>
<td>$n_{\text{eff}}$</td>
<td>402.7</td>
<td>154.5</td>
<td>10.1</td>
<td>155.8</td>
</tr>
<tr>
<td>$\bar{\varepsilon}$ (eV)</td>
<td>0.4107</td>
<td>0.4113</td>
<td>0.4122</td>
<td>0.4121</td>
</tr>
<tr>
<td>$u$ (meV)</td>
<td>0.0241</td>
<td>0.00882</td>
<td>0.0239</td>
<td>0.0824</td>
</tr>
<tr>
<td>$u_a$ (meV)</td>
<td>0.118</td>
<td>0.221</td>
<td>0.613</td>
<td>0.649</td>
</tr>
</tbody>
</table>

the “Base” case. Similarly, the autocorrelations do not depend on the sampling rate, with “$n \times 10$” giving similar results to the base case. Further study is required to determine what, if any, is the significance of this phenomenon.

Throughout this thesis, all time-invariant quantities have been treated in this manner to determine their uncertainty, and the error, where quoted, is the quantity $u_a$.

3.8 Benchmarks

3.8.1 Reid’s ramp model

A very simple benchmark system is the “ramp” model of Reid [111], in which a constant elastic cross section is combined with an inelastic cross section which increases linearly after some threshold, and the system is subject to a constant electric field. This benchmark is widely used due to the known failure of the two-term approximation solution of Boltzmann’s
equation for this collision model. As discussed in 3.7.4, this can be considered a type of pulsed-Townsend system, where the electrons are released all at once and the properties are tracked as a function of time. Given sufficient time, the system reaches a hydrodynamic equilibrium, where the momenta and energy gained by the particles due to the electric field are, on average, balanced by the momenta and energy lost by the particles in collisions with the neutrals. In this system, as in most hydrodynamic systems, the dependent variable is $E/n_0$, the reduced field strength. This is conventionally expressed in Townsends, where $1 \text{Td} = 1 \times 10^{-21} \text{ V m}^2$.

This tests the simulation’s implementation of electric fields (section 3.3) and simple elastic and fixed inelastic scattering (section 3.2.2). Because it reaches a stable hydrodynamic equilibrium, it is also a simple test of the uncertainty estimation and equilibrium testing procedures as discussed previously, and further below.

The physical parameters of the system are as follows:

$$
\begin{align*}
\sigma_{el} (\varepsilon) &= 6 \text{Å}^2 \\
\sigma_{inel} (\varepsilon) &= \begin{cases} 
10(\varepsilon - \varepsilon_i) \text{Å}^2 & \varepsilon \geq \varepsilon_i \\
0 & \varepsilon < \varepsilon_i
\end{cases} \\
\varepsilon_i &= 0.2 \text{eV} \\
m_0 &= 4 \text{amu} \\
T &= 0 \text{K} \\
n_0 &= 1 \times 10^{17} \text{cm}^{-3}.
\end{align*}
$$

(3.14)
Figure 3.9: Thermalisation of the mean energy versus time for $E/n_0 = 24\,\text{Td}$ for the Reid’s ramp model, defined in equation (3.14). Inset: comparison of mean and standard error of the present results (red, and light red respectively), with the results of each of the alternative studies.

It is common to express model cross sections as functions of the collision energy, which is often dimensionally incorrect, as is the case for the inelastic cross section shown here. The implied meaning is invariably that the values within the cross section definition are dimensionless multiples of $1\,\text{eV}$. For example:

$$\sigma_{\text{inel}}(1.2\,\text{eV}) = 10 \times (1.2 - 0.2)\,\text{Å}^2 = 10\,\text{Å}^2.$$ 

The simulations were performed for several strengths of electric field, and in each case were allowed to continue until the system reached a hydrodynamic equilibrium, where the amount of energy lost to collisions is balanced by the amount of energy gained due to the electric field. Table 3.3 lists the results of these simulations, as well as comparisons with the Monte Carlo results of Reid [111], Brennan and Raspopović [99], and the Boltzmann equation solution of White [65]. All of the results are in close agreement, and are within the uncertainties of the simulation. Figure 3.9 demonstrates the convergence over time towards the equilibrium mean energy for the 24 Td case, with an inset diagram showing a comparison with the aforementioned results.

There are two systematic issues that may invalidate the results, if not treated carefully. Firstly, it is necessary to identify the time at which the system reached equilibrium. The criterion for reaching equilibrium is given in section 3.7.4, and involves some trial and error. For the ramp model, the system converges exponentially towards the steady state and
Table 3.3: Coefficients resulting from simulations of Reid’s ramp model. The present MC results are compared with those of Reid’s MC simulation (where available) [111], Brennan’s MC simulation, Raspopović’s MC simulation, [99] and White’s Boltzmann equation solutions [65].

<table>
<thead>
<tr>
<th>$E/n_0$</th>
<th>Author</th>
<th>$\bar{\varepsilon}$ (eV)</th>
<th>$W$ ($10^4$ms$^{-1}$)</th>
<th>$n_0D_\parallel$ ($10^{24}$m$^{-1}$s$^{-1}$)</th>
<th>$n_0D_\perp$ ($10^{24}$m$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reid</td>
<td>0.1013</td>
<td>1.255</td>
<td>-</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>Brennan</td>
<td>0.1015</td>
<td>1.271</td>
<td>0.757</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>0.1015</td>
<td>1.272</td>
<td>0.7591</td>
<td>0.9751</td>
</tr>
<tr>
<td></td>
<td>Raspopović</td>
<td>0.1017</td>
<td>1.273</td>
<td>0.7575</td>
<td>0.966</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>0.1015</td>
<td>1.271</td>
<td>0.7588</td>
<td>0.9749</td>
</tr>
<tr>
<td>12</td>
<td>Reid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Brennan</td>
<td>0.2693</td>
<td>6.833</td>
<td>0.5816</td>
<td>1.138</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>0.2689</td>
<td>6.838</td>
<td>0.5688</td>
<td>1.135</td>
</tr>
<tr>
<td></td>
<td>Raspopović</td>
<td>0.2703</td>
<td>6.834</td>
<td>0.5690</td>
<td>1.140</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>0.2691</td>
<td>6.834</td>
<td>0.5687</td>
<td>1.134</td>
</tr>
<tr>
<td>24</td>
<td>Reid</td>
<td>0.413</td>
<td>9.5</td>
<td>-</td>
<td>1.194</td>
</tr>
<tr>
<td></td>
<td>Brennan</td>
<td>0.4058</td>
<td>8.878</td>
<td>0.4684</td>
<td>1.141</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>0.4079</td>
<td>8.886</td>
<td>0.4609</td>
<td>1.134</td>
</tr>
<tr>
<td></td>
<td>Raspopović</td>
<td>0.4113</td>
<td>8.804</td>
<td>0.4546</td>
<td>1.131</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>0.4111</td>
<td>8.882</td>
<td>0.4606</td>
<td>1.134</td>
</tr>
</tbody>
</table>

remains there indefinitely, so it is relatively easy to determine. Secondly, the sampling of the collision frequency is not exact, due to the presence of the electric field, and is subject to small deviations which depend on the width of the energy bins used. This was compensated for by performing simulations with ever finer energy resolutions until the results were stable.

3.8.2 Ionisation energy-sharing models

A more advanced model includes variable energy losses due to ionisation. When an electron or positron interacts with a molecule and ionises it, an outer shell electron is pulled free of the target molecule. This electron retains some energy and momentum, which has several consequences for transport simulations. Insofar as the simulations are concerned, ionisation collisions are characterised by relatively large, variable energy transfers. Furthermore, as an additional electron is ejected from the collision, the number of electrons in the simulation is increased.

When positrons are the transport particle, these ejected electrons can be stored as initial particle states for a second simulation if necessary. If one is primarily interested in the positronium formation processes, it suffices to know how much energy is lost in the ionisation event. If an excessive number of electrons is produced, it may be necessary to approximate their distribution instead.

When electrons are the transport particle, the ejected electrons are treated as indistinguishable from the primary particles. If the ionisation rate is high, the number of electrons in the simulation can possibly increase to impractical levels. A simple solution to this difficulty can be found in a variation of the attachment variance reduction technique discussed in section 3.4. Whenever an ionisation event occurs, one of the two resulting electrons is picked at random to be tracked for the remainder of the simulation, and its
statistical weight is doubled; this preserves the distribution of electrons, while maintaining the initial number of particles to be tracked.

This section largely summarises Boyle et al. [8], where both a Boltzmann equation solution and the present Monte Carlo code were applied to a simple benchmark system, before comparing increasingly sophisticated implementations of how the collision energy may be split between the initial positron and the secondary electron.

Ness’ step model

The simplest ionisation model shown here is one proposed by Ness and Robson [100], in which the energy partitionings of the ionisation interaction were investigated.

\[
\sigma_{el}^0 - \sigma_{el}^l = 10 \text{ Å}^2, \tag{3.15}
\]

\[
\sigma_{in}^l = \begin{cases} 
1 \text{ Å}^2 & \varepsilon \geq 10 \text{ eV}, \\
0 & \varepsilon < 10 \text{ eV}, 
\end{cases}
\]

\[
\sigma_{ion}^l = \begin{cases} 
1 \text{ Å}^2 & \varepsilon \geq 15 \text{ eV}, \\
0 & \varepsilon < 15 \text{ eV}, 
\end{cases}
\]

\[m_0 = 25 \text{ amu,}\]

\[T_0 = 0 \text{ K}.\]

The energy sharing ratio \(Q\) is defined as:

\[Q = \frac{\varepsilon'}{\varepsilon - \varepsilon_I},\]

where \(\varepsilon\) and \(\varepsilon'\) are the energies of the primary particle respectively before and after the collision and \(\varepsilon_I\) is the threshold energy for ionisation, which for this model is 15 eV. For electrons, ionisation is non-conservative and two indistinguishable electrons leave the event. As such, \(Q\) is symmetric about 0.5 for electrons. Beyond what was tested above with Reid’s ramp model, this model additionally tests the treatment of ionisation energy sharing of section 3.2.2 and, in the case of electrons, the variance reduction technique of section 3.4.

This model was simulated at a range of \(Q\) for both electrons (table 3.4) and positrons (table 3.4). The uncertainty in the Monte Carlo simulations is estimated to be less than 1% for the ionisation collision rates, and less than 0.5% (generally less than 0.3%) for the drift velocity and mean energy. The two approaches give \(\alpha_{ion}/n_0, \bar{\varepsilon}\) and \(W\) values which differ by less than 0.6%, 0.3% and 0.3% respectively, over the range of reduced electric fields and available energy fractions, all of which are within the corresponding Monte Carlo uncertainty. The close agreement supports the validity of both Boltzmann equation and Monte Carlo simulations. As the reduced field is increased, the particles accelerate more rapidly and the higher portions of the cross sections are more frequently sampled, leading to a higher rate of ionisation and consequently a stronger dependence on the energy sharing ratios.
Table 3.4: Comparison of average ionisation rate $\alpha^{\text{ion}}/n_0$, mean energies $\bar{\epsilon}$, and bulk drift velocities $W_{\text{bulk}}$ for electron impact ionisation for Ness’ step model (equation (3.15)) for different reduced fields $E/n_0$ and energy sharing fractions $Q$. The first column lists the kinetic theory results from [8], the second column lists the results of the present Monte Carlo simulations, and the third includes the kinetic theory calculations of Ness and Robson [100]. $Q = \text{AFE}$ corresponds to ‘all fractions equiprobable’. The values enclosed in square brackets have been recalculated using a similar Burnett function expansion to that of Ness and Robson, since there was an error in the AFE case in the original Ness and Robson work.

<table>
<thead>
<tr>
<th>$E/n_0$ (Td)</th>
<th>$Q$</th>
<th>$\alpha^{\text{ion}}/n_0$ $(10^{-15} \text{m}^3\text{s}^{-1})$</th>
<th>$\bar{\epsilon}$ (eV)</th>
<th>$W_{\text{bulk}}$ $(10^5 \text{ms}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Boyle KT</td>
<td>MC</td>
<td>[100]</td>
<td>Boyle KT</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>1.620</td>
<td>1.61</td>
<td>6.739</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>1.598</td>
<td>1.61</td>
<td>6.737</td>
</tr>
<tr>
<td></td>
<td>1/3</td>
<td>1.595</td>
<td>1.596</td>
<td>6.739</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1.591</td>
<td>1.589</td>
<td>6.742</td>
</tr>
<tr>
<td></td>
<td>AFE</td>
<td>1.600</td>
<td>1.606</td>
<td>6.733</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>4.643</td>
<td>4.68</td>
<td>9.009</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>4.504</td>
<td>4.51</td>
<td>9.007</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>4.464</td>
<td>4.452</td>
<td>9.017</td>
</tr>
<tr>
<td></td>
<td>AFE</td>
<td>4.511</td>
<td>4.525</td>
<td>9.000</td>
</tr>
</tbody>
</table>
Table 3.5: Comparison of transport coefficients for positrons using Ness’ step model (equation (3.15)). All other details are as per 3.4.

<table>
<thead>
<tr>
<th>$E/n_0$ (Td)</th>
<th>$Q$</th>
<th>$\alpha^\text{kn}/n_0$ $(10^{-15} \text{m}^3\text{s}^{-1})$</th>
<th>$\varepsilon$ (eV)</th>
<th>$W$ $(10^3 \text{ms}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Boyle KT</td>
<td>MC</td>
<td>Boyle KT</td>
<td>MC</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>1.711</td>
<td>6.869</td>
<td>2.767</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>1.720</td>
<td>1.718</td>
<td>6.919</td>
</tr>
<tr>
<td></td>
<td>1/3</td>
<td>1.725</td>
<td>1.719</td>
<td>6.940</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1.740</td>
<td>1.739</td>
<td>6.983</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>1.757</td>
<td>1.761</td>
<td>7.021</td>
</tr>
<tr>
<td></td>
<td>3/4</td>
<td>1.767</td>
<td>1.774</td>
<td>7.041</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.807</td>
<td>1.804</td>
<td>7.098</td>
</tr>
<tr>
<td>AFE</td>
<td>1.745</td>
<td>1.739</td>
<td>6.979</td>
<td>6.981</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>4.856</td>
<td>6.910</td>
<td>2.767</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>5.060</td>
<td>5.055</td>
<td>9.579</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>5.211</td>
<td>5.208</td>
<td>9.716</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.565</td>
<td>5.599</td>
<td>10.03</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>9.903</td>
<td>13.30</td>
<td>5.260</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>10.21</td>
<td>10.23</td>
<td>13.75</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>10.84</td>
<td>10.83</td>
<td>14.32</td>
</tr>
<tr>
<td></td>
<td>2/3</td>
<td>11.40</td>
<td>11.41</td>
<td>14.79</td>
</tr>
<tr>
<td></td>
<td>3/4</td>
<td>11.68</td>
<td>11.70</td>
<td>15.07</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>12.92</td>
<td>12.95</td>
<td>16.27</td>
</tr>
</tbody>
</table>

Boyle sharing model

Boyle et al. [8] have developed a more sophisticated model for energy partitioning, which is designed to exhibit the following behaviours:

1. At high energies, the scattered positron leaves the collision with almost all of the energy which is available post-collision.

2. For impact energies near the ionisation threshold, it is assumed that there is near equal energy-sharing. It is interesting to note that the positron and electron escape in similar directions with similar energies and are highly correlated, so no clear distinction between ionisation and continuum state positronium can necessarily be made [23].
3. Ionisation at intermediate energies is treated as a combination of the above two effects, i.e. a strong peak in the energy-sharing distribution corresponding to the scattered positron leaving with all the available energy, and a second peak occurring when the positron and electron emerge with similar energy.

A set of parameterised analytic functions was designed to emulate this behaviour, consisting of an exponentially decaying function $g_{\text{high}}(Q)$ at high impact energies, a Lorentz distribution $g_{\text{low}}(Q)$ centred on $Q = 0.5$ for low impact energies, and a smoothly varying weighting function, $w(\varepsilon)$, where $\varepsilon$ is specified in eV, connecting the two:

$$g_{\text{high}}(Q) = A_{\text{high}} \exp(\beta_{\text{high}} Q),$$  \hspace{1cm} (3.16)

$$g_{\text{low}}(Q) = A_{\text{low}} \left[ \frac{1}{\beta_{\text{low}}^2 + (Q - 0.5)^2} \right]^{-1},$$  \hspace{1cm} (3.17)

$$g(\varepsilon, Q) = w(\varepsilon) g_{\text{high}}(Q) + (1 - w(\varepsilon)) g_{\text{low}}(Q),$$  \hspace{1cm} (3.18)

$$w(\varepsilon) = \frac{1}{2} \left[ 1 + \tanh (\gamma (\varepsilon - \varepsilon_1) - \delta) \right],$$  \hspace{1cm} (3.19)

This results in a probability density function that is a function of the positron energy $\varepsilon$. Values for the various parameters are given for a test model:

$$\beta_{\text{high}} = 10,$$

$$\beta_{\text{low}} = 0.05,$$

$$\gamma = 0.05,$$

$$\delta = 3.5,$$

while $A_{\text{low}}$ and $A_{\text{high}}$ are normalisation constants. The resulting $g(\varepsilon, Q)$ has been used to calculate transport coefficients at several reduced field strengths, which are shown in table 3.6. For the 800 Td and 5000 Td cases, the superscripts $a$ and $b$ in that table represent alternative versions of the model where only $g_{\text{low}}$ or $g_{\text{high}}$, respectively, is used over the entire energy range. At 800 Td, the swarm properties for the full energy-partitioning model are close to those which result from the inclusion of only $g_{\text{low}}$, which indicates that the distribution is mostly sampling the equal energy-sharing part of the full energy-partitioning distribution. At the higher field of 4000 Td the swarm properties are now close to those that come from allowing only $g_{\text{high}}$ to have an effect. As the field has increased, the distribution has shifted from sampling mostly the even sharing region, to the region that is heavily biased towards the positron getting large amounts of available energy.
Table 3.6: Comparison of average ionisation rate, $\alpha_{\text{ion}}/n_0$, mean energies, $\bar{\varepsilon}$, and flux drift velocities, $W$, for positron impact ionisation for model (3.20). The superscripts $a$ and $b$ refer to $w(\varepsilon) = 0$ and $w(\varepsilon) = 1$ respectively. Columns ‘Boyle KT’ correspond to the kinetic theory of Boyle et al. [8], and columns ‘MC’ are the results of the present Monte Carlo simulation.

<table>
<thead>
<tr>
<th>$E/n_0$ (Td)</th>
<th>$\alpha_{\text{ion}}/n_0$ $(10^{-15} \text{m}^3\text{s}^{-1})$</th>
<th>$\bar{\varepsilon}$ (eV)</th>
<th>$W$ $(10^5 \text{ms}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Boyle KT</td>
<td>MC</td>
<td>Boyle KT</td>
</tr>
<tr>
<td>800$^a$</td>
<td>10.86</td>
<td>10.85</td>
<td>14.35</td>
</tr>
<tr>
<td>800$^b$</td>
<td>12.48</td>
<td>12.37</td>
<td>15.82</td>
</tr>
<tr>
<td>1600</td>
<td>26.29</td>
<td>26.26</td>
<td>34.12</td>
</tr>
<tr>
<td>2400</td>
<td>40.97</td>
<td>40.88</td>
<td>65.56</td>
</tr>
<tr>
<td>3200</td>
<td>53.97</td>
<td>53.85</td>
<td>104.1</td>
</tr>
<tr>
<td>4000</td>
<td>64.95</td>
<td>64.90</td>
<td>144.8</td>
</tr>
<tr>
<td>4000$^a$</td>
<td>49.18</td>
<td>49.11</td>
<td>86.49</td>
</tr>
<tr>
<td>4000$^b$</td>
<td>66.96</td>
<td>66.64</td>
<td>149.5</td>
</tr>
</tbody>
</table>

3.8.3 Attachment model

Positronium formation is a critical process in positron applications, and so it is important to ensure that loss processes are correctly accounted for in the Monte Carlo simulation. As discussed in section 3.4, loss processes pose a particular challenge for Monte Carlo simulations, because the naive approach of simply removing the particle from the simulation makes it difficult to build up enough measurements to accurately sample the swarm at later times. Instead, the present code uses a variance reduction technique where the particles are treated as having survived every collision, but are statistically weighted to account for their low probability of doing so. It is important to test that this technique works, especially since despite its simplicity it does not appear to have been used in the literature for lepton scattering (although an analogous technique has been used in neutron and photon scattering for many years, e.g. [116]).

Ness and Robson [100] proposed a power-law loss process benchmark model, which has been replicated and extended in a number of studies [117,118]. This model uses a Maxwell model elastic cross section (constant collision frequency), as well as an attachment (loss) cross section:

\[
\begin{align*}
\sigma_{\text{el}} (\varepsilon) &= 10\sqrt{\varepsilon} \text{Å}^2 \\
\sigma_{\text{loss}} (\varepsilon) &= a \varepsilon^p \text{Å}^2 \\
m_0 &= 16 \text{amu} \\
E/n_0 &= 0.4 \text{Td} \\
T_0 &= 293 \text{K},
\end{align*}
\]

where $a$ and $p$ are tunable parameters.

This model has a non-zero background temperature, and as such is also a test of the approximate thermal neutral treatment described in section 3.2.2. Because the total
cross section is (a perturbation of) a Maxwell model with constant collision frequency, the approximate thermal model is sufficient in this case. A more precise model, discussed in section 5.4.6 of chapter 5, must be used when the collision frequency varies with energy.

For $p = \frac{1}{2}, -\frac{1}{2}, -1$, the transport coefficients have been calculated for various values of the attachment amplitude $a$, and listed in table 3.7. These coefficients include both flux and bulk transport coefficients, as defined in 3.6, which can differ significantly when attachment collisions can occur. Briefly, the flux drift velocity is defined as the average velocity of each of the particles in the swarm, while the bulk drift velocity is the average velocity of the centroid of the swarm, and the flux and bulk diffusion coefficients are the higher-order extension of this relation.

When $p = \frac{1}{2}$, the loss process occurs more often as the energy is increased, which means that there is a preference for high-energy particles to be lost from the swarm. This leads to a lowering of the average energy compared to the system without any loss process, a phenomenon called “attachment cooling”. This also shifts the centroid of the swarm as an additional effect beyond the existing flux drift velocity, and so the bulk drift velocity is somewhat lower than the flux drift velocity. The reverse process, “attachment heating”, occurs when $p = -1$, where lower energy particles are preferentially removed, and the bulk quantities are increased relative to the flux quantities. When $p = -\frac{1}{2}$, the collision frequency of attachment events is constant with energy, and particles are lost from all parts of the energy spectrum with equal probability, in which case the bulk and flux quantities are identical.

3.8.4 Other benchmarks

Numerous other minor benchmarks have been conducted but not discussed here, in most cases testing only a subset of the features validated above. However, additional benchmarks are given in chapter 5, where static and dynamic structure effects are added. One of the structure benchmarks, in section 5.3.4 of that chapter, also tests the non-hydrodynamic spatial steady-state features of the simulation with both dilute and dense media.
Table 3.7: Transport coefficients for some variations of the Ness and Robson [100] attachment model defined in equation (3.21). Present Monte Carlo results (MC) are compared with the Boltzmann equation results (BE) of [117]. Uncertainty was not recorded for either dataset.

<table>
<thead>
<tr>
<th>p</th>
<th>*</th>
<th>1/2</th>
<th>1</th>
<th>-1/2</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>1 x 10^{-3}</td>
<td>1 x 10^{-1}</td>
<td>1 x 10^{-5}</td>
<td>5 x 10^{-4}</td>
</tr>
<tr>
<td>α/ν₀</td>
<td>MC</td>
<td>0</td>
<td>80.1</td>
<td>2070</td>
<td>5.8</td>
</tr>
<tr>
<td>[10^{-20}m³s⁻¹]</td>
<td>BE</td>
<td>0</td>
<td>80.92</td>
<td>2079</td>
<td>5.931</td>
</tr>
<tr>
<td>¯ε</td>
<td>MC</td>
<td>0.1545</td>
<td>0.1362</td>
<td>0.1516</td>
<td>0.187</td>
</tr>
<tr>
<td>[eV]</td>
<td>BE</td>
<td>0.1591</td>
<td>0.1355</td>
<td>0.1502</td>
<td>1.195</td>
</tr>
<tr>
<td>Flux</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>MC</td>
<td>1.186</td>
<td>1.186</td>
<td>1.186</td>
<td>1.186</td>
</tr>
<tr>
<td>[10³ms⁻¹]</td>
<td>BE</td>
<td>1.186</td>
<td>1.186</td>
<td>1.186</td>
<td>1.186</td>
</tr>
<tr>
<td>ν₀D_T</td>
<td>MC</td>
<td>3.053</td>
<td>2.699</td>
<td>0.6921</td>
<td>3.058</td>
</tr>
<tr>
<td>[10²³m⁻¹s⁻¹]</td>
<td>BE</td>
<td>3.055</td>
<td>2.697</td>
<td>0.6929</td>
<td>3.055</td>
</tr>
<tr>
<td>ν₀D_L</td>
<td>MC</td>
<td>3.054</td>
<td>2.678</td>
<td>0.6921</td>
<td>3.052</td>
</tr>
<tr>
<td>[10²³m⁻¹s⁻¹]</td>
<td>BE</td>
<td>3.055</td>
<td>2.698</td>
<td>0.6926</td>
<td>3.055</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>MC</td>
<td>1.186</td>
<td>0.9340</td>
<td>0.1512</td>
<td>1.193</td>
</tr>
<tr>
<td>[10³ms⁻¹]</td>
<td>BE</td>
<td>1.186</td>
<td>0.9375</td>
<td>0.1518</td>
<td>1.186</td>
</tr>
<tr>
<td>ν₀D_T</td>
<td>MC</td>
<td>3.064</td>
<td>2.412</td>
<td>0.3932</td>
<td>3.045</td>
</tr>
<tr>
<td>[10²³m⁻¹s⁻¹]</td>
<td>BE</td>
<td>3.055</td>
<td>2.414</td>
<td>0.3910</td>
<td>3.055</td>
</tr>
<tr>
<td>ν₀D_L</td>
<td>MC</td>
<td>3.064</td>
<td>1.715</td>
<td>0.1212</td>
<td>3.052</td>
</tr>
<tr>
<td>[10²³m⁻¹s⁻¹]</td>
<td>BE</td>
<td>3.055</td>
<td>1.730</td>
<td>0.1007</td>
<td>3.055</td>
</tr>
</tbody>
</table>

68
Simulations of pulses in a buffer gas positron trap

This chapter consists primarily of material that has been previously published in the following journal article:


All of the work presented here is my own.

4.1 Introduction

Studies in low-energy positron interactions require a high-resolution source of positrons, as achieved for example in the “Surko” buffer gas positron trap [45, 75, 119], which is a type of Penning trap designed to thermalise positrons in a mixture of buffer gases. A similar trap has been developed for the positron beamlines at the Australian National University (ANU). The general principles and operation of the trap has been extensively described in the literature and outlined in chapter 1, and will not be discussed here. While it is possible to improve the resolution of the beam by adjusting the operation of the trap, such adjustments have hitherto been made on a mostly empirical basis. Previous models have mostly focused on the thermalisation behaviour of the trap, including the cooling time and efficiency [120]. The time-dependent effects of the ‘dump’ stage of the trap have largely been ignored, although the behaviour of this stage effectively determines the energy and time resolution of the final beam.

The content of this chapter has previously been published in [1]. Since then, a comprehensive article by Natisin et al. [121] has been published which largely supersedes the work done here. A brief Monte Carlo investigation by Marjanović et al. [120] is mostly
complementary to the work shown in this chapter: the authors in that case do not consider
the dumping stage of trap, but instead simulate the thermalisation of the positrons in the
earlier stages. Finally, the PhD thesis of Machacek [76] contains some simulations as well
as several experimental investigations of the buffer gas positron trap.

This system can be simulated using the Monte Carlo simulation code described in
chapter 3. Prior to the original publication of this work, there were no published studies of
the arbitrary time-dependent electric fields that exist during the dump stage of the trap.
This chapter describes modelling directed to that end.

4.2 Simulation procedure

Most details of the simulation are as described in chapter 3, and will not be repeated
here. Since the purpose of the simulation is to model the axial behaviour of the positrons,
no magnetic fields are included. Electric fields are included, but only in the form of
instantaneous axial changes in potential (“potential walls”). This introduces a second form
of collision, where a positron “collides” with a change in potential. This is a simpler, less
computationally intensive approach than the continuous electric fields described in chapter
3, yet it is a close approximation of the working design of the trap.

To determine the time until such a collision occurs, the distance between the positron
and the next wall that it could collide with is divided by the positron’s axial speed. This
time is compared to the time until the next gas collision. The particle travels in free-flight
for the smaller of these two times and then undergoes the corresponding collision type.
After each collision, the time to the next wall collision is recalculated from the particle’s
new speed and direction.

When a wall collision occurs, one of two processes may occur. If the positron has a
sufficient axial velocity, it will pass over this wall, gaining or losing axial velocity as required
to maintain conservation of energy. If it has not, then it reflects off the wall in a perfectly
elastic collision that simply reverses the sign of the axial velocity. The time until the
next gas collision is reduced by the time spent travelling to the potential wall, and if the
particle’s energy has changed, it is then rescaled according to the collision frequency at the
particle’s new energy.

The simulation includes time-dependent effects by allowing the height of the potentials
to vary with time while maintaining a zero electric field between the potential walls. Thus
motion between the potential walls is essentially free and kinetic energy is conserved, so the
rate at which particles collide with the gas remains unchanged, simplifying the simulation
considerably.

4.3 Simulation parameters

The simulation was started with the positrons positioned within the dumping electrode, with
an average energy equal to that of the gas within the trap, which is at 23°C. It is initially
assumed that the positrons have thermalised with the trap gases when the simulation
begins, which is the ideal case. A virtual micro-channel plate detector (MCP) was placed two metres from the dumping electrode, as it is in the experiment. The virtual MCP was implemented by adding a zero-potential electrode and simply halting the simulation of each positron when it passed the end of it. If, by the end of the simulation, the positron has not passed the end of the electrode, it is considered lost since this means it has not been ejected from the trap by the dumping electrode. For the purposes of the simulation, the potentials were assumed to have infinitesimal edge widths, and an instantaneous slew rate (a more precise description, with non-zero edge widths, can be found in Machacek’s thesis [76]). Since the simulation was run with positrons that had already been cooled, the loading and cooling phases of the trap were not simulated. The energy and time at which each particle reached the detector was recorded. This allowed the reconstruction of the pulse shape curve and energy cutoff curves that are produced by the experiment.

The pulse shape curve is constructed by measuring the counts of positrons that strike the virtual MCP in consecutive time-intervals. In the experiment, this curve is usually constructed by summing several pulses since the number of positrons passing through a single cycle of the trap would not produce precise statistics. In the simulation, this is unnecessary, since as many positrons as required can be simulated in a single cycle. In the experiment, summing multiple pulses unfortunately introduces some error as the pulses may not be synchronised perfectly. Note that in the experiment, there is no information on the number of positrons. Since the MCP operates through a cascade of electrons, the measured current cannot easily be related to the absolute number of positrons. However, the relative numbers of positrons at different energies should be correct.

As discussed in section 2.3 of chapter 2, the energy cutoff curve is a measure of the energies of the positrons that strike the MCP. In the experiment, it is measured by using a Retarding Potential Analyser (RPA) to prevent positrons of a lower energy from passing through to the MCP. By scanning through a range of potentials, the RPA can be used to construct an array of the relative abundances of positrons at each energy. It follows that the positron counts must be monotonically decreasing as the RPA potential increases, since the RPA is blocking an increasing proportion of the beam. This is reflected in the simulation in terms of a cumulative distribution of positron energies. As with the above pulse timing curve, the experimental energy cutoff curve is constructed by summing several pulses, but in this case time synchronisation is not an issue because the RPA is controlled by the same timing circuits as the measurement.

4.4 Results

Comparisons between experiment and simulation of the pulse shape and energy cutoff curves are shown in figure 4.1. For the pulse shape, one could only claim qualitative agreement between simulation and experiment. As discussed by Natisin et al. [121], differences may arise from the shape of the potential in the last part of the trap, and are also likely compounded by the response rates of the detector and amplifier. Nevertheless, it is reasonable to hope that tuning parameters for improvements in the simulation results can have a similar effect.
Figure 4.1: Comparison between experiment and simulation (a) pulse time profiles and (b) energy cutoffs. All simulation parameters are equal to those known for the experiment. Total gas pressure is 1.1 mTorr, ramping profile is logarithmic, starting at \(-4\) V and increasing to 62 V. The final potential wall is set to 61 V. Positrons are initially thermalised to 300 K. There is presently no convenient way to synchronise the experiment output with the trapping cycle, so the time between the start of the dumping phase and the start of the pulse is unknown. In figure (a), the time of the peak of the experimental pulse has been arbitrarily set to be the same as that of the simulated pulse. Figure (b) does not suffer from this problem.

on experimental results. The energy cutoff shows better agreement, although it is shifted by approximately 0.2 V, which may be indicative of a mismatch between the calibrations of the RPA and the final electrode of the trap, or due in part to other factors such as contact potential differences. It should be noted that this energy cutoff is used for calibrating the experiment every time a set of data is measured, so this energy drift is known and the analysis of the results compensates for it. All in all, one could claim only a qualitative agreement with experiment, but it is nevertheless felt that these initial results help provide physical insight and may prove a useful starting point for optimal tuning of experimental parameters, as outlined in the rest of this chapter.

Several variations on the parameters of the system were considered, with the aim of determining better configurations of the system for optimal pulse shapes. In particular, investigations were made into the effects of the gas density within the trap, the initial positron energy distribution (i.e. thermal distributions at different temperatures) immediately prior to the dumping phase, and the timing of the dumping profile.

4.4.1 Effect of trapping gas density

The simulation was then run again with different gas densities, ranging from no gas at all to a density one thousand times greater than that of the experiment. The effect was to broaden the time and energy distribution of the resultant pulse. This behaviour is to be expected, as collisions with gas molecules can either increase or decrease the time that the positron remains in the dumping stage of the trap, and this increase in variability manifests as a broadening of the curve. The presence of gas does not affect the average energy of the emitted positrons, since the effect is symmetric: positrons which would otherwise leave the trap can collide with a gas molecule and remain in the trap, but positrons which have a
velocity taking them away from the exit of the trap can likewise collide with a gas molecule and hence leave the trap much sooner.

One point of interest is that when the positrons and gas molecules are at the temperature and pressure used in the experiment, the total collision frequency is of the order of $10^5$ Hz. This means there are on the order of 10 gas collisions per positron during the dumping time of the trap (which is 650 $\mu$s), which has a negligible effect on any of the properties of the produced pulse.

Comparisons of the pulse shapes and energy cutoffs are shown in figure 4.2. For the purposes of experiment, a lower gas density is desirable, but this must be balanced against the rate at which thermalisation occurs during the cooling phase.

4.4.2 Effect of initial positron energy distribution

The above simulations were run assuming that the positrons were thermalised with the background gas, at room temperature, when the dumping phase started. This is the case in experiment if the positrons are allowed to cool for a sufficient time. The effects of increasing the average initial energy were simulated for a range of temperatures, from completely thermalised up to a completely uncooled beam that retains an isotropic velocity spread corresponding to 1.5 eV of kinetic energy.

Since higher energies result in a higher collision frequency, gas molecule interactions have a larger impact on the results of the simulation in precisely the same manner that they do in the earlier gas density variations. To avoid conflating these interaction effects with the effects of faster positrons in the time-dependent potential, the gas density was set to zero.

Figure 4.3 shows a comparison of pulse timing and energy cutoffs. A lower initial positron temperature results in less variability in the energies and times at which the positrons are detected. However, the lower velocities of the positrons mean that they travel across the dumping potential relatively slowly and hence have less frequent opportunities to escape the trap, which can lead to a larger energy spread. This is further discussed in the next section.
4.4.3 Effect of dump ramp profile

At room temperature, the average energy of a positron is given by $\varepsilon = \frac{3}{2}kT \approx 0.0388\;\text{eV}$, with a corresponding average speed of $v = \sqrt{\frac{2\varepsilon}{m_e}} \approx 116\;\text{794}\;\text{ms}^{-1}$. The average velocity component along the axis of the beamline is therefore $v_z = v/\sqrt{3} \approx 67\;\text{431}\;\text{ms}^{-1}$. The width of the dumping electrode is 6 cm, so the positron bounces from wall to wall at a frequency of 1.1 MHz. This means that during a typical dumping time of 650 µs, the positron has approximately 365 opportunities to leave the trap. If the dumping potential increases past the potential required to eject a positron from the trap in between two of these opportunities, then the positron will pick up more energy from the potential than necessary, leading to a broadened energy resolution and slightly higher average energy. The details depend on the rate at which the dumping function changes in this period. Ideally, the dumping potential should be increased very slowly, to stop precisely when it has reached the same level as the wall potential, but this is not practical due to fluctuations in the potentials set by the amplifiers and timing considerations.

In the ANU experiment, three different types of functions, shown in figure 4.4, have been used to control the dumping electrode to varying effect. The ‘instant’ dump consists of switching the electrode from low to high as quickly as the equipment allows (the slew rate is approximately 30 V/µs). The result is a pulse of positrons that would have an energy distribution of the same width, but shifted up by an amount corresponding to the potential of the final electrode, were it not for the transport time effect mentioned above. This effect results in 90% of the positrons remaining in the dumping electrode until the end of the ramp, rendering the potential of the final electrode inconsequential, and setting the beam energy to that of the top of the dumping ramp. In addition, every positron will gain sufficient potential within a few microseconds, leading to a high time resolution.

The bilinear ramp style consists of two linear ramps that share a common centre point. The logarithmic ramp is designed to increase quickly at the beginning of the ramp, but only gradually approach the ending value, which reduces the energy variation between positrons located in different parts of the dumping electrode when the dump potential passes the
Figure 4.4: Ramp functions for the dumping electrode for the three cases compared in section 4.4.3.

Figure 4.5: Comparison between the results of different ramping functions for (a) pulse time profiles and (b) energy cutoffs. Ramping functions are as described in section 4.4.3, no gas was included, and all other parameters are as in figure 4.1.

wall potential. The pulse shapes and energy cutoffs for each of these dumping functions are provided in figure 4.5.

4.4.4 Other variables

Several other possible variables were investigated, and found to have little effect on the resultant pulse. Thus, for example, a spatial gradient in the electric potentials has little effect, since the positrons still have to pass the same height wall to escape, so only the potential in the space just prior to the final wall was significant. Modifying the ratio of gases has a similar effect to modifying the gas density, since only elastic interaction channels are significant at thermal energies. The presence of an axially confining magnetic field does not affect the positron’s motion in the axial direction, which is the only direction of significance in forming the pulse, although in practice it is of course necessary to include a field to prevent positrons from annihilating with the sides of the beam tube.
4.5 Conclusion

This study addressed key questions relating to optimising the operation of the traps used in the ANU scattering beamline. Future work may investigate the effect of a slightly non-axial magnetic field, and attempt to determine which parameters are necessary to change in order to reconcile the simulated results with those of the experiment, which may reveal any discrepancies in the calibration of the experiment. This will allow experimentalists to achieve better time and energy resolution for the incident positron pulses, and ultimately result in higher precision cross section measurements.
5

Monte Carlo simulations with structure factors

This chapter contains material that has been previously published in the following journal articles:


5.1 Introduction

This chapter details techniques for simulating charged particles in structured media such as dense gases, liquids, and soft-condensed systems. While the study of electron and positron transport in dilute gases is well understood, and largely limited by the availability of interaction cross sections, there are many effects in denser systems which add considerable complications to accurate transport simulations. The major contributions to these effects arise from highly correlated separations, in both position and velocity, between the neutrals. At low particle energies in a dense medium, the particle effectively interacts with many neutrals simultaneously, so that it is no longer valid to treat transport as a series of binary collisions separated by a typical mean-free path.

While it is tempting to assume that the contributions to multiple scattering due to each neutral would, on average, have no effect, this would only be true if the neutrals were
completely uncorrelated in their positions and velocities. However correlations are always present in all real systems. In a crystalline solid, each neutral has a tightly correlated position relative to others in the crystal lattice, while in a liquid, there are still preferred interatomic distances. It is therefore desirable to model not only the direct scattering by neutrals but also the effects due to correlations in the medium.

The approach taken in this chapter is based on modifying the energy and momentum transfers of elastic collisions so as to include a statistically valid representation of these correlation effects at a macroscopic level. This approach is largely based on the seminal theories of Van Hove [122] and Cohen et al. [123], as well as the Monte Carlo simulations by Wojcik and Tachiya [69] and Sakai et al. [68]. Both simulation techniques have been implemented in the present code, along with a number of modifications which allow the simulation to more closely follow the models of Cohen. A number of benchmark simulations are presented and compared with an alternative Boltzmann equation solution, showing excellent agreement in all cases. The dynamic structure factor technique can also be used to accurately simulate swarm scattering in molecules at non-zero temperatures, which is a surprisingly difficult problem [97].

The derivation and benchmarks of the static structure factor presented in this chapter have been previously published in [3] and [9]. The application of the Monte Carlo static structure procedure to liquid argon has not been previously published, although the model is from [9]. None of the work regarding the dynamic structure factor simulations has been previously published.

5.2 Background and previous models

In a classical sense, the de Broglie wavelength $\lambda$ of a charged particle can be considered the effective radius within which neutrals may interact with the particle. For non-relativistic particles, this is inversely proportional to the speed, and can be significantly large; $\lambda = 1.2 \text{ nm}$ for a $1 \text{ eV}$ electron, and $\lambda = 6.3 \text{ nm}$ for a room-temperature electron. In a gas, the intermolecular spacing is somewhat higher than this (on the order of $10 \text{ nm}$). However, for denser mediums, $\lambda$ may be several orders of magnitude larger than the intermolecular spacing of the neutrals, which means that the charged particle may effectively interact with a large number of neutrals simultaneously.

The dynamic structure factor $S(\Delta k, \omega)$ is based on the seminal work of Van Hove [122], who defined the generalised pair distribution function $G(r, t)$. This function describes the space and time correlations of the positions of particles in a homogeneous but structured medium. Briefly, given a particle with a specified position at a particular time, $G(r, t)$ gives the probability of finding a particle at a displacement $r$ from that particle, at a time $t$ removed from the specified time. This is a natural extension of the more familiar pair distribution function $g(r)$, and, as in that case, is dependent on the interactions between the component molecules of the medium. However, $G(r, t)$ additionally contains information about the temperature of the medium, as well as other effects which depend on the movement of the molecules such as phonon excitations [124]. If we consider a fixed
point in space through which a particle passes at time \( t = 0 \), the density distribution of the system about that point is disturbed not just at that time, but also afterwards.

The dynamic structure factor is defined as the fourier transform, in both space and time, of \( G(\mathbf{r}, t) \) through [124]:

\[
S(\Delta \mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\Delta \mathbf{k}, t) \exp[i\omega t] \, dt
\]

\[
F(\Delta \mathbf{k}, t) = \int G(\mathbf{r}, t) \exp[-i\Delta \mathbf{k}.\mathbf{r}] \, d\mathbf{r},
\]

where \( F(\Delta \mathbf{k}, t) \) represents the “intermediate scattering function” which is directly measured in neutron spin echo spectroscopy [125]. The dynamic structure factor is a bijection with \( G(\mathbf{r}, t) \) so it naturally contains the same information, but it lends itself more naturally to scattering problems. In the above, \( \Delta \mathbf{k} \) is the vector change of wave number, such that \( \hbar \Delta \mathbf{k} \) is the momentum transfer, while \( \omega \) is the change of frequency, such that \( \hbar \omega \) is the transfer of energy. As such, \( S(\Delta \mathbf{k}, \omega) \) can be identified as a probability distribution describing the likely changes of momentum and energy in an elastic collision.

A first approximation to modelling these correlations is the “single scatterer approximation” [123], where the scattered amplitude of the charged particle’s wave is the coherent sum of amplitudes scattered from several individual molecules, but the sum of amplitudes that have scattered from multiple molecules is assumed to be negligible. Under this approximation, the coherent scattering effects can be described entirely by the dynamic structure factor, \( S(\Delta \mathbf{k}, \omega) \).

There have been several previous efforts to incorporate structure factors into scattering simulations and Boltzmann equation solutions. Cohen and Lekner [123] proposed a solution to the Boltzmann equation consisting of the first two terms of a Legendre polynomial expansion, and this was the state of the art for liquids and soft-condensed media for more than 40 years; a topical review by Sakai [126] in 2007 showed the reliance on the two-term expansion at that time. White and Robson had previously shown that this was an insufficient approximation for some cases [127], and subsequently extended the Cohen theory to a full multi-term expansion [16] with anisotropic scattering accounted for systematically. Monte Carlo models have mostly neglected coherent elastic scattering, with the notable exceptions of Sakai [68] and Wojcik and Tachiya [69], whose research directly inspired most of the work described in this chapter.

A fundamentally different approach to multiple scattering can be seen in the dielectric function formalism employed by Kunhardt [128], Dingfelder [129] and Emfietzoglou [57] among others, who essentially start from a solid phase, and extend the formalism to the liquid phase. The dielectric function \( \varepsilon(\Delta k, \omega) \) is a complex valued function\(^1\) where

\[
\text{Im} \left[ \frac{1}{\varepsilon(\Delta k, \omega)} \right] \propto S(\Delta k, \omega), \quad \text{while the real part of } \varepsilon(\Delta k, \omega) \text{ is involved with lagged responses such as energy stored in the medium [92]. The dielectric function is typically measured at the "optical limit", } \Delta k = 0, \text{ and then extended to non-zero } \Delta k \text{ with parametric functions [57]. While not often treated with the Boltzmann equation, this dielectric formalism has formed}
\]

\(^1\varepsilon(\Delta k, \omega) \) is the traditional notation for the dielectric function, but should not be confused with the incident energy \( \varepsilon \) used in the remainder of this thesis.
the basis of several commonly-used Monte Carlo codes including PARTRAC, NOREC [58] and PENELOPE. These models are typically restricted to relatively high energies, above 100 eV, where the Born approximation certainly holds. While it would be desirable to reconcile this formalism with that of the present simulation, doing so is beyond the scope of this thesis.

Throughout this chapter, it is assumed that there are no preferred orientations for the molecules, which means that the structure factor is a function of scalar momentum transfer only, \( S(\Delta k, \omega) \). While this is generally accurate for non-polar neutrals, it is an active area of research for polar molecules such as water. This is especially significant when the medium is subjected to strong magnetic fields, which occurs in PET-MRI (Magnetic Resonance Imaging).

There are several additional effects that modify the transport behaviour in liquids. One such effect is the screening of the atomic dipole by the induced dipoles of the other atoms in the medium. This effect has been implemented by Boyle et al. [17], following the method of Lekner [130]. The principle effect is that it removes the Ramsauer minimum seen in the gas phase cross section. The resulting cross section has been used for the liquid argon system in section 5.3.5.

The work in this chapter focuses on the modifications of the elastic process, which is affected by coherent scattering. Inelastic processes are incoherent and so this extension does not affect them directly, however it is known that collective excitations can occur in dense media [57,131], which will not be considered here. It is also known that the positronium formation and annihilation cross sections are modified by density effects and, in particular, the threshold for positronium formation is reduced [132]. However, all of the benchmark simulations in this chapter are restricted to elastic cross sections only. Additional processes are included in the water model that is the subject of chapter 6.

5.3 Static structure factor

5.3.1 Derivation from Cohen and Lekner transfer rates

The Cohen-Lekner theory of electron transport [123] describes coherent structural effects in terms of two rates of transfer – momentum and energy – which can occur independently. Wojcik and Tachiya [69] have previously calculated effective elastic cross sections that can approximately emulate these energy and momentum transfer rates. Presented here is a modified version of this model, which may additionally account for increased momentum transfer rates.

Cohen and Lekner express the electron distribution function in a basis of spherical harmonics. They modify the standard Boltzmann collision integral to include the dynamic structure factor \( S(\Delta k, \omega) \), as motivated by Van Hove’s definition of the ensemble cross section [122], and then show that when the necessary integrals have been performed, the dependence can be reduced to a static structure factor and a temperature.

Upon solving the equations for the time evolution of the distribution function, they ascribe a physical meaning to two of the mean free path lengths that appear in the collision
integral expansion. The first fully determines the rate of energy transferred from the swarm particles. It is independent of the structure of the medium and is given by the mean free path corresponding to single-particle elastic scattering:

\[ \Lambda_0 = (n_0 \sigma_m)^{-1} = \left( n_0 2\pi \int_0^{\pi} d\chi \sin \chi (1 - \cos \chi) \sigma_{sp}(\varepsilon, \chi) \right)^{-1}, \quad (5.1) \]

where \( n_0 \) is the number density of the neutral molecules, \( \sigma_{sp}(\varepsilon, \chi) \) is the angle-differential elastic cross section for scattering with a single particle (also known as the binary cross section), and \( \sigma_m \) is the usual definition of the momentum transfer cross section in the absence of coherent effects. In the case of non-binary collisions, \( \varepsilon \) refers to the energy in the lab frame and \( \chi \) represents the angle through which the relative velocity is changed.

The second mean free path partly includes the effect of the medium and contains all information about the rate at which momentum is transferred:

\[ \Lambda_1 = (n_0 \tilde{\sigma}_m)^{-1} = \left( n_0 2\pi \int_0^{\pi} d\chi \sin \chi (1 - \cos \chi) \sigma_{sp}(\varepsilon, \chi) S(\Delta k) \right)^{-1}, \quad (5.2) \]

where \( S(\Delta k) \) is the static structure factor as a function of the momentum transferred and \( \tilde{\sigma}_m \) represents a structure modification of the momentum transfer cross section.

Boyle et al. has calculated \[133\] the explicit rates of energy and momentum transfer when structure is included in the Boltzmann equation. The components of this transfer due to the collision term, in the case of zero temperature, are:

\[ \frac{d}{dt} \left\langle n \, m \, v \right\rangle \bigg|_{\text{coll}} = -\left\langle n_0 \psi \tilde{\sigma}_m(v) m v \right\rangle + O(\omega) + O\left( \frac{m}{m_0} \right) = -\left\langle v \Lambda_1^{-1}(v) m v \right\rangle \quad (5.3) \]

and

\[ \frac{d}{dt} \left\langle n \, \varepsilon \right\rangle \bigg|_{\text{coll}} = -2 \frac{m}{m_0} \left\langle n_0 \psi \sigma_m(v) \varepsilon \right\rangle + O(\omega^2) + O\left( \left( \frac{m}{m_0} \right)^2 \right) = -2 \frac{m}{m_0} \left\langle v \Lambda_0^{-1}(v) \varepsilon \right\rangle, \quad (5.4) \]

where \( \langle \ldots \rangle \) represents averaging over velocity space and \( n \) is the number density of the charged particles.

Note that these representative mean free paths should be considered independently, and should be only thought of as an average rate of transfer of the relevant quantity, rather than as a prescription for separate collision events. The ratio \( \Gamma(\varepsilon) \equiv \Lambda_0/\Lambda_1 = \tilde{\sigma}_m/\sigma_m \) can then be defined. In the dilute gas case, \( \Gamma(\varepsilon) = 1 \), because the static structure factor of a dilute gas is unity for all momentum transfers. However, in a structured medium such as a dense gas or a liquid, the ratio can deviate markedly from unity. If \( \Gamma(\varepsilon) < 1 \), there is noticeably less momentum transfer than in the single-particle scattering case, which can be interpreted as a preference towards forward scattering events. In the opposite case of \( \Gamma(\varepsilon) > 1 \), more momentum transfer occurs, which causes the particle to change direction without losing as
much energy as it would in the single-particle scattering. This latter case is neglected by the treatment of Wojcik and Tachiya [69], which leads to an underestimation of momentum transfer in that regime.

In the case of an isotropic single-particle elastic cross section \( \sigma_{sp}(\varepsilon, \chi) = \frac{1}{4\pi} \sigma_{sp}(\varepsilon) \), as in the model described in section 5.3.3, the ratio \( \Gamma(\varepsilon) \) then reduces to:

\[
\Gamma(\varepsilon) = \frac{\Lambda_0}{\Lambda_1} = \frac{1}{2} \int_0^\pi d\chi \sin \chi (1 - \cos \chi) S \left( \frac{2(2m\varepsilon)^{1/2}}{\hbar} \sin \left( \frac{\chi}{2} \right) \right),
\]

(5.5)

where it is assumed that the static structure factor depends only on the magnitude of \( \Delta k \).

We can then write \( |\hbar \Delta k| = \hbar \Delta k \approx 2\sqrt{2m\varepsilon} \sin \frac{\chi}{2} \) in the limit of a small mass ratio \( m/m_0 \). This form of \( \Gamma(\varepsilon) \) is sometimes called the angle-integrated static structure factor, \( \bar{S}(\varepsilon) \), and it is used in several previous works [16,69], however it is important to note that it does not apply when there is a \( \chi \) dependence in \( \sigma_{sp} \). The anisotropic case is considered in section 5.3.5.

In the case of dilute gases where \( S(\Delta k) = 1 \), the energy and momentum transfer rates converge, yielding the single-scattering model in which every energy transfer is accompanied by a momentum transfer. When the transfer rates differ, however, this theory is not directly applicable to Monte Carlo modelling because it does not give a microscopic description of how much energy and momentum is transferred in each collision between swarm particles and neutral particles.

5.3.2 Sampling coherent scattering in Monte Carlo simulations

As described in chapter 3, the present Monte Carlo simulation is built around sampling sets of scattering cross sections, \( \sigma \), that define the probabilities of all interactions between the charged particles and the medium. When a collision is simulated, a specific cross section is randomly selected according to the relative probabilities of the available cross sections [134]. In the case of single-scattering collisions with cold independent gas molecules, the amount of energy and momentum transferred is fully determined by the initial energy and the selected scattering angles.

For structured materials, an approximate theory has been developed by Wojcik and Tachiya [69], who propose a mechanistic model of electron transport in rare gas liquids. In what follows, Wojcik and Tachiya’s model has been extended to be more generally applicable to other systems by removing a small approximation and associated error.

The presence of structure requires the introduction of additional microscopic processes that, at a macroscopic level, produce the same rate of energy and of momentum transfer as in the Boltzmann equation formalism detailed in section 5.3.1. This is performed by separating the original, single-particle elastic cross section into three different processes depending on the ratio \( \Gamma(\varepsilon) \), as illustrated in figure 5.2. These processes have cross sections, labelled by the quantities that are modified in the collision: \( \sigma_{both}, \sigma_{momentum} \) and \( \sigma_{energy} \). The result of a collision from the process corresponding to \( \sigma_{both} \) is identical to that of a regular single-particle scattering collision. For \( \sigma_{energy} \), a regular single-particle scattering collision is performed, but after the collision the direction of motion of the particle is
set to be the same as it was before the collision. This has the effect of transferring a minimal amount of momentum whilst maintaining the same energy transfer as in \( \sigma_{\text{both}} \). For \( \sigma_{\text{momentum}} \), a regular single-particle scattering collision is performed, but the post-collision particle speed is scaled to be equal to that before the collision. This results in exactly zero transfer of energy, but some change of vector momentum.

The path lengths \( \Lambda_0 \) and \( \Lambda_1 \) in section 5.3.1 correspond to transfer rates of \( \nu_m = v n_0 \sigma_m = v / \Lambda_0 \) and \( \bar{\nu}_m = v n_0 \bar{\sigma}_m = v / \Lambda_1 \) for energy and momentum respectively, where \( v \) is the speed of the charged particle. To achieve these rates, the cross sections are combined in various ratios depending on the value of \( \Gamma(\varepsilon) = \Lambda_0 / \Lambda_1 \). If \( \Gamma(\varepsilon) < 1 \) the rate of momentum transfer must be decreased, while maintaining energy transfer, and so the cross sections are chosen as \( \sigma_{\text{both}}^{\Gamma<1} = \Gamma(\varepsilon) \sigma_{sp} \), \( \sigma_{\text{energy}}^{\Gamma<1} = (1 - \Gamma(\varepsilon)) \sigma_{sp} \), and \( \sigma_{\text{momentum}}^{\Gamma<1} = 0 \). In the opposite case, \( \Gamma(\varepsilon) > 1 \), an increased rate of momentum transfer is achieved by setting \( \sigma_{\text{both}}^{\Gamma>1} = \sigma_{sp} \), \( \sigma_{\text{momentum}}^{\Gamma>1} = (\Gamma(\varepsilon) - 1) \sigma_{sp} \), and \( \sigma_{\text{energy}}^{\Gamma>1} = 0 \). This gives a total elastic cross section of \( \sigma_{\text{tot}} = \max(1, \Gamma(\varepsilon)) \sigma_{sp} \). The complete Monte Carlo procedure is shown as a flowchart in figure 5.1.

It must be emphasised that these collision processes do not individually represent multiple scattering interactions between the electrons and the medium. In particular, the
Figure 5.2: Schematic diagram of the various elastic cross-sections used in simulating a Percus-Yevick liquid ($\phi = 0.4$). All quantities are given relative to the elastic cross-section for a single particle. Note that $\sigma_{\text{tot}} \geq \sigma_{\text{sp}}$.

Momentum and energy-only collisions would require rather contrived circumstances to achieve momentum energy conservation between the electron and the medium. Instead, the additional collision processes are designed to reproduce the rates of energy and momentum transfer in equations (5.1) and (5.2) when considered as the average of a series of selected collisions. It is shown in [3] that a sampling process involving these cross sections does indeed satisfy these requirements, to within the order of the mass ratio $m/m_0$ as mentioned earlier. These differences are small enough that they are unlikely to affect electron-atom simulations, though they may be significant in systems where ions serve as the charged particles.

Wojcik and Tachiya [69] studied liquid argon according to the method described above but their mechanistic model effectively caps the value of $\Gamma(\varepsilon)$ such that it never exceeds unity. This meant that their total collision frequency was unaltered from the single-particle scattering case, and simulation of the particles in the energy regions where $\Gamma(\varepsilon)$ exceeded 1 could only be considered approximately accurate. The difference between their method and the present is shown in figure 5.2, where the regions labelled $\sigma_{\text{momentum}}$ are absent in their model, and the total cross section modified accordingly, so that it is simply $\sigma_{\text{sp}}$.

For the aforementioned study of liquid argon, such modifications were only required in a small energy range for the structure factor that they employed. One of the purposes of the present work is to determine how this approximation affects the results for a benchmark Percus-Yevick model, where the approximation is more significant.
5.3.3 Percus-Yevick model

Structure factor

To demonstrate and benchmark the new simulation procedure and code, it is applied to a simple model system that requires a correct treatment of structured media. One such model, frequently found in the literature [16, 135], is that of a structure for hard-sphere potentials obtained by applying the Percus-Yevick approximation as a closure to the Ornstein-Zernike equation, which yields a pair-correlation function [136, 137], which in turn can be transformed into a static structure factor via a Fourier transform and used in the simulation. The Verlet and Weiss [138] version of the structure factor includes some corrections to better emulate the structure of a real liquid, and takes the form:

\[
S(\Delta k) = \left(1 + \frac{24\eta}{\Delta k^2} \left[ \frac{2}{\Delta k^2} \left( \frac{12\zeta}{\Delta k^2} - \beta \right) \right] \right)^{-1} \sin(\Delta k) \Delta k \left( \alpha + 2\beta + 4\zeta - \frac{24\zeta}{\Delta k^2} \right) + \cos(\Delta k) \left( \frac{2}{\Delta k^2} \left( \beta + 6\zeta - \frac{12\zeta}{\Delta k^2} \right) - \alpha - \beta - \zeta \right)
\]

where \( \eta = \phi - \frac{\phi^2}{16} \), \( \alpha = \frac{(1+2\eta)^2}{(1-\eta)^2} \), \( \beta = \frac{-6\eta(1+\frac{2}{\eta})^2}{(1-\eta)^4} \) and \( \zeta = \frac{n_0}{2} \). This includes a packing density parameter, \( \phi \), which specifies how closely the hard spheres are packed and can be written in terms of the hard sphere radius \( r \) and the neutral number density \( n_0 \) as \( \phi = \frac{4}{3}\pi r^3 n_0 \).

This structure factor depends only on the magnitude of the momentum exchange during a collision.

In this chapter, systems with a range of densities have been modelled, ranging from \( \phi \approx 0 \), which is a dilute gas (\( S(\Delta k) = 1 \)), to \( \phi = 0.4 \), which describes a system in which 40% of the volume is excluded by the hard-sphere potentials of the neutral molecules. The angle-integrated forms of each of these structure factors as described in equation (5.5) are shown in figure 5.3.

Other parameters

The simulations performed here are intended to be compared with a Boltzmann equation approach published in [16]. Each simulation is a drift-tube style of simulation with a hydrodynamic equilibrium, similar to the earlier benchmarks in chapter 3. As with those benchmarks, this system has been simulated across a range of reduced electric field strengths and several steady-state transport coefficients have been calculated. The transport coefficients are defined in detail in section 3.6 of chapter 3.

As the Percus-Yevick structure model is intended to model molecules with a hard-sphere potential, the cross sections are chosen accordingly. Specifically, there is only one type of interaction, an elastic collision with a cross-section of \( \sigma_{el}(\varepsilon) = 6 \text{ Å}^2 \). The charged particles are treated as electrons, with a mass of \( m = m_e \). The neutrals are assigned a mass of \( m_0 = 4 \text{ amu} \), the mass of a helium atom, as used in the comparison study. In most similar
benchmarks, the transport coefficients depend only on the reduced electric field, $E/n_0$, but in this case $n_0$ is specified by the combination of $\sigma_{el}$ and $\phi$, which indirectly specifies $E$ as well for all but the $\phi \approx 0$ case.

**Transport coefficients**

The Percus-Yevick hard-sphere system has been previously studied in [16], and a comparison with those results provides a test of our simulation\footnote{An error in the calculation of the Percus-Yevick structure factor used in [16] means that the structure factor would be correct for a fluid where the molecules have a hard-sphere cross-section of $\sigma = 1.5 \, \text{Å}^2$, not the reported cross-section of $\sigma = 6 \, \text{Å}^2$, although the cross-sections themselves were as reported. The Boltzmann equation results presented here have been recalculated with the correct structure factor, as described in section 5.3. The phenomenology reported in [16] remains correct, however.}. Figure 5.4 shows the various transport coefficients obtained using the present method, using the approach which overcomes Wojcik and Tachiya’s approximation. It is instructive to compare this figure with figure 5.3, to see the field strengths that are affected most strongly by the features of the structure factors employed. The complete set of all of the results is included in the original article [3]. Enough particles have been simulated so that in general the Monte Carlo statistical error (as defined in section 3.7.5 of chapter 3) is not visible at these scales, being less than 1% in all cases. Agreement with the Boltzmann equation results is to within 1% in all cases, so the datasets would not be distinguished from each other at the scale of the above figures, but a detailed comparison is presented in section 5.3.3.

The features of the results are discussed in detail in [16], and that discussion will not be repeated in depth here. One key feature is the presence of structure-induced negative-differential conductivity (defined in [139]) which is apparent in the drift velocity:

Figure 5.3: Angle integrated Percus-Yevick structure factors, from equations (5.6) and (5.5), as a function of collision energy and volume fraction.
Figure 5.4: Mean energy $\bar{\epsilon}$, drift velocity $W$, and diffusion coefficients $D_L$ and $D_T$ for Percus-Yevick model simulations, as a function of reduced electric field $E/n_0$ and Percus-Yevick packing ratio $\phi$. Error bars are not visible at this scale. Circles (and for $D_T$, diamonds) are the present Monte Carlo results, and lines are Boltzmann equation solutions by White and Robson [16].
at moderate field strengths of 1-10 Td, the drift velocity is inversely proportional to the field strength. This is because at low field strengths, the presence of coherent scattering causes an anisotropy in particle scattering which allows the particles to be affected more consistently by the field, raising their velocity in comparison to the structure-free case. At higher field strengths, the mean particle energy is higher, leading to a reduced de Broglie wavelength, which means that the charged particles interact with fewer neutral molecules, so the coherent effects are reduced. This results in a net reduction of forward motion despite a higher average energy.

Also of note is the variation in the anisotropic diffusion as a function of $\phi$. In the case of a hard-sphere gas with no structure, the ratio $D_{L}/D_{T} = 0.5$ is expected [20], which, as shown in figure 5.5, is demonstrated by the present simulations. When structure is introduced, this ratio changes significantly. This effect has been previously explored in [16] and [133] through the extended Generalized Einstein Relation. It is notable that a multi-term Boltzmann equation solution is required to achieve accuracy in this regard, while the present simulations have no difficulties in accurately representing this anisotropy in the velocity distribution function.

**Comparison with Boltzmann equation solution**

In figure 5.6, the percentage difference is shown between the present results, results calculated with Wojcik and Tachiya’s approximation, and the Boltzmann equation solution. The present implementation of Wojcik and Tachiya’s method shows good agreement over most regions of field strength, however for some larger field strengths, errors of up to 5% in the mean energy and up to 35% in the diffusion coefficients become apparent. These differences
Figure 5.6: Mean energy $\bar{\epsilon}$ and longitudinal diffusion $D_L$ percentage difference for each Monte Carlo model versus the Boltzmann equation (BE) model, for the Percus-Yevick structure factor at $\phi = 0.4$. 
occur when the energies of the electrons are within the regions that are truncated by that method. Two competing factors have an effect when the particle’s energy is in these regions, causing differences between the two methods. Firstly, the collision frequency is enhanced, and since every collision has a chance of both removing some energy from the particle and changing the direction of the particle away from the direction of the electric field, this means that particles will tend to lose energy at a greater rate. However, this is balanced by the presence of the new momentum-only collision, which can occur up to 28% of the time in these regions. The presence of such collisions will tend to decrease the energy transfer rate. Nevertheless, figure 5.6 clearly shows that the net effect is observable for the Percus-Yevick $\phi = 0.4$ case, with a peak difference at approximately 8 Td. This corresponds to a mean energy of about 5 eV (see figure 5.4), which is at the peak of the $\Gamma (\varepsilon)$ function where Wojcik and Tachiya’s approximation is least accurate.

For the present model, the disagreements with the Boltzmann equation results are less than 1% over all field strengths considered. Such differences are of the order of the numerical schemes used in the Monte Carlo and Boltzmann equation methods. The remaining differences are likely a result of the granularity of the energy meshes used in the Monte Carlo codes and Boltzmann equation numerical solutions.

5.3.4 Step model spatial benchmark

System parameters

In this section, a second benchmark for the static structure approach is presented. The simulations were performed for a collaborative article with Boyle et al. [9], which was focussed on novel techniques for solving a space-time Boltzmann equation. Presented here are the Monte Carlo implementations of these systems. This benchmark employs the above Percus-Yevick structure factor, but additionally includes a step-like excitation cross section:

\[
\sigma_{\text{exc}} = \begin{cases} 
0 & \varepsilon < 2 \text{ eV} \\
0.1\sigma_0 & \varepsilon \geq 2 \text{ eV}
\end{cases}
\]

, where $\sigma_0 = 1 \text{ Å}^2$.

In order to test whether the simulation can accurately capture non-hydrodynamic (transitory) behaviour, this model is loosely based on a Franck-Hertz experiment, where the excitation cross section causes periodic oscillations in the spatial behaviour of the swarm [140,141]. As above, an electric field is included, however instead of scanning across a range of field strengths and reporting steady-state behaviour, only a single field is used and the spatial variation of the steady-state swarm properties is analysed.

While the majority of this thesis employs S.I. units where possible, both the step model and liquid argon static structure factor model simulations are intended for comparisons.
Figure 5.7: Spatial variation of the average energy (A) and velocity (B) under steady state Townsend conditions for the step model described in section 5.3.4 for various Percus-Yevick volume fractions $\Phi$. The dashed lines are results of the present Monte Carlo simulation, while the solid lines are solutions of a Boltzmann equation. Reproduced with permission from [9].

with the results of Boyle et al [9], which use a dimensionless unit system given by

$$z^* = n_0 \sigma_0 z,$$
$$t^* = n_0 \sigma_0 \sqrt{\frac{2e}{m}} t,$$ and
$$n^* = \frac{n}{n_0 \sigma_0 N},$$

(5.7)

where $N$ is the total number of particles simulated.

As in section 5.3.3, the neutral number density $n_0$ is derived from the volume fraction $\phi$ (ranging from $\sim 0$ to 0.4) and the size of the hard sphere elastic cross section (always 6 Å$^2$). The reduced electric field strength is set to a constant $E/n_0 = 3$ Td, which thus specifies the electric field strength. The initial position of the electrons is sampled from a Gaussian distribution centred on the origin with a standard deviation of $0.1 z^*$; a delta function distribution is trivial for the Monte Carlo code, but is not practical for a Boltzmann equation solution. The initial velocity $v_0$ of the electrons is sampled from a drifted Maxwellian distribution

$$f_{DM}(v_0) = \left( \frac{m}{2 \pi k_B T} \right)^{\frac{3}{2}} \exp \left[ -\frac{m}{2 k_B T} (v_0 - W)^2 \right],$$

where the velocity drift is given by $W = 1 \times 10^5 \text{ms}^{-1} \hat{E}$ (equivalent to 0.028 eV, parallel to the electric field), and $T$ is set to $1 \times 10^4 \text{K}$ (for an energy spread of 1.29 eV).

Results

Figure 5.7 shows the spatial profiles of the average energy (A) and velocity (B) under steady state Townsend conditions for a step model cross section set and Percus-Yevick
structure factors of varying volume fractions $\phi$. The resulting spatial profiles exhibit damped spatially-periodic structures which are qualitatively similar to those observed in the Franck-Hertz experiment. Loosely speaking, they occur because each electron undergoes a repeated sequence of gaining energy from the electric field, then losing the threshold energy $\varepsilon_t = 2\text{eV}$ in an inelastic collision. Because all of the electrons start from the same origin and rapidly thermalise to be of the same order in energy, the energies and densities of the particles have strong spatial similarities. In the limit of no elastic scattering, the width between the peaks in these profiles, $\lambda$, is proportional to the threshold energy of the inelastic process [142] through

$$\lambda = \frac{\varepsilon_t}{E/n_0}. \quad (5.8)$$

In this particular case, $\lambda = 6.66z^*$. In the actual results, however, the wavelength varies from $8.24 \pm 0.02$ for $\phi \sim 0$ to $6.67 \pm 0.02$ for $\phi = 0.4$. The differences arise from the inclusion of elastic scattering, and in particular with the variations in momentum transfer due to the static structure factor. With a greater volume fraction, the momentum transfer rates are reduced as the majority of elastic scattering events are effectively forward-scattering. This agrees with the approximation of weak elastic scattering that was used to derive equation (5.8), so it is unsurprising that the agreement is so close. In contrast, the $\phi \sim 0$ case has more frequent changes in direction for each electron, so that the electric field is unable to impart energy to it as quickly, which means the oscillation wavelength is increased.

The internal resolution of the particle’s position within the simulation is very high, since double precision floating point arithmetic is used throughout, so the spatial structures can be accurately modelled regardless of the scale (which is in contrast to the Boltzmann equation solutions with which these results were compared). The spatial sampling resolution for recording the results, however, is limited. As discussed in section 3.5, spatial samples are taken by interpolating the particle properties of interest at pre-specified times, and accumulating the values in space-indexed arrays. If the particle motion is not sampled often enough, this will affect the results with a type of aliasing effect. It is still accurate, in the sense that the simulation is still self-consistent and no conservation laws are broken. However, the temporal sampling is analogous to a video camera trying to capture the motion of a rapidly changing scene, and any average over the resulting images is likely to be meaningless if the frame rate is too low. To have confidence in the results, it suffices to repeatedly increase the temporal sampling rate until the summed results no longer change. It is possible to check the convergence with just one run of the simulation if the temporal samples are stored separately, in which case subsets of the samples (e.g. every 2nd sample) can be summed, and if they agree with the summation of the entire set, the sampling rate is sufficient.

5.3.5 Liquid argon

Background

Electron transport in liquid argon is of fundamental interest for high-energy particle detectors such as the liquid argon time projection chamber (LArTPC). In this system,
high-energy particles such as neutrinos ionise argon atoms in a detector. The ejected electrons are transported through the liquid argon, accelerated by a weak electric field. An arrangement of detector meshes intercept the electrons and the current thus produced is measured, allowing the precise localisation of the electrons. Using electron transport theory, the velocity and position of the original high-energy particle can be inferred. At present, these calculations are often performed using the LArSoft software package from Fermilab [143].

Cross sections

A recent publication by Boyle et al. [9] made use of novel theoretical calculations that calculate the fully-differential cross sections for electrons elastically scattering from argon. These cross sections may be used directly in the present Monte Carlo simulation. In this system, the energies of the electrons remain below the first electronic excitation at 8.9 eV, and there are no vibrational or rotational excitations due to the atomic nature of the target. In this case, elastic and spin-exchange interactions are the only interaction modes, and they have been combined into an angle-differential pseudo-elastic cross section, with specific modifications to account for the liquid phase. A full description of this cross section is outside of the scope of the present work but is given in [17]. These differential cross sections are reproduced in figure 5.8 as polar plots. Note the symmetry about the horizontal, as discussed in section 3.2.2 of chapter 3.
Figure 5.9: Static structure factor for liquid argon, integrated as per equation 5.9. The dilute gas structure is independent of the cross sections, as $\Gamma(\varepsilon) = S(\Delta k) = 1$. The other three cross sections are the two anisotropic cross sections shown in figure 5.8, and an arbitrary isotropic cross section: $\Gamma(\varepsilon)$ is independent of $\sigma_{el}(\varepsilon)$ if the latter has no $\chi$ dependence (it reduces to equation (5.5)).

As with the Percus-Yevick case above, the total scattering frequency depends on a structure-modified total cross section through $\sigma_{tot} = \max(1, \Gamma(\varepsilon))\sigma_{el:sp}(\varepsilon)$, where $\Gamma(\varepsilon)$ is the static structure modification defined in the next section and $\sigma_{el:sp}(\varepsilon)$ is the total elastic cross section for single-particle (gas-phase) scattering. The latter quantity is obtained from the above differential data by integration:

$$\sigma_{tot:sp}(\varepsilon) = \int_0^\pi \sigma_{el}(\varepsilon, \chi) \sin \chi d\chi.$$ 

This can be contrasted with the momentum-transfer cross section,

$$\sigma_{mt:sp}(\varepsilon) = \int_0^\pi \sigma_{el}(\varepsilon, \chi) (1 - \cos \chi) d\chi,$$

which is the input that is most relevant for Boltzmann equation solutions and presented in Boyle’s work.

**Structure factor**

To account for the spatial correlations of the scattering species in the liquid medium, a procedure similar to that in section 5.3.2 is employed. A liquid argon static structure factor has been measured over a broad range of momenta by Yarnell [144] and can be integrated...
over all allowable changes in momentum for each collision energy:

\[ \Gamma (\varepsilon) = \frac{\int_0^\pi \sigma_{\text{el}} (\varepsilon, \chi) \sin \chi (1 - \cos \chi) S \left( \frac{2(2m\varepsilon)^{1/2}}{\hbar} \sin \left( \frac{\chi}{2} \right) \right) d\chi}{\int_0^\pi \sigma_{\text{el}} (\varepsilon, \chi) \sin \chi (1 - \cos \chi) d\chi} , \quad (5.9) \]

where \( m \) is the positron’s mass. This form differs from equation (5.5) because it accounts for the differential nature of the elastic cross section by ensuring that the contributions from all possible momentum transfers at the given energy are weighted accordingly. In the gas phase, this reduces to 1, while for an isotropic cross section in the liquid phase, it takes the same form as equation (5.5). The resulting factor is shown in figure 5.9 for both the screened and unscreened variants of the elastic cross section.

**Initial conditions**

Measurements by Foxe et al. [145] have shown that electrons ejected by high energy ionisations in liquid argon are typically at energies of less than 1 eV. Therefore, the initial energy is sampled from a uniform distribution below 1 eV, with an isotropic distribution in the initial direction of the electrons’ velocities. There is also a Gaussian distribution of initial positions, with a standard deviation of \( \sqrt{10} z^* \).

**Results**

Figure 5.10 shows the spatial profile of the axial density of the swarm at \( t^* = 1, 10 \) and 100. These results are in good agreement with the results of Boyle et al.’s kinetic theories, shown in figure 7 of [9]. At later times, the liquid-phase experiences the greater diffusion rate, even despite its lack of Ramsauer minimum. This research is very recent – at the time of writing, still in review – so the Monte Carlo comparison is currently limited to these few profiles. Nevertheless, there is no reason to expect any differences from the remaining profiles published in [9], and it does serve as a test for the combination of anisotropic elastic gas-phase cross sections and the static structure factor.

**5.4 Dynamic structure factor**

**5.4.1 Background**

While the static structure factor can capture the modified momentum transfer rates due to coherent elastic scattering, it contains no information about energy transfer rates. In a real liquid, there are a number of complex ways in which a charged particle can interact with the medium as a whole and these can be summarised by the dynamic structure factor. Just as the static structure factor can be defined as the Fourier transform of the radial pair-correlation function \( g(r) \), the dynamic structure factor is the Fourier transform in two dimensions of the time-dependent (generalised) pair-correlation function \( G(r, t) \) [122]. Thus the dynamic structure factor accounts for not only the relative positions of the neutrals within the medium, but also for their relative velocities. It follows that the dynamic
Figure 5.10: Single-slice time snapshots of the spatial distribution of the number of electrons at three successive times, \( t^* = 1, 10 \) and 100, for simulations with no structure factor or screening correction ("gas"), with a structure factor but no screening correction ("gas-coh"), and with both a structure factor and screening correction (liquid-coh). Time and space measures are scaled as per equation (5.7). Note that the three curves in the first snapshot coincide.

structure factor can account for thermal effects, as well as any homogeneous disruptions to the liquid such as sound waves (phonon propagation).

There has been little study of how an elastic cross section might be modified by the dynamic structure factor. The methods presented in this chapter are largely influenced by the work of Sakai \[68\], who directly employed a dynamic structure factor to investigate elastic scattering in liquid argon. This chapter presents a more general method which makes fewer approximations with regards to the integrals and takes detailed balancing into account.

This method applies equally well to gases. However, in a dilute gas, neutrals are uncorrelated, so the dynamic structure factor serves only to account for the thermal motion of individual neutrals, which can be treated in a more direct manner by modelling the velocity of each target neutral as the collision occurs \[97\]. As discussed in section 3.2.2 of chapter 3, there are drawbacks to that procedure and the present method is an attractive alternative.

5.4.2 Properties of the dynamic structure factor

We begin with the definition of the dynamic structure factor, \( S(K,\omega) \). In neutron scattering experiments, it is defined as that proportion of neutrons with initial momentum \( \hbar k \) and initial energy \( \varepsilon \) that, post-collision, have a momentum of \( \hbar (k - K) \) and \( \varepsilon - \hbar \omega \). The quantity \( K \) is often referred to as the momentum transfer, although it is strictly speaking a change in wave number, while \( \omega \) is referred to as the energy transfer, in both cases neglecting the reduced Planck constant \( \hbar \). The dynamic structure factor is a property of the medium, and independent of the particles that are scattering within it, which allows the results of neutron or x-ray scattering experiments to be generally applicable to scattering with any particle. In homogeneous media that have no preferred direction, the dependence on the
vector momentum transfer $\mathbf{K}$ can be reduced to a dependence on merely its magnitude $K$, a simplification that shall be maintained throughout the rest of this chapter.

There is a series of integral moments of the dynamic structure factor which were first described by Cohen and Lekner [123, equations (2)-(4)]. The first three of these are

\[
\langle 1 \rangle = \int_{-\infty}^{\infty} S(K, \omega) \, d\omega = S(K), \quad \langle \omega \rangle = \int_{-\infty}^{\infty} \omega S(K, \omega) \, d\omega = \frac{hK^2}{2M_0}, \quad \text{and} \quad \langle \omega^2 \rangle = \int_{-\infty}^{\infty} \omega^2 S(K, \omega) \, d\omega = 2k_B T \langle \omega \rangle + O\left(\langle \omega \rangle^2\right).
\]

The first of these is the definition of the static structure factor, the second describes the mean energy transfer, and the third is related to the spread of energy transfers and contains information about the temperature of the medium. As explained by Cohen and Lekner, the higher order moments are smaller again by a factor $\Theta_D/T$, where $\Theta_D$ is the Debye temperature of the gas\(^3\), so the first three moments allow the system to be well described when the temperature is sufficiently high.

It is important to appreciate that these integral moments are only exact when $K$ and $\omega$ are independent. In the case of a single swarm particle interacting with the medium, $K$ and $\omega$ can be shown [68] to be related through

\[
K = \sqrt{\frac{2m}{\hbar} \left( -2\sqrt{\varepsilon} \cos(\chi) \sqrt{\varepsilon - \hbar \omega - \hbar \omega + 2\varepsilon} \right)} / \hbar, \quad (5.10)
\]

and the above integral moments may no longer apply.

### 5.4.3 Defining the ensemble cross section

The differential elastic scattering cross section for particles scattering within the medium is dependent on both the dynamic structure of the medium and the single-particle scattering cross section $\sigma_{sp}$, and these two factors can be multiplied to provide the differential scattering cross section for the ensemble of scattering particles,

\[
\sigma_{ens}(\varepsilon, \chi, K, \omega) = \sqrt{\frac{\varepsilon - \hbar \omega}{\varepsilon}} \sigma_{sp} \left( \varepsilon - \frac{\omega}{2}, \chi \right) S(K, \omega). \quad (5.11)
\]

This definition is based on that of Van Hove in [122], but generalised to apply to any arbitrary single-particle cross-section.

At thermal equilibrium, the principle of detailed balance requires that every energy-loss interaction must be matched by a corresponding energy-gain interaction. This requirement holds true even when the interactions are due to coherent scattering, as they still satisfy

\(^3\)Debye temperature is usually considered in the context of solids, being the temperature of a crystal’s highest normal mode of vibration [146]. However, it can also be derived in terms of the speed of sound within the material, which is well-defined even for an ideal gas.
microscopic reversibility. As such, the term $\sqrt{\frac{\varepsilon - \omega}{\varepsilon}}$ must be included in the ensemble cross section, and the cross section should be evaluated at a collision energy of $\varepsilon - \frac{\hbar \omega}{2}$.

Note that this ensemble cross section applies also in neutron scattering [147]. However the cross section for neutron scattering is essentially uniform at all energies and scattering angles, because neutrons interact primarily via the strong nuclear force. This means neutron scattering is an effective means of measuring the dynamic structure factor.

Equation (5.10) reduces the dependence of $\sigma_{\text{ens}}(\varepsilon, \chi, K, \omega)$ to $\sigma_{\text{ens}}(\varepsilon, \chi, \omega)$, however it also means that the integral moments above cannot be used to simplify the integrals of $\sigma_{\text{ens}}$ described in the next section. Nevertheless, Sakai uses the first integral moment in [68], without justification.

### 5.4.4 Sampling the ensemble cross section

For the simulations presented here, the energy transfer $\omega$ and collision angle $\chi$ are sampled using an inverse cumulative transform technique as described in 3.2.2 of chapter 3. Several integrals of the ensemble cross section defined in (5.11) must therefore be evaluated before the simulation begins.

The first such integral is the total ensemble cross section,

$$\sigma_{\text{ens:total}}(\varepsilon) = \int_{0}^{\pi} \int_{\varepsilon}^{\varepsilon - \infty} \sigma_{\text{ens}}(\varepsilon, \chi, \omega) \, d\omega \, \sin \chi \, d\chi,$$

which is used to define the collision frequency for elastic scattering. This cross section is used in the same manner as the total cross sections in a structure-free simulation, and is hence equivalent to, for example, the measured total cross sections from chapter 2. Note that the energy transfer integral has the energy of the particle as the upper limit, which is automatically enforced by the energy-momentum conservation equation (5.10).

To select the scattering angle during a collision, a partial integral over the angles is also necessary:

$$\sigma_{\text{ens:}\chi}(\varepsilon, \chi_0) = \int_{\chi_0}^{\chi_0 + \pi} \int_{0}^{\varepsilon} \sigma_{\text{ens}}(\varepsilon, \chi, \omega) \, d\omega \, \sin \chi \, d\chi,$$

which must be performed repeatedly for many $\chi_0$.

The energy transfer probability distribution is similarly based on a partial integral over the energies:

$$\sigma_{\text{ens:}\omega}(\varepsilon, \chi_0, \omega_0) = \int_{0}^{\chi_0} \int_{\omega_0}^{\omega_0 + \pi} \sigma_{\text{ens}}(\varepsilon, \chi, \omega) \, d\omega \, \sin \chi \, d\chi,$$

noting that $\omega_0$ will at times be negative (meaning that the particle gains energy from the coherent scattering event) when close to thermal equilibrium.

With these definitions, look-up tables can be produced so that $\omega$ and $\chi$ can be quickly sampled during scattering events. The first table is a two-dimensional table of collision energy versus a random variate from a uniform distribution, with values that indicate the corresponding scattering angle, i.e. $L_\chi(\varepsilon, R_1) = \chi_0$ such that
5.4.5 Evaluating the integrals

In general, the integrals defined in section 5.4.4 are not analytic; even if both the dynamic structure factor and single scattering cross section are analytic models, the energy-momentum relation (equation (5.10)) has a complicated dependency on \( \omega \), leading to an intractable integral. In addition, the dynamic structure factor has a sharp central peak along the \( \omega \) axis, which becomes a delta function in the limit of \( K = 0 \).

The algorithm for calculating the look-up tables is loosely based on a secant method. In each case, the goal is to determine several upper bounds of each integral such that the results of the integrals are equal to a series of \( R \), which are themselves equal divisions on \([0, 1]\). As each integrand is strictly positive, extending the range of the integral will increase the result. A first guess at the upper bounds is the range of the integral split into equal divisions. Afterwards, for each \( R \), the secant method is used on the closest known bounds to iterate towards the correct bounds. As the results of each guess are also stored, subsequent points can often be found more quickly.

The integrals themselves are performed using adaptive Gaussian quadrature as implemented in the Mathematica software package, with some fine-tuning to avoid known discontinuities and to ensure that the peak is detected. The symbolic nature of Mathematica allows for some dynamic inspection of the functional form to identify the locations of the peaks, which is a significant advantage over purely numerical computation.

5.4.6 Ideal thermal gas benchmark

Several model systems have been simulated as a benchmark of the dynamic structure procedure. The hard sphere model has a constant cross section \( \sigma_{HS} = 6 \text{ Å}^2 \), while the Maxwell model ensures a constant collision frequency by including a dependence on the collision energy, \( \sigma_{Mx} = 6 \varepsilon^{-1/2} \text{ Å}^2 \). In both cases, the dynamic structure factor is that of a dilute thermal ideal gas.

Dynamic structure factor

The classical dynamic structure factor for a dilute ideal gas is derived by starting with the thermal distribution of each cartesian component of the wave number, which is given by

\[
f_0(\xi) = \sqrt{\frac{\hbar^2}{2\pi k_B T M_0}} \exp\left[\frac{\hbar^2 \xi^2}{2 M_0 k_B T}\right],
\]
where $\xi$ is the wave number, $T$ is the temperature of the gas, and $M_0$ is the mass of each molecule in the gas. It is normalised so that $\int_{-\infty}^{\infty} f_0(\xi) \, d\xi = 1$.

To calculate the dynamic structure factor, the wave number distribution is weighted by a delta function that represents the allowed changes in momentum and energy during a collision, and then integrated over all possible wave numbers:

$$S(K, \Delta \omega) = \int_{-\infty}^{\infty} f_0(\xi) \delta(g(\xi, K, \Delta \omega)) \, d\xi,$$

where $\delta$ is the Dirac delta function, and $g$ and its parameters are defined below.

In an elastic collision, the change of energy of the charged particle is

$$\hbar \Delta \omega = \frac{\hbar^2}{2M_0} (\xi_f^2 - \xi_i^2) = \frac{\hbar^2}{2M_0} ((\xi_i + K)^2 - \xi_i^2) = \frac{\hbar^2}{2M_0} (K^2 - 2K\xi_i)$$

where $\xi_i$ and $\xi_f = \xi_i + K$ are the wave numbers before and after a collision, respectively. Without loss of generality, the direction of momentum change is chosen to be aligned with the cartesian $z$-axis.

A dynamic structure factor must have units of reciprocal frequency, so the delta function must have units of reciprocal frequency because $f_0(\xi) \, d\xi$ is dimensionless and

$$g(\xi, K, \Delta \omega) = \Delta \omega - \frac{\hbar}{2M_0} (K^2 - 2K\xi_i),$$

giving

$$S_{th}(K, \omega) = \int_{-\infty}^{\infty} f_0(\xi) \delta(\omega - \frac{\hbar}{2M_0} (K^2 - 2K\xi_i)) \, d\xi = \frac{M_0 \exp \left[ -\frac{(K^2\hbar - 2\omega M_0)^2}{8K^2 M_0 k_B T} \right]}{\sqrt{2\pi K} \sqrt{M_0 k_B T}}.$$ 

It can be shown analytically that this satisfies the first three integral moments as defined in Cohen and Lekner’s theory

\begin{align*}
\langle 1 \rangle &= \int_{-\infty}^{\infty} S_{th}(K, \omega) \, d\omega = 1 \\
\langle \omega \rangle &= \int_{-\infty}^{\infty} \omega S_{th}(K, \omega) \, d\omega = \frac{\hbar K^2}{2M_0} \\
\langle \omega^2 \rangle &= \int_{-\infty}^{\infty} \omega^2 S_{th}(K, \omega) \, d\omega = 2k_B T \frac{\hbar K^2}{2M_0} + \left( \frac{\hbar K}{2M_0} \right)^2,
\end{align*}

where the second term of the last moment is very small compared to the first, except for the case of hot electrons at low temperatures. For the general case $\langle \omega^n \rangle$, the MATHEMATICA
software package was able to find a general solution, although it is quite complicated and requires the use of confluent hypergeometric functions $\text{$_1F_1$}(a; b; z)$ and Euler gamma functions $\Gamma(z)$:

$$\langle \omega^n \rangle = 2^{n-2} \frac{(M_0 k_B T)^{\frac{1}{2}(-n-1)}}{\sqrt{\pi}k_B T} e^{-\frac{K^2\hbar^2}{8k_B T M_0}} \left\{ 2\sqrt{M_0 k_B T} \left( \frac{n+1}{2} \right) \left( (-k_B TK)^n + (k_B TK)^n \text{$_1F_1$}(\frac{n+1}{2}; \frac{1}{2}; \frac{K^2\hbar^2}{8k_B T M_0}) - \sqrt{2}((-1)^n - 1) \hbar K^{n+1} \Gamma\left(\frac{n+1}{2}\right) \times \text{$_1F_1$}\left(\frac{n+1}{2}; \frac{1}{2}; \frac{K^2\hbar^2}{8k_B T M_0}\right) \right\}.$$ 

Results

The above dynamic structure factor was used to model a gas of neutral mass 4 amu at a temperature of 293 K. The model was integrated to give the total cross section, energy transfer and scattering angle meshes described in section 5.4.4.

The total cross section for the hard sphere thermal model is shown in figure 5.11, where it is also compared with the thermal distribution of energies of the neutrals in a gas. The ensemble cross section is notably increased at energies below the thermal energy (the peak of the black curve). However, even at the lowest energies considered, the difference between the cold gas and thermal gas total cross section is less than 5%. By contrast, the Maxwell model (not shown) does not change for the ensemble cross section case, because the constant collision frequency of that model ensures that the additional energy introduced by the thermal motion has no effect on the collision frequency.

Figure 5.11: Hard sphere total elastic cross section, with and without the inclusion of thermal effects via the ideal gas structure factor. The energy distribution of the neutrals is shown for comparison.
Figure 5.12: Mean energy at hydrodynamic equilibrium $\varepsilon$, as a function of reduced electric field $E/n_0$, for thermal Dilute Gas Hard Sphere and Maxwell models. The solid lines represent Boltzmann equation solutions by Boyle (unpublished), which also include solutions for $T = 0$ (straight lines). The uncertainty in the Monte Carlo results is not visible at this scale.

Figure 5.12 presents the hydrodynamic equilibrium mean energies for the two dilute gas benchmark models, as a function of reduced electric field strength. For comparison, the zero-temperature results calculated without a dynamic structure are also shown. As expected, both thermal models approach to the thermal energy of 0.038 eV as the electric field is reduced, while at high fields, the thermal motion is insignificant so the thermal and cold gas models converge in each case.

5.4.7 Thermal Percus-Yevick structure benchmark

**Combining thermal properties with any static structure factor**

It is possible to construct an analytic dynamic structure factor for which the first integral moment results in any arbitrary static structure factor, and which satisfies the next two integral moments as in the thermal gas case. Such a structure factor takes the form

$$S(K, \omega) = S(K) S_{th}\left(K/\sqrt{S(K)}, \omega\right).$$

If $K$ and $\omega$ are independent, this satisfies these first three integral moments as listed in Cohen and Lekner’s theory [123, equations (2)-(4)]:

102
CHAPTER 5. MONTE CARLO WITH STRUCTURE

W. Tattersall

Figure 5.13: Mean energy at hydrodynamic equilibrium $\varepsilon$, as a function of reduced electric field $E/n_0$, for thermal Dilute Gas Hard Sphere and Percus-Yevick models. The solid lines represent Boltzmann equation solutions by Boyle (unpublished), including the $T = 0$ cases (darker lines).

\[ \langle 1 \rangle = \int_{-\infty}^{\infty} S(K, \omega) \, d\omega = S(K) \]
\[ \langle \omega \rangle = \int_{-\infty}^{\infty} \omega S(K, \omega) \, d\omega = \frac{\hbar K^2}{2M_0} \]
\[ \langle \omega^2 \rangle = \int_{-\infty}^{\infty} \omega^2 S(K, \omega) \, d\omega = 2k_B T \frac{\hbar K^2}{2M_0} + \left( \frac{\hbar K^2}{2M_0} \right)^2 \frac{1}{S(K)}. \quad (5.12) \]

This dynamic structure factor models a dense liquid of hard-spheres, just as the static version does. However, it also includes thermal effects identical to that of a dilute gas. It is thus a natural extension of both the gas-phase thermal hard-sphere model above as well as the condensed-phase cold Percus-Yevick fluids in section 5.3.3. While these Boltzmann equation solutions do not use the dynamic structure factor directly, they can use a static structure factor (the first moment), and include temperature by forcing the value of the third moment. It is therefore possible to test the present Monte Carlo simulation against equivalent Boltzmann equation results.

Results

Figure 5.13 presents mean energy in the hydrodynamic equilibrium for the thermal Percus-Yevick benchmark model at a temperature of 293 K and a volume fraction (see section 5.3.3).
of $\phi = 0.4$. The Boltzmann equation model of the same system is also shown, which includes temperature effects by fixing the second integral moment. The cold Percus-Yevick results of section 5.3.3 are shown for comparison, as well as both the thermal and cold hard-sphere model results of section 5.4.6, which are equivalent to the $\phi \sim 0$ case of this model.

The behaviour of the system is consistent with the earlier models: at low fields, the thermal effects increase the mean energy so that the system converges to the thermal energy of 0.038 eV. At high fields, the thermal effects are negligible, and the results match the cold gas case. It is notable that the scattering implementation is quite distinct from the static structure factor. Where the static structure model implements the momentum and energy transfer modifications by fixing either the direction or speed of the swarm particle post-collision, the dynamic model samples from continuous distributions of scattering angle and energy transfer, which encapsulates all of the elastic scattering dynamics implicitly.

5.4.8 Conclusions and future work

In this chapter the Monte Carlo transport simulations have been extended to include coherent elastic scattering, using either a static or dynamic structure factor. The flexibility of this technique lies in its ability to combine a structure factor, which is independent of the particle type, with a single particle cross section. As experimental measurements of cross sections are usually performed in the gas phase while many applications of particle transport occur in a liquid, solid, or soft-condensed phase, the ability to apply knowledge from one setting to the problems of another is very convenient. The static structure factor approach is simpler, and correctly accounts for the modified momentum transfer rates. The dynamic structure factor approach is considerably more difficult to implement because it requires that a number of difficult integrals are computed before the simulation can begin. In addition, there are very few dynamic structure factors that have been measured with the necessary precision and range to model systems of interest in this thesis.

Both techniques have been tested against a number of benchmark models. The Percus-Yevick model serves as a simple test of modified momentum-transfer, and when combined with a model containing an inelastic process, the spatial profiles of transport coefficients are also modified by the structure. A preliminary model of liquid argon shows excellent agreement with the equivalent Boltzmann equation formalism.

A dilute gas with a non-zero temperature is the first of the benchmarks for the dynamic structure factor simulations, yielding results which agree perfectly with Boltzmann equation solutions for both hard-sphere and Maxwell models. This structure has been combined with the Percus-Yevick static structure to form a new benchmark model that exhibits thermal effects as well as the features of the Percus-Yevick model.

Work is well under way to apply the latter technique to liquid argon, which requires the provision of a dynamic structure factor at very low momenta. It is not sufficient to apply higher-$K$ dynamic behaviour to the low-$K$ static structure factor used in this chapter, because it is at low $K$ that some of the most interesting dynamical responses occur, including phonon excitations [124] which can enable discrete quanta of energy to be transferred either to or from the medium.
6

Spatial simulations of liquid water

This chapter is adapted from the following journal article which is currently under consideration for publication:


All of the work described in this article is my own.

6.1 Introduction

In this chapter, simulations are made of positron transport in liquid water. This is a combination of the techniques described in chapter 5, where coherent elastic scattering was introduced into the Monte Carlo scattering model, as well as the measured water vapour elastic cross sections presented in chapter 2. The chapter begins by collating a set of water cross sections from various sources, including the aforementioned measurements. These cross sections are largely based on those used in previous studies [14], but additionally incorporate updated integral and differential quasi-elastic cross sections, as well as several alternative models of ionisation energy sharing. They are then used as inputs to the Monte Carlo simulation to model the transport of a beam of positrons that are injected into liquid water with energies of 60 eV. Several variations of the cross sections are considered, consisting of alternative ionisation energy sharing and anisotropic scattering models. The results take the form of comparative profiles of positron number density, energy deposition, positronium formation, and secondary electron generation.
At the time of writing, there are no previous positron Monte Carlo studies that explicitly include the effects of coherent elastic scattering in liquid water by using a static structure factor. As discussed in chapter 5, this effect, which arises from the spatially and temporally correlated structures within liquids, is potentially significant at low energies where the de Broglie wavelength is comparable to the inter-molecular spacing [7,148]. For liquid water, Boltzmann equation modelling of hypothetical swarm experiments has been performed [7], and a Boltzmann equation solution to the spatial diffusion of positrons in gaseous and liquid water is also available [148]. However, there have been very few swarm experiments for positrons in any medium, and none in water. A recent experiment by Alva-Sánchez [149] used a micro-PET machine to perform several measurements of the most common positron sources emitting into several biological-substitute materials, including solid water. However, the positrons are emitted at energies that are too high to compare with the present model.

There are several aspects of transport in the liquid phase that have been neglected. Polarisation screening [17], while important, requires detailed knowledge of the scattering potential. Similarly, the modification of the Ps binding energy [132] can shift the formation cross section, but the required modification is unknown. Similarly, there is evidence that the ionisation and electronic excitation cross sections are altered in the liquid phase [57,131], but there are no studies of how this might occur for positrons in liquids although theoretical predictions [150] exist for several solids at energies above 40 eV. Finally, localisation in density fluctuations is ignored, as this is significant only at near-thermal energies [151]. While these phenomena are undoubtedly important, they are not well understood and are beyond the focus of the current work.

The system that is simulated in this chapter is aimed at improving Monte Carlo simulations of PET by focusing on the low-energy regime. This is partly done to eliminate the non-local effects that arise from the radiation chemistry of the positron track [23], which are a complex topic and are difficult to accurately simulate. The proper inclusion of these effects requires the tracking of the electrons and ions created during the relaxation of the positron. These can then influenced the path of the positron as the electrons and ions diffuse (the so-called “blob” model [151]), as well as provide an alternate mechanism for positronium formation with the secondary electrons. Hence in this chapter, it is assumed that the positrons are injected into the medium at 60 eV, rather than having reached this energy from a relaxation process. Furthermore, for simplicity the positronium atoms that are formed are not tracked, even though they may later break-up into a positron and electron, effectively producing a delayed ionisation event. However, the information which is obtained from these low-energy simulations is of relevance to the radiation tracks of positrons injected at high energies as, for example, a greater rate of diffusion can imply that a positron can more readily escape its radiation track.

Section 6.2 describes a comprehensive set of positron-water cross sections, including both integral and differential cross sections for all of the collisional processes that are included in the simulations. In section 6.3 the structure factor for liquid water is introduced, along with the integrated form which is needed for the simulation. The chosen definitions for energy deposition are in section 6.4. Following this, in section 6.5, the various simulation
parameters are described, including spatial outputs, system geometry, liquid density, and the duration of the simulations. Section 6.6 presents the results of the simulation, highlighting the sensitivity of the results to the microscopic cross-sections and scattering dynamics, as well as the structure of the liquid. Concluding remarks are presented in section 6.7.

6.2 Cross sections for positrons in water

6.2.1 Integral cross-section sets

The cross sections used here are a modification of a cross section set employed in several earlier Monte Carlo simulations [7, 14, 18]. For the simulations considered here, the integral elastic cross section from that set has been replaced with the experimentally measured integral and differential elastic cross sections presented in chapter 2. The resulting set of integral cross sections is shown in figure 6.1, and described in detail below.
Figure 6.2: Comparison of the integral elastic and grand total cross sections that are available for positrons in gas-phase $\text{H}_2\text{O}$. The Set B elastic cross section is used in the present simulations. See text for more details.

Elastic cross-section set

The integral elastic cross section was previously obtained by subtracting the above inelastic cross sections (which include electron cross-sections in the absence of positron values) from the grand total cross section measured in reference [5]. Since that original set was constructed, there have been new measurements performed which directly measure the elastic cross section [2]. It is worth noting that the measured “quasi-elastic” cross section also includes low-threshold inelastic processes due to the experimental energy resolution of approximately 100 meV. As in previous models [7, 14, 148], this “quasi-elastic” cross section is treated as purely elastic, in the absence of a better approximation.

A comparison of the quasi-elastic cross sections from the previous (set A) and current (set B) cross section data sets is shown in figure 6.2. Also shown in that figure are the grand total cross sections (GTCS) from the corresponding data sets, which are in good agreement with each other. The magnitude of the directly measured elastic integral cross section in set B is considerably lower than the derived cross section of set A. For example, at higher energies, set B is less than one third of the magnitude of set A. As the elastic cross sections of set A were calculated indirectly, they are impacted by a lack of knowledge of any of the inelastic processes such as neutral dissociation [70], which would cause the elastic cross section to be overestimated. By contrast, the elastic cross sections of set B were directly measured and so they may be more accurate. The measured elastic cross section has been modified with a forward-scattering correction as discussed in section 2.5 of chapter 2.
CHAPTER 6. SPATIAL SIMULATIONS OF WATER

W. Tattersall

Inelastic cross-section sets – ionisation and excitation

The inelastic cross sections are unchanged from those previously used in the earlier Monte Carlo simulations [7, 14, 18]. The positron ionisation cross section was calculated by Tóth et al. [15] using a distorted-wave model. Theoretical vibrational excitation cross sections were calculated by Nishimura and Gianturco [90], although they are unavailable for energies above 3.2 eV and so do not contribute to most of the simulations. The electronic excitation cross sections are experimentally inaccessible at this time, so are instead sourced from electron scattering measurements by Thorn et al. [91]. Note that triplet excitation processes from the electron set have been excluded, since electrons are distinguishable from positrons and this excludes exchange interactions, while the spin-orbit interaction is negligible for positrons. As such, the ground electronic state of the water molecule, a singlet state, cannot be excited into a triplet state as a result of positron impact [23]. Liquid effects are not included in the inelastic cross sections because there are no published data for low-energy positrons in liquid water, and the published data for electrons [57] include exchange interactions and incompatible models for ionisation that cannot be easily separated from the total.

Positronium formation and direct annihilation cross-section sets

Positronium formation is a process that is unique to positrons, whereby a positron may bind with an electron from a water molecule to form an exotic atom. The positronium travels through the medium until it self-annihilates, releasing gamma rays. Compared to direct annihilation, discussed below, the positronium formation cross section is much larger and occurs at higher energies, although both types of annihilation are important for positron detection in PET. For the simulations in this chapter, the measured positronium formation cross sections from chapter 2 are used, specifically those of the first experiment.

Following the positronium formation, it is possible that the Ps atom can break apart, after which the positron is released and continues on its path through the medium. The cross section for this process is unknown but it can be assumed to be reasonably large [152, 153]. The Ps atom is able to avoid break-up only if it can thermalise sufficiently quickly to a kinetic energy less than the Ps binding energy. There are some measurements of Ps scattering in the noble gases [154], but it is difficult to predict a Ps thermalisation rate for water. As the focus is on the low-energy behaviour, this process is neglected and it is instead assumed that Ps formation is unconditionally followed by Ps annihilation. This will grossly overestimate the Ps formation fraction, but it allows for the easy identification of the contribution that coherent elastic scattering makes to the spatial diffusion of the positron distribution. This is in contrast to the well-known Ore gap model [23] which assumes Ps atom dissociation is very large and hence suppresses Ps formation for energies above the ionisation threshold.

The break-up of positronium also depends heavily on its environment. In the gas phase, the binding energy is 6.8 eV but in a liquid such as water with a high-frequency dielectric permittivity of \( \epsilon_\infty \approx 2 \), the binding energy can be reduced to 1.7 eV [151]. This means that the positronium break-up process is available for a larger fraction of the thermalisation
as the focus in this chapter is on the effects of structure on the positron’s elastic cross section, these considerations are neglected.

Direct annihilation occurs when a positron and an electron in the molecule interact directly, producing gamma rays without the intervening step of positronium formation. This occurs mostly at energies of much less than 1 eV, with a cross section magnitude which is between five and six orders of magnitude smaller than the integral cross section for pseudo-elastic scattering [155]. Whilst all of the positrons that do not form positronium will inevitably undergo this process, given sufficient time, the lack of known cross sections for rovibrational excitations means that we cannot accurately simulate positrons at the low energies where direct annihilation is relevant. Consequently, this process is excluded from the simulations.

6.2.2 Differential cross sections

Measured quasi-elastic differential cross sections (DCS) for positrons in water vapour are presented in chapter 2. These cross sections are not, however, sufficiently extensive to serve as the input for the simulation. However, both the IAM-SCAR [2] and R-Matrix [13] calculations also shown in that chapter are in reasonably good agreement with the experimental cross sections. Figure 6.3 shows this agreement in a different form, allowing a direct comparison at all energies and angles simultaneously. The IAM-SCAR model shows better agreement with the measured DCS, particularly at the lower energies. The simulation has been performed with both theoretical models, as well as an isotropic case, and comparison between the three are shown. For the other results, the anisotropy is defined by the IAM-SCAR cross sections.

There are no experimental measurements or complete theoretical results for differential cross sections for the excitation processes. The present model uses an empirical theory by Fuss et al. [156]. This provides an estimate of the angle-differential nature of the cross section for each excitation process:

\[ \sigma_{\text{inel}} (\epsilon, \chi) \propto \sigma_{\text{el}} (\epsilon, \chi)^{1 - \frac{\Delta \epsilon}{\epsilon}}, \]  

(6.1)

where \( \epsilon \) is the collision energy, \( \chi \) is the scattering angle, and \( \Delta \epsilon \) is the energy threshold of the excitation process in question. The constant of proportionality is set so that the angle-differential cross section integrates to give the integral cross sections as described in section 6.2.1. Namely

\[ 2\pi \int_0^\pi \sigma_{\text{inel}} (\epsilon, \chi) \sin \chi d\chi = \sigma_{\text{inel}} (\epsilon). \]

6.2.3 Ionisation energy sharing

In a positron-impact ionisation event, the energetic incident positron ionises the molecule and, in the process, loses an amount of energy equivalent to the binding energy of the molecule, while the remaining kinetic energy is shared between the scattered positron and the ejected electron (the small contribution to the ion’s motion is neglected in this study).
Figure 6.3: Comparison between the two available theoretical elastic differential cross sections: IAM-SCAR [2] and R-Matrix [13]. Experimental values [2] are plotted as circles, using the same colour scale. The dashed white lines denote the energies for which the DCSs have been explicitly calculated, while intermediate values use a linear interpolation. The angular resolution of the theoretical DCSs is 1°.

Note that in this case the first ionisation energy is considered, which in water has an energy threshold of 12.6 eV. In this study, comparisons have been made between five models of ionisation energy sharing, in which the kinetic energy of the ejected electron and the post-collision positron is distributed in different ratios:

1. All to positron, in which the scattered positron retains as much of the energy as possible, leaving the ejected electron with (an unphysical) zero energy,
2. 50/50 sharing, where the remaining energy is always split evenly between the ejected electron and the scattered positron,
3. Equi-probable (uniform) sharing, where the remaining energy has an equal probability of being split in any ratio between the ejected electron and the scattered positron,
4. Parametric model, as detailed in reference [8], which is an energy-dependent parameterised combination of models (1) and (2) above and is based on experiments with H₂, and
5. An experimentally measured energy sharing distribution for H₂O, from Arcidiacono et al. [157].

Most of the previous studies have assumed either that the ejected electron receives none of the residual energy (model 1) [7], or that the scattered positron and ejected electron can share any ratio of the resulting energy [18] (model 3). A recent study by Boyle et al. [8] has highlighted the importance of the energy sharing behaviour when calculating transport
coefficients for particles in an electric field, and so several of the models from that article have been included as an estimate of how positron and electron energy is distributed after an ionisation event. The most complete model in that article is a parametric fit to measurements [158, 159] of energy sharing for positron impact ionisation of molecular hydrogen (model 4).

For the present simulation, the most useful data concerning positron-water ionisation comes from the experiments from the UCL group led by Laricchia [157]. They have measured post-collision positron energies for positron impact ionisation of water at 100 eV and 130 eV, in the case where the positron is scattered into angles of less than 15°. The Monte Carlo simulations start at 60 eV and decrease from there but, in the absence of other data or relevant theories, the aforementioned 100 eV distribution is used for all of the energies that occur in the simulations and for all scattering angles. Note that for both positron and electron ionisation in water, there is a theoretical treatment by Tóth et al. [160] which calculates the triple differential cross-section for an incident positron of 250 eV. This work is quite restricted in the range of kinematic variables studied, however, so it cannot be used here.

All of these energy sharing models are shown in Figure 6.4, where the possible energy fractions which can be sampled are indicated with a line. Note that the results of Model 4 are only shown for a pre-collision energy of 60 eV; see reference [8] for analytic equations that describe the complete distribution, which is what governs the ionisation energy sharing in the present simulation.

An alternative model for ionisation (and general inelastic processes) makes use of energy-loss spectra [57], focusing entirely on the dynamic response of the liquid and using a Born approximation treatment for an incoming electron. As previously mentioned, it is non-trivial to obtain a positron equivalent from existing water calculations, and it is preferable to use scattering calculations which explicitly include the differences between an electron or a positron scattering from the molecule.

6.3 Inclusion of coherent elastic scattering in liquid water

To account for the spatial and temporal correlations of the scattering species in the liquid water medium, a static structure factor is implemented in the simulation with the procedure detailed in chapter 5. This requires a knowledge of the static structure factor $S(\Delta k)$, which for liquid water is sourced from Badyal et al. [19]. Since the simulation requires a static structure factor which is a function of positron energy, equation 5.9 of chapter 5 is used to integrate over all allowable changes in momentum for each collision energy.

The result of this process, for the IAM-SCAR, R- Matrix and isotropic scattering cross-section sets, is shown in figure 6.5. For a forward-peaked differential cross section, the probability of low momentum transfer is larger, so that the low momentum transfer part of $S(\Delta k)$, which is much less than 1, is sampled more, leading to a smaller $\bar{S}(\epsilon)$. For completely uncorrelated scatterers, as in the dilute gas case, the static structure factor $S(\Delta k) = 1$ by definition. In that case, $\bar{S}(\epsilon) = 1$ for all energies, regardless of the angular
Figure 6.4: Ionisation energy sharing distributions for positrons in water. Each line corresponds to one of the energy sharing ratios that can be sampled by the Monte Carlo simulation. For the H\(_2\) and H\(_2\)O models, each line represents an energy-sharing ratio sampled with equal probability for any ionisation event with an initial positron energy of 60 eV.

dependence of \(\sigma_{el}(\epsilon, \chi)\). Any differences due to coherent scattering are most pronounced at low energies, where the small structure factor leads to a propensity for strongly reduced momentum transfer, and thus more forward-peaked collisions. However, \(\bar{S}(\epsilon)\) deviates considerably from unity in the entire energy range when the anisotropy of the IAM-SCAR and R-Matrix is taken into consideration.

6.4 Definition of energy deposition

A common procedure in radiation therapy is to measure energy deposition, otherwise known as radiation dosimetry. The dosimetry is used to estimate the likely degree of cellular damage due to the transport through tissue of the positron and its associated secondary electrons. There are a number of related measures of dose, but in this case what is presented is an approximation of the “absorbed dose”, which is simply the amount of energy deposited per kilogram of water. This does not take into account the biological effectiveness of the radiation, although the results have been differentiated into categories based on the type of interaction, and could be used to calculate such an effective dose if desired.

Each collision that a positron undergoes will transfer some energy to the medium. For all collisions except positronium formation, there is an elastic energy transfer proportional to the mass ratio of the positron and a water molecule, which for the present energy ranges
Figure 6.5: Angle-integrated static structure factor for liquid water, derived from the static structure measured by Badyal et al. [19] and calculated using equation (5.9). The lines correspond to calculations for both of the theoretical differential elastic cross section sets discussed in section 6.2.2, as well as for isotropic scattering.

are less than 1 meV. Because each excitation process has a separate cross section defined, the water molecule will always gain the threshold energy of the chosen process. In water, these thresholds range between 0.2 and 12.6 eV.

In an ionisation event, the resulting ionised molecule gains the ionisation energy of 12.6 eV. The electron produced in the ionisation event will also deposit energy into the medium and, lacking an annihilation pathway, must eventually deposit enough energy to at least reach thermal equilibrium. The transport of the electron is not included in this study, so it is not possible to predict the locality of the deposited energy. As such, the energy deposition profile shows the energy of the electrons at the locations where the ionisation events take place. However, the presented results maintain a distinction between electron energy and ionisation threshold energy.

Positronium formation occurs by ionising the molecule, so it also deposits 12.6 eV of energy. This occurs even when the kinetic energy of the positron is lower than the ionisation threshold, as there is some potential energy supplied by the bound state of the positronium. The transport and eventual annihilation of the resulting positronium is outside of the scope of this thesis, and it is difficult to predict how much of the kinetic energy of the positronium would be absorbed by the water molecules and how much would remain with the positronium until it decays into a pair of gamma rays. The gamma rays contain any remaining kinetic energy as well as the mass energy of the positronium, and thus have an energy of approximately $2 \times 511$ keV, which is vastly higher than any of the other energies.
CHAPTER 6. SPATIAL SIMULATIONS OF WATER

W. Tattersall

considered here. However, the gamma rays are unlikely to interact strongly with the local water molecules – it is indeed this feature that allows them to be detected for use in PET. As such, the absorbed dose for each positronium formation event is treated as 12.6 eV at the site of the event, ignoring any remaining energy. This is in contrast to Marjanović et al. [18], who state that the entirety of the positron’s energy (which is often less than 12.6 eV) is deposited at the site of the event.

6.5 Simulation parameters

The simulation begins with all of the positrons having an initial energy of 60 eV, because this is the highest of the experimentally measured energies in reference [3]. This is relatively low compared to most other studies [60], however this is the energy regime in which the Born approximation is insufficient and empirical cross sections are increasingly necessary [122]. The positrons are emitted isotropically from the source, so the swarm is spherically symmetric, even though individual particles require fully specified 3D coordinates.

As the energy deposition behaviour of the particles is the primary interest, the simulation was halted as soon as the energy of the positron became lower than the positronium formation threshold. This decision was made in order to satisfy equation (3.11) in chapter 3, which is required to determine time-independent spatial distributions. If low energy positrons are not removed from the simulation, and there are no means by which they may gain energy (which is the case with the field-free, cold medium system that is simulated here), the positrons slow to arbitrarily low energies and continue to accumulate within a finite volume around the source, which means there can be no time independent steady-state distribution. Removing positrons below the positronium formation threshold prevents this problem and does not significantly affect results above the threshold energy. As shown in the results, in most of the simulations approximately 97% of the positrons undergo positronium formation. It is very unlikely that those that remain would re-enter the higher-energy regime, as they can only gain energy from thermal energy, which is generally much smaller than the threshold. Other models have treated such positrons as annihilating locally [71]. However, later simulations demonstrate that the positrons may still travel distances that are significant on the relatively fine spatial scale that is employed here. As such, lower energies are explicitly excluded from the domain of the model; quantities such as mean energy can no longer be calculated, but distributions of energy and annihilation profiles above the cutoff energy are still accurate.

To estimate the effects of coherent scattering, which are most significant at very low energies, several simulations have been performed that are instead cut off at a thermal energy of 0.04 eV. These latter simulations are somewhat counter-intuitive, as the vast majority of the collisions are elastic interactions of those very few positrons that avoid forming positronium. They are nevertheless useful for demonstrating how the range of near-thermal positrons can be affected by coherent scattering, which has implications for direct annihilation profiles.
Table 6.1: Measurements presented in this study, represented in terms of the factors in equations (3.9) (time-averaged space distributions) and (3.10) (collision moments, marked with a ‘*’). The value of $\psi$ for the energy deposition measurement depends on the type of process, as discussed in section 6.4. The quantity $\epsilon_{e^-}$ is the energy of the secondary electron emitted from the ionisation event, which is sampled from the distributions in section 6.2.3.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Symbol</th>
<th>Symbol</th>
<th>$\psi$</th>
<th>$y(r', v', t_m)$</th>
<th>Collisional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positron density</td>
<td>$\rho(r)$</td>
<td>1</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Positron energy distribution</td>
<td>$\rho(r, \epsilon)$</td>
<td>1</td>
<td>$\frac{1}{2}m_\gamma^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collision count per process</td>
<td>$N_j(r)$</td>
<td>1</td>
<td>$\frac{\nu_j(v)}{\nu_{tot}(v)}$</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Energy deposition per process</td>
<td>$\Delta\epsilon_j(r)$</td>
<td>Varies</td>
<td>$\frac{\nu_j(v)}{\nu_{tot}(v)}$</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Electron production</td>
<td>$N_I(r, \epsilon_{e^-})$</td>
<td>1</td>
<td>$\frac{1}{2}m_\gamma^2 \epsilon_{e^-} \cdot \frac{\nu_I(v)}{\nu_{tot}(v)}$</td>
<td>*</td>
<td></td>
</tr>
</tbody>
</table>

In all cases, the density of water molecules has been chosen to emulate that of liquid water at standard temperature and pressure, which corresponds to a molecular number density $n_0$ of $3.3 \times 10^{28} \text{ m}^{-3}$. This applies even when there is no coherent scattering, the “dilute gas” case, so that is possible to distinguish the effects of coherent elastic scattering independently from density effects.

### 6.6 Results

This section contains a variety of density measurements, all of which are specific cases of the spatially-binned collision- and space-moment distributions described in section 3.5. These are related to the steady-state phase-space distribution function through equations (3.8) and (3.10), respectively, of that chapter.

The values of the discriminant $y(r', v', t_m)$ corresponding to the various measurements are listed in table 6.1.

#### 6.6.1 The standard simulation

Not every possible combination of cross sections and scattering parameters has been simulated. Instead, the focus was on variations of what is the most realistic simulation of liquid water out of the variations in this chapter. The standard simulation comprises of the updated set of integral cross sections, along with IAM-SCAR differential elastic cross sections, the Fuss et al. [156] approximation for inelastic differential cross sections, the $\text{H}_2\text{O}$ model for ionisation energy sharing (ionisation model 5 in section 6.2.3), and the experimentally-measured static structure factor of Badyal et al. [19] to account for coherent scattering effects. As all of the quantities reported depend linearly on the positron emission rate, the results are scaled to correspond to a positron emission rate of $\alpha = 1 \text{ Hz}$. All of the spatial density results are presented in terms of a linearised density, as discussed in section 3.7.3, so that they have units of inverse length rather than inverse volume.

The steady-state spatial distribution of the density of positrons, $\rho(r)$, is shown in figure 6.6. In the steady state, with a continuously-emitting source which began emitting a long time ago, this value does not change with time for small $r$. Because positrons which
survive below the Ps formation threshold are no longer simulated and the energy of the positrons is monotonically decreasing with time, the distance that the positrons can travel is finite and the total number of positrons in the system eventually reaches a steady state. This occurs when the number of incoming positrons is matched by the number of positrons that reach the energy threshold. The peak of the density distribution lies at the source, dropping off rapidly with distance as the positrons are removed from the source due to positronium formation. The absolute magnitude of the density is very small, for the present emission rate of $\alpha = 1 \text{ Hz}$, because the positrons last on average $1 \times 10^{-16}$ s before forming positronium and being removed from the distribution.

Figure 6.7 shows the spatial profile of energy deposition for the above parameters. This is equivalent to the quantity given in equation 3.10, summed over all energy bins, with $y$ set to discriminate based on the collision process, and $\psi$ set to the energy deposited by each collision as defined in section 6.4. The amount of energy transferred due to elastic collisions is not even visible on this scale. Instead, energy deposition is dominated by positronium formation and ionisation. This is to be expected: both positronium and ionisation events transfer at least 12.6 eV to the medium, and while the ionisation cross section has a larger cross section at higher energies, positronium formation can continue to occur at lower energies. As the H$_2$O model is being used for ionisation energy sharing, most collisions result in only a small amount of energy transferred to the ionisation electron, hence the total energy in the ejected electrons is considerably smaller than the energy retained by the ionised molecules.
Figure 6.7: Stacked line chart showing spatial profiles of the rate of energy deposition for the standard simulation parameters. Note that “Ionisation e−” represents the initial energy of the emitted electrons, while all other depositions are at the locations of the interaction events. Total energy deposition is included in parentheses in the figure legend. Energy deposition due to elastic and vibrational excitation collisions is not visible at this scale.

Figure 6.8 represents the spatial distribution of collision events. This is equivalent to equation (3.10), once again summed over all energy bins, with \( y \) set to discriminate based on the collision process, and \( \psi = 1 \). Even though only positrons at energies above the positronium formation threshold are simulated, elastic interactions are still the most common collision process. The vibrational and electronic excitation processes are relatively rare, while ionisation and positronium formation together constitute half of the collisions close to the source.

To evaluate the effects of the ionisation energy sharing model, the type of anisotropic scattering and the presence of coherent scattering, several variations of the standard parameters have been considered. To determine the total positronium formation rate, equation (3.10) has been used, this time summing over both spatial and velocity bins, with \( y \) set to allow only positronium formation events, and \( \psi = 1 \). Figure 6.9 shows a comparison of the total percentage of positronium formation for all of these models, which is effectively a measure of the time that the positrons spend at energies where the positronium formation is larger. As expected, the form of the differential cross sections has no impact on the rate of positronium formation, as without any external forces the energies of the positrons are not dependent on the direction of their travel. Similarly, coherent scattering does not directly affect energy transfer rates, and likewise leaves the positronium rate constant. The greatest rate of positronium formation occurs when ionisation energy sharing gives all of
the remaining energy to the scattered positron, because the higher energy allows more positronium formation events to subsequently occur.

As the dissociation of the Ps atom is neglected after it has formed, the amounts shown in figure 6.9 are an overestimate of the total positronium formation fraction. Hence, these values should not be directly compared to experiment, in which a significant fraction of the annihilation is always observed to originate from direct positron annihilation. Additionally, the simulation does not correspond to typical experimental conditions because the positron is injected at low energies instead of high energies.

6.6.2 Effect of anisotropic scattering

The presence of anisotropy in the scattering cross-sections has a significant effect on the spatial profiles of the positron energy distribution. Figure 6.10 shows a comparison of these energy profiles, and it is clear that while the relative number of positrons at each energy is unchanged, the particles travel significantly further when scattered anisotropically. The IAM-SCAR model predicts cross-sections that are slightly more forward-peaked than those from the R-Matrix approach, and the corresponding distance profiles reflect this. However, the difference is much smaller than it would be in the presence of an electric field [161], such as in swarm studies [7, 162], because there is no preferred direction. With an applied electric field, particles that oppose the direction of the field do not do so for long, so forward-scattering enhances its motion in the direction of the field considerably. In
Figure 6.9: Comparison of the fraction of positrons that undergo positronium formation at least once, for each of the variations of the standard parameters. The standard parameter set is red, while green represents variation in the ionisation energy sharing behaviour and cyan represents variants of the anisotropy for scattering events. The fraction reported here is not representative of the total Ps annihilation rate that would be obtained in experimental conditions, as it neglects break-up of the Ps atom.

the present case, where there is no field, forward scattering increases the diffusion of the swarm in all directions.

Figure 6.11 shows the density of positronium formation events as a function of distance from the source. As expected, the isotropic elastic cross section has a much sharper distribution, while the more forward-peaked anisotropic cross sections (IAM-SCAR and R-Matrix) lead to the broadest positronium formation distribution, even though the total formation rate is the same.

The broadening of the spatial positron distribution is of importance in the “blob” model [151] of the positron track for the injection of high-energy positrons. As the relaxation of the positron leads to significant densities of secondary ions along the positrons path, then the diffusion of the positron out of the radiation track will change the processes available to the positron. This can occur even if the distance the positron diffuses at the end of the path is much smaller than the entire high-energy track. In the blob model, the size of the blob at the end of the positron track is on the order of nm [151].

6.6.3 Effect of ionisation energy sharing

Ionisation energy sharing distributions determine the amount of energy that is allocated to the positron and the ejected electron after an ionising collision event. The spatial dependence
Figure 6.10: Steady-state positron number distributions, as a function of positron energy and distance from source. This is measured over an energy space of equal divisions, such that $\rho(r) = \int \rho(r, \epsilon) d\epsilon$ gives the total number of positrons as shown in figure 6.6. The simulations use the standard parameters listed in section 6.6.1, except that different differential cross sections, as listed in section 6.2.2, are used for both elastic and inelastic scattering.

of the scattered positron and ejected electron energy density distribution functions are presented in figures 6.12 and 6.13 respectively. The positron energy distribution was sampled by recording the instantaneous energy of the positron at evenly spaced time intervals, while the electron energy was recorded after each ionisation event. The transport of the emitted electrons is not simulated in this study. For a complete picture of energy deposition and micro-dosimetry, the tracks of the emitted electrons should be simulated as well, however it should be noted that in the H$_2$O model, the electrons are emitted with relatively low energies and are unlikely to contribute significantly to the total energy deposited. Such a simulation is therefore deferred to future, higher-energy studies.

Several interesting features can be identified in these results. Figure 6.1 lists the threshold energies of the various inelastic processes, and in figure 6.12 these specific values have a clearly visible impact in the positron energies, particularly for the “50/50” and “all to positron” models. Because the initial positron distribution is a monochromatic 60 eV beam, there are several horizontal bands of high density in the energy-distance coordinates, which occur at $(60 \text{ eV} - \epsilon_p)$ where $\epsilon_p$ is the threshold energy for each excitation process.
Figure 6.11: Positronium formation rate as a function of the radial distance from the source. The results are presented for the different cross-section anisotropies.

Figure 6.12: Steady-state positron number distributions, similar to figure 6.10. The variants employ different distributions of post-collision energy sharing in ionisation events, as described in section 6.2.3.
Figure 6.13: Steady-state number distributions of the secondary electrons emitted in ionisation events, as a function of initial electron energy and distance from source. Note that this only includes electrons when they are first emitted. The simulations use the standard parameters listed in section 6.6.1, but with variations of the post-collision energy sharing in ionisation events according to the models listed in section 6.2.3. A precise definition of $N_I(r, \epsilon_{e^-})$ is given in section 3.7.3.

These represent positrons that have undergone only a single excitation collision, and the intensity of these bands is therefore proportional to the magnitudes of the corresponding integral cross sections at the initial energy. For the “50/50” model, there is a similar band for ionisation at 23.7 eV, which is half of the remaining energy after an ionisation event that was initialised by a 60 eV positron, and the “all to positron” model shows distinct bands for every multiple of the threshold energy below the initial energy. Subsequent bands are not distinct for the continuous models of ionisation energy sharing, because assigning the ejected electron a variable amount of energy broadens the energy distribution of the positron swarm. However, the H$_2$ model does show a small increase in density in the region close to 23.7 eV, a consequence of its physical preference towards sharing energy evenly. The H$_2$O model shows similarly broad bands that match the energies of the “all to positron” bands, as its energy sharing distribution is dominated by a tendency to give almost all of the energy to the positron. These bands of high density are seen in other swarm transport simulations, such as [7,120], but it is notable that they are an artefact of the monochromatic initial energy, and will not be seen in a realistic system where the positrons are emitted with a broad spectrum of energy.

The positions at which ionisation events occur have an electron energy distribution that depends heavily on the ionisation model in question. As can be seen in figure 6.13, the “50/50” and “H$_2$” models’ distributions are bi-modal, one peak being at the aforementioned 23.7 eV while the other appears at 5.5 eV. The latter arises in the case where there are two ionisation events that both share energy approximately equally with their ejected electrons.
Figure 6.14: The rate of ionisation events for positrons in H$_2$O, as a function of the distance from the positron source. The effects of several ionisation energy sharing models are compared.

In figure 6.14, it can be seen that the energy-integrated ionisation rate is significantly enhanced for the “all to positron” and “H$_2$O” models, as these models lose less energy to the positrons. This results in both a greater ionisation rate and a higher velocity that allows the positrons to cover more distance. For completeness, the (trivial) electron energy distribution for the “all to positron” ionisation model is also included.

Positronium formation is shown in figure 6.15. In all cases, positronium formation is negligible beyond 7 nm from the source. The “H$_2$O” and “all to positron” models yield the greatest total positronium formation rates, but within the very short range, they have a somewhat lower rate than the alternative models. Within 1 nm of the source, the “50/50” and “H$_2$” models have a lower energy, as seen in figure 6.12, and the positronium formation cross section is larger at lower energies.

6.6.4 Impact of coherent elastic scattering from correlated water molecules in the liquid phase

The inclusion or removal of coherent elastic scattering processes is used to assess the significance of the effect for the transport of positrons. In this case, the density of the medium is unaltered, so including these effects adjusts only the momentum transfer rate for elastic collisions. The magnitude of the effect is largest at low energies, where the structure factor deviates significantly from 1 (as shown in Figure 6.5), i.e. below about 1 eV, although the difference still exceeds 10% at energies as high as 10 eV. Nevertheless, the effect is negligible.
Figure 6.15: Spatial distribution of the positronium formation rate for each of the ionisation models.

Figure 6.16: Steady-state positron number distributions, similar to figure 6.10, but comparing the correlated (liquid) and uncorrelated (gas-like, but with liquid density) systems.
at the higher energies where most of the simulations were conducted, partly because the momentum transfer is small due to the forward-peaked differential cross sections. To analyse for the effects at lower energies, simulations have been performed in which the positrons are allowed to reach approximately thermal levels. This is, strictly speaking, somewhat less accurate than the shorter-duration simulation, because the rotational excitation cross sections that are treated quasi-elasitically (see section 6.2.1) are likely to be significant at such low energies.

In figure 6.16, the positron energy distribution (as a function of distance from the source) is presented for the gas and liquid (coherent scattering) phases. It is clear that for energies below about 3 eV the positrons in the liquid diffuse to roughly twice the distance compared to the gas phase, reaching thermal energies. This is because coherent scattering reduces the momentum transfer cross-section when the structure factor is less than unity (see section 5.3.2 in chapter 5), which is true for energies below 8 eV (as seen in figure 6.5). This physically manifests itself as an increased scattering probability at forward scattering angles, so that positrons do not change their direction of velocity as often, leading to a greater random-walk diffusion. Since this effect, in water, is only significant below the positronium formation threshold, coherent scattering does not significantly alter the ionisation or positronium formation dosimetry. It should be mentioned, however, that solids have much longer-range structural correlations, and as such these effects may become significant when simulating positron transport through, for example, bone.

The positrons spend most of the simulation time at an energy below that of the lowest vibrational excitation threshold (bending mode) of $\sim 0.2$ eV, so they are free to travel a relatively long distance. This explains the apparent increase in diffusion at those low energies, compared to the standard simulation. Note, however, that since the cross section set currently lacks explicit rotational excitation cross sections, this effect is unlikely to be as large in real gases, although a similar effect would occur at thermal energies.

6.7 Concluding remarks

This chapter has presented a collated set of vapour-phase water cross sections, as well as results from a series of Monte Carlo simulations employing said cross sections. Several variations have been compared to quantify the effects of ionisation energy sharing, anisotropic scattering, and coherent elastic scattering. The resultant spatial distributions include comparisons of energy deposition, ionisation events and Ps formation. For the variations that were compared, the strongest effect is seen in the choice of post-ionisation energy sharing, which can lead to differences of up to 20% in the positronium formation rate. Even though the positronium break-up process is neglected, the differences that are observed are likely to effect experimentally observed positronium annihilation rates. The choice of energy sharing model also affects how far the positrons diffuse from the source. The anisotropic elastic cross sections calculated using the IAM-SCAR method have a small, but detectable effect on the spatial profiles as compared with the earlier R-Matrix calculation cross sections. Both of these theoretical data sets present a much larger diffusion compared
to the commonly-assumed case of isotropic scattering. This is important in the context of the tracks of positrons injected at high energies, because a positron that has diffused out of its radiation track has a very different environment and dynamics. The significance of coherent elastic scattering is relatively limited: while it has essentially no effect on the positronium formation or ionisation dosimetry profiles, it can increase the diffusion significantly at lower energies.

These models provide clear evidence that an accurate description of scattering at the atomic level is crucial for a quantitative understanding of the macroscopic behaviour of the system in question. The accuracy of future transport simulations is primarily limited by the availability of the molecular cross sections, particularly the fully-differential ionisation cross sections. For accurate predictions of positron annihilation due to direct annihilation, it would be necessary to simulate the transport at very low energies, which would in turn require substantial information about the rotational excitation cross sections. True dosimetry determinations and molecular damage estimates would also require electron cross sections, as well as effective dose models to estimate the damage caused by specific types of energy deposition. Future transport work should also aim to include other effects of the liquid phase, such as potential screening and density fluctuations, as well as the tracking of the formed positronium atoms including their break-up and recombination processes.
7.1 Summary

The behaviour of charged particles in gases and structured media is of critical importance in a variety of technologies and applications. Electron applications are ubiquitous in modern technologies and processes, while the unique ability of positrons to annihilate with electrons can be exploited in positron-annihilation spectroscopy and positron emission tomography. There is a need to be able to quantify the macroscopic effects that these particles may have on their environment, especially for medical applications, where ionising radiation is of particular concern. The intent of this thesis has been to (i) contribute to the knowledge base of single particle positron cross sections with water, and (ii) to develop a Monte Carlo simulation which can accurately and efficiently model charged particles in gases, and incorporate a structure factor to model the effects of coherent elastic scattering in liquids or soft-condensed matter. A particular focus has been on liquid water and argon: the former for its biological applications, while the latter is a well-described system with practical applications in particle detectors.

Cross sections for positrons in water vapour have been measured [2, 5], spanning a range of energies from 1 to 60 eV. These include the first measurements of both total and differential elastic scattering, and total inelastic scattering. The agreement between experiment and theory in all cases is acceptable, particularly when the significant omission of forward-scattering effects is accounted for. Several interesting comparisons have also been made with other data sets, including the elastic and inelastic cross sections used in a number of previous studies [7, 14]. Finally, the forward scattering corrections to the elastic data, previously only applied at select energies, have now been extrapolated over the entire range, allowing the direct use of the total elastic cross sections in positron transport models.
CHAPTER 7. CONCLUSION

An original Monte Carlo code which can model electrons and positrons in a variety of conditions has been developed. It has been extensively benchmarked in both diffusive systems and highly non-equilibrium hydrodynamic systems. Several novel techniques have been included in the code, including several methods for calculating the charged particle motion in an electric field, and a variance reduction technique that allows for efficient simulations of particles when a strong non-conservative process exists, such as electron impact ionisation or positronium formation. This independent code has already proven useful as a benchmark comparison for Boltzmann equation solutions, as well as modelling aspects of the positron scattering beamline including the dumping behaviour of a Surko positron accumulator [1] and the expected cutoff curve for positrons leaving the scattering chamber.

The Monte Carlo code has been extended to model the effects of coherent elastic scattering in materials which have notable spatial and temporal correlations between their constituent molecules. Two different techniques were employed: a static structure approach based on a formalism by Wojcik and Tachiya, and a dynamic structure approach based on Sakai et al. Both techniques improve the accuracy of the simulation when applied to liquids and soft-condensed materials, and the latter has the added advantage of correctly treating gases with a non-zero temperature. Further benchmarks were used to validate the code, including a system similar to a Franck-Hertz experiment [9] where the structure effects modify the oscillation wavelength. This code also represents one of the few implementations of coherent elastic scattering that models both energy and momentum transfers precisely. While it has yet to be employed with real systems, two benchmark models have validated the technique and demonstrated its utility for non-zero gas temperatures.

In the final chapter, a sophisticated Monte Carlo model of positron thermalisation in liquid water has been developed, employing the newly measured cross sections as well as the non-conservative transport and coherent elastic scattering techniques in the liquid phase. It is limited to modelling the transport of the positrons only, and therefore extends only to the first positronium formation event, while not simulating the transport of any secondary electrons. Nevertheless, this model has been used to produce spatial profiles of energy deposition, the types of collisions that occur, and the expected sites of ionisation and positronium formation, all of which are of interest for medical dosimetry models of positron emission tomography.

7.2 Recommendations for future work

The ubiquity of charged particle transport naturally offers a wide variety of applications and opportunities for transport models. The work that has been presented in this thesis is only a small part of that which is required to accurately model transport in many systems.

Positron scattering experiments continue to improve, studying different interactions and materials with new techniques. The recent example of measurements of positrons in water by Loreti et al. [163] which minimises forward scattering effects is very welcome. Meanwhile, fully-differential ionisation cross sections are being measured [93] with a reaction microscope
experiment which would significantly improve the expected accuracy of transport models. Experiments in positronium scattering are also under way [154], which is relevant for most positron applications as positronium may break-up and reform several times before annihilating and being detected.

The future of Monte Carlo models of charge transport is very likely to be largely subsumed by the GEANT4 simulation framework, which at this point in time is likely the most complex particle transport code in the world. Due to its open source nature, many independent researchers have contributed large amounts of code, including many of the same features that appear in the present work. A direct dynamic structure factor approach has not yet been implemented in that model, although an indirect approach based on a dielectric formalism is part of GEANT4-DNA [61]. Being able to combine arbitrary dynamic structure factors with arbitrary cross sections may be useful from the viewpoint of developing an understanding of the emergent properties of the system, while the thermal ideal gas models may be effective for low energy thermalisation of ions.

Direct simulation of clinical and experimental applications relies on the availability of high-quality, complete cross sections, and unfortunately these are quite difficult to measure. For clinical use in positron emission tomography to be reliable, the type of transport simulation presented here would require at the least fully-differential ionisation cross sections for positrons in water, and a clearer picture of the sub-electronic excitation processes would also be very welcome. The transport of positronium itself is also very important, as its processes of break-up and recombination can significantly increase its diffusion and hence increase the spread of gamma ray emission.

There are several modifications to transport behaviour in dense media in general, and human tissue in particular, which have not been considered here. Localised density effects such as bubbles and clusters [124] and spur model recombination effects [151] are generally applicable in dense media. Meanwhile, the polar nature of water and the strong magnetic fields of combined PET/MRI scanners suggest that orientational effects [164] may play a significant role for medical applications. The development of scattering models for other biomolecules [165,166] such as THF [156], and pyrimidine [47] would also improve models of transport in human tissue analogues.


[53] Christophe Champion, Cindy Le Loirec, and Borko Stosic. EPOTRAN: a full-differential Monte Carlo code for electron and positron transport in liquid and


The simulation code is written in the Fortran language, but benefits from an extensive pre-processor stage based around a Python language templating system. Listing 1 shows a typical sample of the simulation code, in this case the set of statements that selects the process for interaction in a scattering event. Lines beginning with a “#” are interpreted as Python code, along with variables prefixed with “$”, and they are run before the Fortran code is compiled. This allows the selective inclusion of program features, with all of the attendant optimisations that the compiler can then make. In this example, lines 3 to 5 will only be included in the compiled Fortran code if positronium formation exists in the cross section set and $\text{conserve_positronium}$ is set to True, which is a pre-processing flag that enables the variance reduction feature described in subsection 3.4. Lines 8 and 9 will only be included if trace-level logging is switched on. The pre-processor variable $\text{gas}$ is replaced with the compile-time variable “\text{gas}” if there is only one, or with a reference to “\text{gases(chosen_gas)}” for gas mixtures.

Once the template has been filled, the resulting pure Fortran code has no dependencies on Python or any third-party libraries, and is thus very portable, allowing it to be run on any system that has a Fortran90 compiler. All of the inputs and outputs are processed by an extensive set of Python scripts, which allows for free-form inputs of simulation variables as well as simulation scheduling and aggregation across multiple computers and extensive analysis of the output data, including automatic figure generation.
The simulation begins by loading all inputs from a single file. The inputs consist of the following:

- A grand total cross section, for calculating the collision frequency.
- Normalised single cross sections, $\sigma_j/\sigma_{\text{GTCS}}$, to select which one occurs in a collision.
- In some cases, normalised angle or energy-differential cross sections.
- Existing particle properties, if continuing a previous simulation.

Most other parameters are compiled into the code, including configuration options for features such as the non-conservative attachment technique or electric fields, as well as all of the output specifications. In doing so, the Fortran compiler is able to make significant optimisations, such as not setting a variable that will never be used in the output.

Measurements can be performed selectively, and are integrated into the simulation code at several “join points” within the code, which are functionally similar to aspect-oriented programming [167]. These points have read-only access to the particle’s properties, and this level of isolation prevents inadvertent modification of the system when performing observations.

**Code Listing 1** Sample of the simulation code, showing interleaving of pre-processed Python template variables with standard Fortran code.

```fortran
1 coll_chooser: DO proc = offset+1, offset + ${gas}%process_count
2 #if "POSITRONIUM_FORMATION" in $interaction_kinds and $conserve_positronium
3 IF (processes(proc)%interaction_kind == POSITRONIUM_FORMATION) THEN
4   CYCLE
5 END IF
6 #end if
7 prob = prob + process_probability(proc, en_bin)
8 $tr("Process:", "proc")
9 $tr("Total/prob:", "prob")
10 IF (prob >= coll_type_random) THEN
11   chosen_proc = proc
12   EXIT coll_chooser
13 END IF
14 END DO coll_chooser
```

In retrospect, greater care should have been taken to distinguish the pre- and post-compilation code, as the interleaving of expressions at two separate phases of compilation rapidly becomes very confusing and error-prone. Nevertheless, the technique does allow for a useful degree of flexibility with regards to simulation features, without compromising the execution speed of the simulation at run time.

While “lines of code” is rarely a good metric for code complexity, the following does provide some perspective. In total, the Monte Carlo simulation templated Fortran code is around 3,500 lines and confined to one file. Meanwhile, the Python framework surrounding it amounts to 26,000 lines, with another 70,000 lines used to describe inputs and analysis scripts, all spread across 500 files. Only built-in functions were used in the Fortran code, while the Python code employs functions from several 3rd-party libraries: “numpy” for numerical calculations, “scipy” for some of the more advanced numerical algorithms.
including numerical integration and root-finding, “matplotlib” for producing figures, “traits” for enforcing consistency in the simulation variables, and the “cheetah” templating engine for pre-processing the Fortran code.
This appendix comprises cross section data from the two experiments described in chapter 2. In all cases, the cross sections have units of Å² = 10 x 10⁻¹⁶ cm², and each result is formatted as [value] ± [error], where the error is the estimated uncertainty of the measurement, which is almost entirely statistical. Each measurement is shown to 3 decimal places, although the uncertainty is often larger than this.

As discussed in section 2.5, the experiments can not detect scattering into small angles, so at low energies, the directly measured data represents a partial cross section over a limited range of scattering angles. A correction factor has been applied, based on theoretical DCS from [13], which estimates the total cross section where necessary. While the original publication [2] only included adjusted values at the energies for which a DCS is known, here the correction has been applied at all energies, based on an interpolation over the known values. The forward-scattering corrected values quote an uncertainty that is scaled up by the same amount as the measurement.
Table B.1: Measured grand total and positronium formation cross sections from the first experiment, as well as the forward-scattering adjusted grand total cross section. All energies are in eV, and all cross sections are in $\text{Å}^2$. The corresponding results of the second experiment are in reasonable agreement, when forward scattering is accounted for, and have a larger uncertainty, so there is little value in reproducing them here, although they are included in the figures of chapter 2.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\sigma_{\text{GTCS (measured)}}$</th>
<th>$\sigma_{\text{GTCS (estimated total)}}$</th>
<th>$\sigma_{\text{Ps}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>63.756 ± 1.148</td>
<td>174.021 ± 3.133</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>50.348 ± 1.019</td>
<td>148.493 ± 3.005</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>39.751 ± 1.050</td>
<td>116.400 ± 3.075</td>
<td>-</td>
</tr>
<tr>
<td>1.25</td>
<td>35.157 ± 1.080</td>
<td>95.711 ± 2.940</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>29.762 ± 1.076</td>
<td>76.665 ± 2.772</td>
<td>-</td>
</tr>
<tr>
<td>1.75</td>
<td>28.941 ± 1.057</td>
<td>71.961 ± 2.628</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>22.882 ± 0.473</td>
<td>56.283 ± 1.163</td>
<td>-</td>
</tr>
<tr>
<td>2.25</td>
<td>23.941 ± 1.043</td>
<td>59.285 ± 2.583</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>19.648 ± 0.469</td>
<td>49.134 ± 1.173</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>16.658 ± 0.516</td>
<td>41.707 ± 1.292</td>
<td>-</td>
</tr>
<tr>
<td>3.5</td>
<td>14.744 ± 0.511</td>
<td>34.317 ± 1.189</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>14.539 ± 0.493</td>
<td>30.591 ± 1.037</td>
<td>-</td>
</tr>
<tr>
<td>4.5</td>
<td>12.886 ± 0.499</td>
<td>25.266 ± 0.978</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>11.141 ± 0.130</td>
<td>20.932 ± 0.244</td>
<td>-</td>
</tr>
<tr>
<td>5.5</td>
<td>11.466 ± 0.503</td>
<td>20.948 ± 0.919</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>10.951 ± 0.130</td>
<td>19.498 ± 0.231</td>
<td>0.750 ± 0.103</td>
</tr>
<tr>
<td>6.5</td>
<td>10.850 ± 0.470</td>
<td>18.870 ± 0.817</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>10.462 ± 0.125</td>
<td>17.800 ± 0.213</td>
<td>1.448 ± 0.104</td>
</tr>
<tr>
<td>7.5</td>
<td>10.325 ± 0.478</td>
<td>17.216 ± 0.797</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>10.066 ± 0.136</td>
<td>16.470 ± 0.223</td>
<td>1.683 ± 0.103</td>
</tr>
<tr>
<td>9</td>
<td>9.879 ± 0.130</td>
<td>15.661 ± 0.206</td>
<td>2.174 ± 0.104</td>
</tr>
<tr>
<td>10</td>
<td>9.813 ± 0.127</td>
<td>15.183 ± 0.196</td>
<td>2.418 ± 0.106</td>
</tr>
<tr>
<td>11</td>
<td>9.446 ± 0.135</td>
<td>14.331 ± 0.205</td>
<td>2.425 ± 0.101</td>
</tr>
<tr>
<td>12</td>
<td>9.509 ± 0.133</td>
<td>14.159 ± 0.198</td>
<td>2.665 ± 0.103</td>
</tr>
<tr>
<td>13</td>
<td>9.203 ± 0.129</td>
<td>13.467 ± 0.189</td>
<td>2.686 ± 0.104</td>
</tr>
<tr>
<td>14</td>
<td>9.305 ± 0.133</td>
<td>13.392 ± 0.191</td>
<td>2.756 ± 0.102</td>
</tr>
<tr>
<td>15</td>
<td>9.191 ± 0.132</td>
<td>13.016 ± 0.187</td>
<td>2.918 ± 0.104</td>
</tr>
<tr>
<td>16</td>
<td>9.103 ± 0.139</td>
<td>12.691 ± 0.194</td>
<td>2.813 ± 0.104</td>
</tr>
<tr>
<td>17</td>
<td>9.172 ± 0.135</td>
<td>12.600 ± 0.185</td>
<td>2.820 ± 0.109</td>
</tr>
<tr>
<td>18</td>
<td>8.991 ± 0.130</td>
<td>12.172 ± 0.176</td>
<td>2.736 ± 0.102</td>
</tr>
<tr>
<td>19</td>
<td>9.009 ± 0.130</td>
<td>12.022 ± 0.173</td>
<td>2.804 ± 0.107</td>
</tr>
<tr>
<td>20</td>
<td>8.967 ± 0.133</td>
<td>11.799 ± 0.175</td>
<td>2.726 ± 0.105</td>
</tr>
<tr>
<td>21</td>
<td>8.849 ± 0.134</td>
<td>11.490 ± 0.174</td>
<td>2.696 ± 0.105</td>
</tr>
<tr>
<td>22</td>
<td>8.666 ± 0.123</td>
<td>11.106 ± 0.158</td>
<td>2.664 ± 0.102</td>
</tr>
<tr>
<td>23</td>
<td>8.825 ± 0.129</td>
<td>11.173 ± 0.163</td>
<td>2.650 ± 0.103</td>
</tr>
<tr>
<td>24</td>
<td>8.659 ± 0.120</td>
<td>10.836 ± 0.150</td>
<td>2.593 ± 0.092</td>
</tr>
<tr>
<td>25</td>
<td>8.985 ± 0.119</td>
<td>11.120 ± 0.147</td>
<td>2.672 ± 0.098</td>
</tr>
<tr>
<td>26</td>
<td>8.598 ± 0.120</td>
<td>10.539 ± 0.147</td>
<td>2.495 ± 0.096</td>
</tr>
<tr>
<td>27</td>
<td>8.694 ± 0.125</td>
<td>10.559 ± 0.152</td>
<td>2.424 ± 0.099</td>
</tr>
</tbody>
</table>

*Continued on next page*
### Table B.1 – Continued from previous page

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\sigma_{\text{GTCS}}$ (measured)</th>
<th>$\sigma_{\text{GTCS}}$ (estimated total)</th>
<th>$\sigma_{\text{PS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>$8.569 \pm 0.136$</td>
<td>$10.327 \pm 0.164$</td>
<td>$2.519 \pm 0.100$</td>
</tr>
<tr>
<td>29</td>
<td>$8.432 \pm 0.125$</td>
<td>$10.094 \pm 0.150$</td>
<td>$2.253 \pm 0.099$</td>
</tr>
<tr>
<td>30</td>
<td>$8.361 \pm 0.060$</td>
<td>$9.952 \pm 0.071$</td>
<td>$2.278 \pm 0.048$</td>
</tr>
<tr>
<td>31</td>
<td>$8.307 \pm 0.058$</td>
<td>$9.863 \pm 0.069$</td>
<td>$2.229 \pm 0.047$</td>
</tr>
<tr>
<td>32</td>
<td>$8.394 \pm 0.061$</td>
<td>$9.945 \pm 0.072$</td>
<td>$2.206 \pm 0.047$</td>
</tr>
<tr>
<td>33</td>
<td>$8.279 \pm 0.059$</td>
<td>$9.788 \pm 0.070$</td>
<td>$2.108 \pm 0.044$</td>
</tr>
<tr>
<td>34</td>
<td>$8.160 \pm 0.072$</td>
<td>$9.629 \pm 0.085$</td>
<td>$2.040 \pm 0.055$</td>
</tr>
<tr>
<td>35</td>
<td>$8.121 \pm 0.071$</td>
<td>$9.566 \pm 0.084$</td>
<td>$1.974 \pm 0.055$</td>
</tr>
<tr>
<td>36</td>
<td>$8.136 \pm 0.068$</td>
<td>$9.566 \pm 0.080$</td>
<td>$1.965 \pm 0.053$</td>
</tr>
<tr>
<td>37</td>
<td>$8.091 \pm 0.067$</td>
<td>$9.495 \pm 0.079$</td>
<td>$1.942 \pm 0.053$</td>
</tr>
<tr>
<td>38</td>
<td>$8.086 \pm 0.068$</td>
<td>$9.474 \pm 0.080$</td>
<td>$1.853 \pm 0.052$</td>
</tr>
<tr>
<td>39</td>
<td>$7.921 \pm 0.068$</td>
<td>$9.266 \pm 0.080$</td>
<td>$1.772 \pm 0.053$</td>
</tr>
<tr>
<td>40</td>
<td>$7.916 \pm 0.068$</td>
<td>$9.245 \pm 0.079$</td>
<td>$1.708 \pm 0.053$</td>
</tr>
<tr>
<td>41</td>
<td>$7.897 \pm 0.067$</td>
<td>$9.208 \pm 0.078$</td>
<td>$1.704 \pm 0.053$</td>
</tr>
<tr>
<td>42</td>
<td>$7.892 \pm 0.067$</td>
<td>$9.187 \pm 0.078$</td>
<td>$1.707 \pm 0.053$</td>
</tr>
<tr>
<td>43</td>
<td>$7.910 \pm 0.066$</td>
<td>$9.196 \pm 0.077$</td>
<td>$1.644 \pm 0.051$</td>
</tr>
<tr>
<td>44</td>
<td>$7.879 \pm 0.068$</td>
<td>$9.144 \pm 0.079$</td>
<td>$1.657 \pm 0.051$</td>
</tr>
<tr>
<td>45</td>
<td>$7.766 \pm 0.066$</td>
<td>$9.001 \pm 0.076$</td>
<td>$1.538 \pm 0.050$</td>
</tr>
<tr>
<td>46</td>
<td>$7.706 \pm 0.067$</td>
<td>$8.919 \pm 0.078$</td>
<td>$1.492 \pm 0.052$</td>
</tr>
<tr>
<td>47</td>
<td>$7.776 \pm 0.065$</td>
<td>$8.987 \pm 0.075$</td>
<td>$1.527 \pm 0.049$</td>
</tr>
<tr>
<td>48</td>
<td>$7.574 \pm 0.064$</td>
<td>$8.741 \pm 0.074$</td>
<td>$1.397 \pm 0.050$</td>
</tr>
<tr>
<td>49</td>
<td>$7.672 \pm 0.065$</td>
<td>$8.842 \pm 0.075$</td>
<td>$1.417 \pm 0.050$</td>
</tr>
<tr>
<td>50</td>
<td>$7.507 \pm 0.066$</td>
<td>$8.642 \pm 0.076$</td>
<td>$1.305 \pm 0.050$</td>
</tr>
<tr>
<td>51</td>
<td>$7.574 \pm 0.067$</td>
<td>$8.706 \pm 0.077$</td>
<td>$1.267 \pm 0.052$</td>
</tr>
<tr>
<td>52</td>
<td>$7.533 \pm 0.069$</td>
<td>$8.649 \pm 0.079$</td>
<td>$1.300 \pm 0.051$</td>
</tr>
<tr>
<td>53</td>
<td>$7.499 \pm 0.068$</td>
<td>$8.600 \pm 0.078$</td>
<td>$1.248 \pm 0.050$</td>
</tr>
<tr>
<td>54</td>
<td>$7.490 \pm 0.065$</td>
<td>$8.580 \pm 0.074$</td>
<td>$1.238 \pm 0.049$</td>
</tr>
<tr>
<td>55</td>
<td>$7.490 \pm 0.067$</td>
<td>$8.587 \pm 0.077$</td>
<td>$1.221 \pm 0.048$</td>
</tr>
<tr>
<td>56</td>
<td>$7.373 \pm 0.063$</td>
<td>$8.423 \pm 0.072$</td>
<td>$1.141 \pm 0.048$</td>
</tr>
<tr>
<td>57</td>
<td>$7.382 \pm 0.062$</td>
<td>$8.427 \pm 0.071$</td>
<td>$1.192 \pm 0.046$</td>
</tr>
<tr>
<td>58</td>
<td>$7.339 \pm 0.060$</td>
<td>$8.368 \pm 0.068$</td>
<td>$1.124 \pm 0.045$</td>
</tr>
<tr>
<td>59</td>
<td>$7.380 \pm 0.056$</td>
<td>$8.404 \pm 0.064$</td>
<td>$1.124 \pm 0.044$</td>
</tr>
<tr>
<td>60</td>
<td>$7.292 \pm 0.061$</td>
<td>$8.294 \pm 0.069$</td>
<td>$1.088 \pm 0.041$</td>
</tr>
</tbody>
</table>
Table B.2: Measured and corrected total elastic cross sections, as well as the measured total inelastic cross sections. All energies are in eV, and all cross sections are in Å².

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\sigma_{\text{El}}$ (measured)</th>
<th>$\sigma_{\text{El}}$ (estimated total)</th>
<th>$\sigma_{\text{Inel}}$ (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>6.875 ± 0.186</td>
<td>22.409 ± 0.606</td>
<td>0.026 ± 0.111</td>
</tr>
<tr>
<td>5</td>
<td>6.641 ± 0.180</td>
<td>19.964 ± 0.541</td>
<td>−0.063 ± 0.111</td>
</tr>
<tr>
<td>5.5</td>
<td>6.343 ± 0.178</td>
<td>18.295 ± 0.514</td>
<td>0.251 ± 0.113</td>
</tr>
<tr>
<td>6</td>
<td>6.181 ± 0.179</td>
<td>17.108 ± 0.496</td>
<td>0.014 ± 0.109</td>
</tr>
<tr>
<td>6.5</td>
<td>6.140 ± 0.174</td>
<td>16.508 ± 0.469</td>
<td>0.005 ± 0.109</td>
</tr>
<tr>
<td>7</td>
<td>5.503 ± 0.170</td>
<td>14.369 ± 0.446</td>
<td>0.122 ± 0.110</td>
</tr>
<tr>
<td>7.5</td>
<td>5.520 ± 0.172</td>
<td>14.038 ± 0.439</td>
<td>0.111 ± 0.112</td>
</tr>
<tr>
<td>8</td>
<td>5.301 ± 0.167</td>
<td>13.134 ± 0.414</td>
<td>0.121 ± 0.112</td>
</tr>
<tr>
<td>8.5</td>
<td>5.232 ± 0.165</td>
<td>12.627 ± 0.400</td>
<td>0.273 ± 0.113</td>
</tr>
<tr>
<td>9</td>
<td>5.028 ± 0.163</td>
<td>11.832 ± 0.384</td>
<td>0.380 ± 0.116</td>
</tr>
<tr>
<td>9.5</td>
<td>4.849 ± 0.162</td>
<td>11.112 ± 0.371</td>
<td>0.460 ± 0.112</td>
</tr>
<tr>
<td>10</td>
<td>4.864 ± 0.134</td>
<td>11.122 ± 0.307</td>
<td>0.481 ± 0.098</td>
</tr>
<tr>
<td>10.5</td>
<td>4.642 ± 0.160</td>
<td>10.222 ± 0.353</td>
<td>0.560 ± 0.114</td>
</tr>
<tr>
<td>11</td>
<td>4.437 ± 0.131</td>
<td>9.884 ± 0.294</td>
<td>0.782 ± 0.101</td>
</tr>
<tr>
<td>11.5</td>
<td>4.524 ± 0.160</td>
<td>9.697 ± 0.343</td>
<td>0.718 ± 0.122</td>
</tr>
<tr>
<td>12</td>
<td>4.352 ± 0.128</td>
<td>9.472 ± 0.279</td>
<td>0.644 ± 0.099</td>
</tr>
<tr>
<td>12.5</td>
<td>4.223 ± 0.155</td>
<td>8.835 ± 0.325</td>
<td>0.657 ± 0.114</td>
</tr>
<tr>
<td>13</td>
<td>4.120 ± 0.125</td>
<td>8.730 ± 0.266</td>
<td>0.862 ± 0.101</td>
</tr>
<tr>
<td>13.5</td>
<td>3.984 ± 0.157</td>
<td>8.142 ± 0.321</td>
<td>0.974 ± 0.121</td>
</tr>
<tr>
<td>14</td>
<td>4.031 ± 0.130</td>
<td>8.360 ± 0.270</td>
<td>1.269 ± 0.106</td>
</tr>
<tr>
<td>14.5</td>
<td>4.128 ± 0.156</td>
<td>8.236 ± 0.312</td>
<td>0.967 ± 0.125</td>
</tr>
<tr>
<td>15</td>
<td>3.693 ± 0.110</td>
<td>7.531 ± 0.182</td>
<td>1.302 ± 0.091</td>
</tr>
<tr>
<td>16</td>
<td>3.608 ± 0.110</td>
<td>7.231 ± 0.177</td>
<td>1.570 ± 0.095</td>
</tr>
<tr>
<td>17</td>
<td>3.567 ± 0.109</td>
<td>6.938 ± 0.172</td>
<td>1.380 ± 0.091</td>
</tr>
<tr>
<td>18</td>
<td>3.254 ± 0.108</td>
<td>6.393 ± 0.167</td>
<td>1.835 ± 0.096</td>
</tr>
<tr>
<td>19</td>
<td>3.305 ± 0.108</td>
<td>6.234 ± 0.161</td>
<td>1.756 ± 0.094</td>
</tr>
<tr>
<td>20</td>
<td>3.184 ± 0.105</td>
<td>5.839 ± 0.153</td>
<td>1.827 ± 0.095</td>
</tr>
<tr>
<td>21</td>
<td>2.935 ± 0.104</td>
<td>5.458 ± 0.151</td>
<td>2.282 ± 0.098</td>
</tr>
<tr>
<td>22</td>
<td>3.093 ± 0.104</td>
<td>5.397 ± 0.149</td>
<td>2.088 ± 0.096</td>
</tr>
<tr>
<td>23</td>
<td>3.095 ± 0.102</td>
<td>5.451 ± 0.143</td>
<td>2.011 ± 0.096</td>
</tr>
<tr>
<td>24</td>
<td>3.047 ± 0.106</td>
<td>5.358 ± 0.146</td>
<td>2.114 ± 0.095</td>
</tr>
<tr>
<td>25</td>
<td>2.750 ± 0.105</td>
<td>4.597 ± 0.177</td>
<td>2.643 ± 0.104</td>
</tr>
<tr>
<td>26</td>
<td>2.644 ± 0.105</td>
<td>4.350 ± 0.174</td>
<td>2.668 ± 0.104</td>
</tr>
<tr>
<td>27</td>
<td>2.868 ± 0.105</td>
<td>4.646 ± 0.172</td>
<td>2.342 ± 0.098</td>
</tr>
<tr>
<td>28</td>
<td>2.752 ± 0.105</td>
<td>4.403 ± 0.169</td>
<td>2.670 ± 0.104</td>
</tr>
<tr>
<td>29</td>
<td>2.922 ± 0.102</td>
<td>4.591 ± 0.163</td>
<td>2.665 ± 0.102</td>
</tr>
<tr>
<td>30</td>
<td>2.746 ± 0.102</td>
<td>4.250 ± 0.160</td>
<td>2.818 ± 0.102</td>
</tr>
<tr>
<td>31</td>
<td>2.507 ± 0.102</td>
<td>3.873 ± 0.160</td>
<td>3.245 ± 0.108</td>
</tr>
<tr>
<td>32</td>
<td>2.723 ± 0.102</td>
<td>4.182 ± 0.159</td>
<td>2.962 ± 0.104</td>
</tr>
<tr>
<td>33</td>
<td>2.464 ± 0.099</td>
<td>3.785 ± 0.154</td>
<td>3.170 ± 0.107</td>
</tr>
<tr>
<td>34</td>
<td>2.616 ± 0.100</td>
<td>3.996 ± 0.155</td>
<td>3.071 ± 0.106</td>
</tr>
<tr>
<td>35</td>
<td>2.305 ± 0.099</td>
<td>3.517 ± 0.153</td>
<td>3.359 ± 0.107</td>
</tr>
<tr>
<td>36</td>
<td>2.498 ± 0.099</td>
<td>3.806 ± 0.153</td>
<td>3.167 ± 0.107</td>
</tr>
<tr>
<td>37</td>
<td>2.530 ± 0.100</td>
<td>3.848 ± 0.153</td>
<td>3.162 ± 0.104</td>
</tr>
</tbody>
</table>

Continued on next page
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\sigma_{\text{El}}$ (measured)</th>
<th>$\sigma_{\text{El}}$ (estimated total)</th>
<th>$\sigma_{\text{Inel}}$ (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>$2.278 \pm 0.101$</td>
<td>$3.450 \pm 0.154$</td>
<td>$3.282 \pm 0.106$</td>
</tr>
<tr>
<td>39</td>
<td>$2.393 \pm 0.099$</td>
<td>$3.612 \pm 0.151$</td>
<td>$3.308 \pm 0.109$</td>
</tr>
<tr>
<td>40</td>
<td>$2.457 \pm 0.098$</td>
<td>$3.694 \pm 0.149$</td>
<td>$3.499 \pm 0.109$</td>
</tr>
<tr>
<td>41</td>
<td>$2.388 \pm 0.113$</td>
<td>$3.539 \pm 0.170$</td>
<td>$3.272 \pm 0.126$</td>
</tr>
<tr>
<td>42</td>
<td>$2.493 \pm 0.112$</td>
<td>$3.684 \pm 0.168$</td>
<td>$3.195 \pm 0.122$</td>
</tr>
<tr>
<td>43</td>
<td>$2.532 \pm 0.114$</td>
<td>$3.733 \pm 0.170$</td>
<td>$3.407 \pm 0.125$</td>
</tr>
<tr>
<td>44</td>
<td>$2.576 \pm 0.116$</td>
<td>$3.789 \pm 0.172$</td>
<td>$3.343 \pm 0.122$</td>
</tr>
<tr>
<td>45</td>
<td>$2.382 \pm 0.115$</td>
<td>$3.493 \pm 0.170$</td>
<td>$3.358 \pm 0.125$</td>
</tr>
<tr>
<td>46</td>
<td>$2.603 \pm 0.113$</td>
<td>$3.810 \pm 0.168$</td>
<td>$3.411 \pm 0.123$</td>
</tr>
<tr>
<td>47</td>
<td>$2.515 \pm 0.117$</td>
<td>$3.676 \pm 0.173$</td>
<td>$3.447 \pm 0.125$</td>
</tr>
<tr>
<td>48</td>
<td>$2.389 \pm 0.114$</td>
<td>$3.492 \pm 0.169$</td>
<td>$3.560 \pm 0.127$</td>
</tr>
<tr>
<td>49</td>
<td>$2.330 \pm 0.116$</td>
<td>$3.406 \pm 0.171$</td>
<td>$3.674 \pm 0.125$</td>
</tr>
<tr>
<td>50</td>
<td>$2.400 \pm 0.112$</td>
<td>$3.491 \pm 0.165$</td>
<td>$3.682 \pm 0.128$</td>
</tr>
<tr>
<td>51</td>
<td>$2.633 \pm 0.115$</td>
<td>$3.821 \pm 0.169$</td>
<td>$3.593 \pm 0.127$</td>
</tr>
<tr>
<td>52</td>
<td>$2.369 \pm 0.111$</td>
<td>$3.427 \pm 0.162$</td>
<td>$3.712 \pm 0.125$</td>
</tr>
<tr>
<td>53</td>
<td>$2.605 \pm 0.115$</td>
<td>$3.767 \pm 0.168$</td>
<td>$3.752 \pm 0.127$</td>
</tr>
<tr>
<td>54</td>
<td>$2.529 \pm 0.114$</td>
<td>$3.650 \pm 0.166$</td>
<td>$3.536 \pm 0.125$</td>
</tr>
<tr>
<td>55</td>
<td>$2.560 \pm 0.119$</td>
<td>$3.690 \pm 0.173$</td>
<td>$3.654 \pm 0.124$</td>
</tr>
<tr>
<td>56</td>
<td>$2.517 \pm 0.116$</td>
<td>$3.622 \pm 0.169$</td>
<td>$3.724 \pm 0.126$</td>
</tr>
<tr>
<td>57</td>
<td>$2.696 \pm 0.115$</td>
<td>$3.875 \pm 0.168$</td>
<td>$3.743 \pm 0.128$</td>
</tr>
<tr>
<td>58</td>
<td>$2.513 \pm 0.115$</td>
<td>$3.610 \pm 0.167$</td>
<td>$4.020 \pm 0.131$</td>
</tr>
<tr>
<td>59</td>
<td>$2.635 \pm 0.111$</td>
<td>$3.771 \pm 0.161$</td>
<td>$4.095 \pm 0.129$</td>
</tr>
<tr>
<td>60</td>
<td>$2.675 \pm 0.118$</td>
<td>$3.826 \pm 0.171$</td>
<td>$4.186 \pm 0.131$</td>
</tr>
</tbody>
</table>
Table B.3: Measured quasi-elastic differential cross sections. First published in [2], and also presented in figures 2.8 and 2.9 in chapter 2. All collision energies are in GeV, all angles are in degrees, and the units of the cross sections are in mb/sr.

\[(\chi - \chi^\prime) \sigma + (\chi^\prime) \sigma = (\chi^\prime \chi) \sigma \]