Theoretical and Experimental Studies of the Gas-Liquid Interface

Daniel M. Packwood

A Thesis submitted for the degree of Doctor of Philosophy

Department of Chemistry

University of Canterbury

Submitted to examiners on July 5 2010

Final copy submitted on September 29 2010
Abstract

A theoretical model describing the motion of a small, fast rare gas atom as it passes over a liquid surface is developed and discussed in detail. A key feature of the model is its reliance on coarse-grained capillary wave and local mode descriptions of the liquid surface. Mathematically, the model is constructed with several concepts from probability and stochastic analysis. The model makes predictions that are quantitative agreement with neon-liquid surface scattering data collected by other research groups. These predictions include the dominance of single, rather than multiple, neon-liquid surface collision dynamics, an average of 60% energy transfer from a neon atom upon colliding with a non-metallic surface, and an average of 25% energy transfer upon colliding with a metallic surface. In addition to this work, two other investigations into the gas-liquid interface are discussed. The results of an experimental investigation into the thermodynamics of a gas flux through an aqueous surface are presented, and it is shown that a nitrous oxide flux is mostly due to the presence of a temperature gradient in the gas-liquid interface. Evidence for a reaction between a carbon dioxide flux and an ammonia monolayer on an aqueous surface to produce ammonium carbamate is also found. The second of these is an investigation into the mechanism of bromine production from deliquesced sodium bromide aerosol in the presence of ozone, and involves a sensitivity and uncertainty analysis of the computer aerosol kinetics model MAGIC. It is shown that under dark, non-photolytic conditions, bromine production can be accounted for almost exclusively by a reaction between gas-phase ozone and surface-bound bromide ions. Under photolytic conditions, bromine production instead involves a complicated interplay between various gas-phase and aqueous-phase reactions.
Preface

For the most part, this work describes my own view on gas-liquid collisions. While it serves as my doctoral thesis, I want it to have a wider appeal and so have presented it as a monograph (complete with preface). This also provides a chance to draw together several scattered papers into a coherent story. I hope that readers from outside of the field will find the theory to be elegant and sensible, and that gas-liquid collision researchers find it to be a compelling alternative view of their subject. The last two chapters describe some experimental and computational work that is unrelated to the gas-liquid collision theory but still maintains the ‘gas-liquid interface’ theme.

The development of the theory relies heavily on concepts from probability and statistics. While most of this work only uses simple results from these fields, set notation is regularly used and for this reason the reader is recommended to read through the ‘Set Notation’ section which is provided after this preface. At first, the use of set notation may seem unnecessary. However, I am certain the reader will find that set notation makes light work out of messy sentences. The second half of Chapter 3 recasts the ideas from the first half in a way which is mathematically meaningful. While this section is optional reading and is not necessary to work through subsequent chapters, it would be unfortunate if nobody ever looked at it. For this reason I have provided an Appendix (Chapter 10) which introduces the key mathematical ideas in a descriptive way.

This work has left me indebted to many people. Profs. Barbara Finlayson-Pitts and Donald Dabdub, and their research student (now Dr.) Paul Nissenson were a pleasure to work with during my time at UC Irvine in 2008, and are thanked for providing such a welcoming environment. The latter thanks is extended to the rest of Dabdub group, namely Wayne Chang, Marc Carreras-Sospedra, Alex Cohan, Prasad Pokkunuri and Satish Vutukuru, as well as the rest of the AirUCI researchers. Prof. Finlayson-Pitts is further thanked for an all expenses paid trip to SoCal earlier this year so that I could talk at the AirUCI Annual Meeting. Katrin Siefermann (now Dr.) is thanked for looking after me during my trip to Göttingen last year and introducing me to Hubertusbrot. While I only spent two days at Madison, the (vigorous) discussions that I had with Prof. Gilbert Nathanson and his group significantly affected the direction of my research, and I am enormously grateful for my time spent there. Shortly after Madison, I went on to Boulder for a couple of days and have Prof. David Nesbitt and his group to thank for their hospitality and engaging discussions. It was impressive to see so much talent in one research group. I also wish to thank Profs. Yoshitaka Tanimura and Tianyan Yan for an exciting trip to Japan and China last August. I have had the pleasure of sharing
an office with some zany people. In rough chronological order, this includes David Bones, Andy Sykes, Don Hastie, Omar El-Hadad, Lisa Graham, James Bull and Rachel Hanover-O’connor. From David Bain to hunger strikes, there was never a dull moment. I also wish to thank Pamela Phillips, whose delicious weekly (not weakly) meals provided the stamina to make it through to the next meal, and who kindly took me grocery shopping every Friday.

Finally, I wish to thank Professor Leon Phillips, who has been supervising me since my honours project in 2007. I’ve been incredibly privileged to work with somebody with such a strong grasp of physical chemistry and so much enthusiasm for research. If any of this has rubbed off on me, then I’m sure that everything will work out well.

D.M.P. (28 / 10 / 10)
Set Notation

- Consider the elements $x_1, x_2, \ldots$. The collection of these elements is denoted by \{x_1, x_2, \ldots\}.

- \{x_1, x_2, \ldots : C\} is the collection of all elements in \{x_1, x_2, \ldots\} which fulfil the condition $C$.

- Let $X = \{x_1, x_2, \ldots\}$. $x_i \in X$ is read as ‘$x_i$ is an element of the collection $X$’.

- Let $T$ be a collection. Then \{x_t \mid t \in T\} denotes all elements $x_n \in X$ such that $n \in T$.

- \{x_1, x_2\} is the collection of all elements in \{x_1, x_2, \ldots\} which fulfil the condition $C$. ‘$\subseteq$’ means that \{x_1, x_2\} is either a subset of or is equivalent to $X$.

- The collection of real numbers is denoted by $\mathbb{R}$. When given the subscript ‘+$’, it denotes the collection formed from all positive real numbers and zero.

- Let $z_1$ and $z_2$ be real numbers and $z_2 > z_1$. Then $[z_1, z_2]$ denotes all real numbers in the interval $z_1 \leq r \leq z_2$, $(z_1, z_2]$ all numbers in the interval $z_1 < r \leq z_2$, $[z_1, z_2)$ all numbers in the interval $z_1 \leq r < z_2$, and $(z_1, z_2)$ all numbers in the interval $z_1 < r < z_2$.

- Let $X$ and $Y$ be two (possibly identical) collections. The product collection $X \times Y$ denotes the collection of all ordered pairs $(x_i, y_i)$, where $x_i \in X$ and $y_i \in Y$. Similarly, $X^n$ denotes the collection of all ordered $n$-tuples $\left(x_1^1, x_2^2, \ldots, x_n^n\right)$, where $x_1^1 \in X_1, x_2^2 \in X_2, \ldots$ and $x_n^n \in X_n$.

- $X \cup Y$ is the collection formed by merging the collections $X$ and $Y$ together (the union of $X$ and $Y$). $X \cap Y$ is the collection formed from the elements which are contained in both $X$ and $Y$ (the intersection of $X$ and $Y$).

- Let $Y$ be the largest set which contains $X$. $X^C$ is the elements of $Y$ which are not contained in $X$ (the complement of $X$).

- Let $X = x_1, x_2, \ldots$ be a collection of real-valued elements. The infimum of $X$, $\inf_{x_i \in X} x_i$, is the greatest lower bound to $X$ (largest number $q$ such that all $x_i \in X$ are greater than $q$). The supremum of $X$, $\sup_{x_i \in X} x_i$, is the least upper bound to $X$ (smallest number $q$ such that all $x_i \in X$ are less than $q$).
## Contents

1 Introduction ........................................... 1
   1.1 The Current Picture of a Gas-Liquid Collision ............ 1
   1.2 Key Results from Molecular Beam Studies ................ 3
      1.2.1 The IS and TD channels ........................... 5
      1.2.2 Collisional energy transfer in the IS channel .......... 6
      1.2.3 Angular distributions of scattered rare gases ........ 7
      1.2.4 The role of liquid composition .................... 8
      1.2.5 The role of liquid temperature .................... 8
   1.3 Insights from Theoretical and Computational Studies ...... 9
      1.3.1 MD simulations and the role of multiple gas-liquid collisions 9
      1.3.2 The basic tenet of gas-liquid collisions ............ 10
      1.3.3 Classical scattering theory applied to liquid metals .... 10
   1.4 Guide to the Rest of this Work ........................ 11

2 The Local Mode Model of a Liquid Surface .................... 14
   2.1 Fluid Dynamics of Surface Waves ........................ 15
      2.1.1 Gravity and capillary waves ........................ 15
      2.1.2 Damping of short wavelength capillary waves .......... 19
      2.1.3 Local mode displacements ........................... 19
   2.2 The Random Local Mode Model ............................ 23
      2.2.1 Three approximations .............................. 23
   2.3 Test of the Random Local Mode Model ...................... 25
      2.3.1 Formulation of the model ........................... 27
      2.3.2 Calculation of an angular distribution ............... 29
      2.3.3 Results and Discussion ............................ 34
      2.3.4 Final remarks ................................... 37

3 The Random Walk on Parabolas ................................ 40
   3.1 Pictorial Construction ............................... 41
      3.1.1 Improvements on the random local mode model .......... 41
      3.1.2 Construction of the random walk on parabolas .......... 43
   3.2 Rigorous Construction of the Random Walk on Parabolas .... 48
      3.2.1 Basic definitions ................................. 48
      3.2.2 Isotropy and continuity conditions .................. 49
      3.2.3 The pure jump process $Z$ .......................... 50
      3.2.4 Integration w.r.t a random walk on parabolas .......... 53
   3.3 The Random Walk on Polynomials .......................... 54
      3.3.1 Construction of the process ........................ 55
      3.3.2 Convergence to a Wiener Process .................... 58
### 4 Impulsive Energy Loss Constraints

4.1 A Statistical Treatment of Energy Loss ................................................. 65  
4.1.1 Derivation of a collisional energy loss distribution ......................... 66  
4.1.2 Comparison with experimental data ............................................. 69  
4.2 Extension to Liquid Metal Surfaces ................................................. 73  
4.2.1 Energy loss distribution for capillary wave excitation ....................... 75  
4.2.2 Comparison with experimental data ............................................. 77  
4.3 Final Remarks .................................................................................. 81  

### 5 Motion of an Atom Over a Liquid Surface

5.1 The Equations of Motion .................................................................. 84  
5.1.1 Derivation ..................................................................................... 84  
5.1.2 Interpretation ................................................................................ 87  
5.2 Numerical Solutions to the Equations of Motion ............................... 90  
5.2.1 Implementation of the Runge-Kutta algorithm ................................ 90  
5.2.2 Interaction potential and the local mode half width ....................... 93  
5.2.3 Time step and initial conditions ................................................... 94  

### 6 Analysis of Neon Scattering Dynamics

6.1 Neon Scattering from Squalane ......................................................... 97  
6.1.1 Key dynamical results .................................................................. 97  
6.1.2 Squalane surface profile ............................................................... 105  
6.1.3 Sensitivity of the dynamics to model parameters ............................ 106  
6.2 Extrapolation to Neon Scattering from Perfluorinated Polyether .......... 112  
6.3 Final Remarks .................................................................................. 113  

### 7 Conclusions and Future Work

7.1 The Local Mode Picture of a Gas-Liquid Collision ............................. 116  
7.1.1 Contrasts with the ‘current’ picture .............................................. 117  
7.1.2 What is a typical neon-liquid surface collision? .............................. 118  
7.2 Future Work ................................................................................... 119  
7.2.1 Looking beyond neon-squalane collisions .................................... 119  
7.2.2 Possible projects for a more developed theory ......................... 120  
7.3 Extension to Rotor Scattering ......................................................... 122  
7.3.1 Rotational excitation and the local mode model ............................ 122  

### 8 Irreversible Thermodynamics of a Gas-Liquid Interface

8.1 Irreversible Thermodynamics and the Gas-Flux Problem .................. 129  
8.1.1 The linear formulation .................................................................. 131  
8.1.2 The heat of transport and the gas flux equation ............................ 133  
8.2 Measuring the Heat of Transport ..................................................... 134  
8.2.1 Apparatus and procedures .......................................................... 134  
8.2.2 Summary of results from previous studies .................................... 138  
8.3 Heat of Transport Measurements for N2O and CO2 .......................... 140  
8.3.1 N2O measurements .................................................................... 140  
8.3.2 CO2 measurements ................................................................. 141  
8.3.3 Final remarks ............................................................................. 145  
8.4 Appendix ......................................................................................... 146  
8.4.1 Energy balance equation ............................................................. 146  
8.4.2 Mass balance equation ............................................................... 147  
8.4.3 Entropy generation equation ...................................................... 148
9 Bromine Production from the Oxidation of Sea Salt Aerosol 150
  9.1 The MAGIC Model of Aerosol Kinetics .................................. 153
  9.1.1 Gas-phase chemistry ..................................................... 153
  9.1.2 Mass transfer .............................................................. 153
  9.1.3 Aqueous-phase chemistry .............................................. 154
  9.1.4 Interfacial reactions .................................................... 156
  9.2 Analysis Methodology ....................................................... 156
  9.2.1 Latin hypercube sampling .............................................. 157
  9.2.2 Linear regression and uncertainty analysis .............................. 158
  9.3 Results and Discussion ................................................... 160
  9.3.1 Bromine production in the dark ....................................... 162
  9.3.2 Bromine production in the light ...................................... 167
  9.4 Final Remarks ............................................................... 173

10 Appendix: A Crash Course on Stochastic Processes 175
# List of Figures

1.1 Two-body picture of a gas-liquid collision ........................................... 2  
1.2 Diagram of the molecular beam technique ................................................ 4  
1.3 Illustration of the IS/TD channels .......................................................... 5  

2.1 Comparison of sinusoidal capillary waves and Bessel function local mode  
    displacements ......................................................................................... 20  
2.2 Amplitude of a local mode as a function of time .......................................... 22  
2.3 Field of randomly superimposed local mode displacements .......................... 23  
2.4 Scattering model for testing the random local mode model .......................... 26  
2.5 Diagrams illustrating the process \((A_t, C_t)\) .............................................. 29  
2.6 A representative sample path of the process \((A_t, C_t)\) ............................... 30  
2.7 Diagram defining the processes \(X_t, Z_t\) and \(E_t\) ..................................... 31  
2.8 Calculation of the scattering angle from the slope of a local mode. .............. 32  
2.9 Angular distributions predicted by the test model .................................. 35  
2.10 Sample paths of the process \(E_t\) ............................................................ 38  
2.11 The local mode picture of a gas-liquid collision 1 ...................................... 39  

3.1 Illustration of the isotropy condition .......................................................... 44  
3.2 Sample paths of the random walk on parabolas ......................................... 46  
3.3 The local mode picture of a gas-liquid collision 2 ....................................... 47  
3.4 Venn diagrams illustrating the isotropy conditions in terms of symmetric  
    differences .................................................................................................. 51  
3.5 Sample path of the random walk on polynomials ....................................... 58  

4.1 Illustrating of the energy loss model ........................................................... 65  
4.2 Trapping probabilities predicted with the energy loss model ......................... 70  
4.3 Energy loss curves predicted with energy loss model ................................. 72  
4.4 Model of energy loss in neon-liquid metal collisions .................................... 74  
4.5 Energy loss curves predicted for liquid metal surfaces .............................. 78  
4.6 Trapping curves predicted for liquid metal surfaces ................................... 79  
4.7 Plot of energy loss distribution for neon-liquid metal collisions .................... 80  
4.8 The local mode picture of a gas-liquid collision 3 ....................................... 81  

5.1 An atom approaching a curved surface ....................................................... 88  
5.2 Illustration of the approximation \(\Omega(X_t, Y_t) \sim \Omega(R_t)\) ......................... 89  
5.3 The final local mode picture of a gas-liquid collision ................................ 90  
5.4 Simulated energy losses .............................................................................. 93  
5.5 Calculated trajectory of a neon atom approaching a squalane surface ........... 94  

6.1 Predicted angular distributions for neon scattering from squalane .................. 99  
6.2 Representative trajectories of neon during a neon-squalane surface collision. 100
List of Tables

2.1 Parameters used to test the random local mode model. . . . . . . . . . . . . 36
5.1 Accuracy of various time steps. . . . . . . . . . . . . . . . . . . . . . . . . . 95
6.1 Parameters and initial conditions used for neon-squalane calculations. . . 98
6.2 Dynamical statistics for various neon-squalane calculations. . . . . . . . . 104
8.1 Some heat of transport measurements from the literature. . . . . . . . . . . 139
9.1 Scenarios examined for the sensitivity and uncertainty analysis. . . . . . . 161
9.2 Initial conditions for the base case. . . . . . . . . . . . . . . . . . . . . . . . 161
9.3 Regression coefficients and uncertainty contributions for the Base Case. . 163
9.4 Regression coefficients and uncertainty contributions for the LightT600 sce-
nario. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 168
Chapter 1

Introduction

Collisions between gas-phase species and liquid surfaces play a key role in all processes involving a gas-liquid interface. For example, respiration involves the uptake of oxygen molecules from the air into the alveoli of the lungs, which in turn requires collisions between gas-phase oxygen molecules and liquid films on the inner surfaces of the lungs [12]. Gas-liquid collisions are involved in all industrial processes which dissolve a high pressure gas into a liquid, such as in the carbonation of a soft drink. Well-documented examples can be found in the aerosol literature. For example, clouds grow via gas-phase water molecules colliding with and accommodating at the surfaces of their constituent aerosol droplets [37]. Recently, it has been shown that interfacial reactions between gas-phase oxidants and ions bound to the surface of aerosol particles often dominate over other aqueous- and gas-phase chemical reactions [49, 119]. Although the mechanistic details of interfacial reactions are unknown, it is clear that a gas-liquid collision would be their first step. If processes such as these are to be thoroughly understood, then it is crucial that the dynamics of a gas-liquid collision event can be described in an accurate and simple way.

The major contribution of this work is the development of a theory describing the dynamics of gas-liquid collision events. However, before setting off in this direction it will be worthwhile to review the current picture of a gas-liquid collision. Much of this picture has been elucidated from molecular beam data collected by the Nathanson group at Madison, Wisconsin in the early ’90s. While the picture is somewhat qualitative, it provides a good account of key experimental trends.

1.1 The Current Picture of a Gas-Liquid Collision

Suppose that a gas-liquid collision is a localised, impulsive, two-body event between a gas-phase particle of mass $m_g$ and a discrete molecular fragment of mass $m_s$ of the liquid surface (Figure 1.1). For simplicity, we restrict ourselves to the case of an incoming atom, rather than a molecule. The surface fragment may consist of a few neighbouring atoms of a surface molecule, an entire surface molecule, or several closely interacting surface
molecules. This picture of a gas-liquid collision is obviously idealised. The impulsive assumption requires the incoming particle to be moving fast enough for the surface fragment to be approximately static during the entire collision, such that only the kinetic energy of the incoming particle and the surface fragment changes during the collision. Moreover, it seems unreasonable to expect that the degrees of freedom of a real liquid surface could be so cleanly partitioned into fragments. Note that the model does allow for the possibility of energy to be dispersed amongst other fragments some time after the collision event. Despite its shortcomings, the model does have some hallmarks of a good theory. It is based on a simple, comprehensive picture that can enter into discussion very easily. Moreover, the picture is intuitive, appealing to a chemist’s molecular view of the world. The model also contains an unknown parameter, \( m_s \), which may be possible to determine experimentally once a set of equations are extracted from the picture. Measured values of this parameter would give some insight into the molecular structure of the liquid surface. Hence, the model is a useful tool, serving as a means to an end rather than an end in itself. Simple, intuitive and useful are the three hallmarks that we will strive to include in our own theory.

To put the model on quantitative footing, we suppose that the incoming atom collides with the surface with a velocity \( \mathbf{v}_i \) and at an angle \( \phi_i \) to the normal to the point of impact on the surface fragment, and that it rebounds at an angle \( \phi_f \) to the normal and with a velocity \( \mathbf{v}_f \). Since the impulsive forces of the collision are along the normal to the point of impact, the momentum of the incoming atom is conserved in the direction perpendicular to the normal, that is,

\[
m_g v_i \sin \phi_i = m_g v_f \sin \phi_f.
\]  

Momentum is transferred to the surface fragment along the normal. Let \( \mathbf{v}_s \) be the velocity of the surface fragment immediately after the collision. Since the total momentum of the system along the normal must be conserved during the collision, we have...
$m_g v_i \cos \phi_i = m_g v_f \cos \phi_f + m_s v_s.$ \hfill (1.2)

Conservation of energy during the collision event implies that

$$\frac{1}{2} m_g v_i^2 = \frac{1}{2} m_g v_f^2 + \frac{1}{2} m_s v_s^2. \hfill (1.3)$$

Finally, the fraction of energy lost to the surface by the incoming particle due to the collision is

$$\frac{\Delta E}{E_i} = \frac{m_g v_i^2/2 - m_g v_f^2/2}{m_g v_i^2/2}. \hfill (1.4)$$

where $E_i$ is the initial energy of the incoming atom. Equations (1.1) - (1.4) are four equations in four unknowns, namely $\phi_f$, $v_f$, $v_s$ and $\Delta E/E_i$. Solving them simultaneously gives [65]

$$\frac{\Delta E}{E_i} = \frac{4\mu}{(1+\mu)^2} \cos^2 \phi_i \hfill (1.5)$$

where $\mu$ is the mass ratio $m_g/m_s$. This result only holds when $\mu \leq 1$, beyond which the collision would not cause the particle to change direction. This result is often referred to as the Baule formula, after the author who developed this equation to study gas-solid collisions in 1914 [5].

Despite being almost a century old, the Baule formula still makes regular appearances in the gas-solid collision literature. This is testament to the versatility of the underlying model. It has been extended in a number of ways [34, 122, 35], but still retains the basic two-body picture shown in Figure 1.1 in each case. Hence, when the first reliable gas-liquid collision data became available in the early ‘90s, it was hardly surprising that the Baule formula was immediately put to work [108]. In fact, the Baule formula can qualitatively account for most experimental trends relating to collisional energy transfer from a gas-phase particle to a liquid surface [75], at least for the case of a high-energy gas-phase atom. The current picture of gas-liquid collisions is therefore summarised remarkably well by Figure 1.1; it amounts to an impulsive collision between the gas-phase particle and a discrete molecular fragment of the liquid surface.

Of course, there is more to gas-liquid collisions than what is entailed by the Baule formula alone. The next section highlights the essential experimental results relating to gas-liquid collisions, which will enhance the picture shown in Figure 1.1 and illustrate the predictions of the Baule formula.

### 1.2 Key Results from Molecular Beam Studies

Experimentally, the dynamics of gas-liquid collisions are studied by molecular beam methods. This involves directing a nearly monoenergetic beam of atoms or molecules at a
liquid surface at fixed incidence angle and detecting the scattered product by time-of-flight (TOF) mass spectrometry at various exit angles. The entire assembly is kept under high vacuum conditions and the liquid is thermostatted close to room temperature. A highly simplified diagram is shown in Figure 1.2, which will be sufficient for our purposes; technical details are given in reference [75]. The current experimental apparatus is limited to having the molecular beam source, mass spectrometer and target aligned in the same plane. Thus, molecular beam methods are restricted to probing dynamics which occur within plane. This is not the case for methods employing rotatable infrared laser detection systems [88], although these cases are restricted to small molecules with simple infrared spectra. The molecular beam technique is best suited for low vapour pressure liquids, for which the chance of a collision with a vapour molecule is minimal. Liquids that have been investigated include squalane, glycerol [46, 109], sulfuric acid [6], perfluorinated polyethers (PFPE) [46, 110], and various liquid metals [104, 64]. Very recently, this list has been extended to include certain ionic liquids [127]. Investigations with these liquids range from rare gas scattering [46, 109, 110], reactive scattering of oxygen atoms [33, 127] and small inorganic acids [101], through to analyses of rotational state distributions of scattered carbon dioxide molecules [88]. Of these, rare gas scattering data provides the clearest illustration of the key experimental trends, so we focus attention on that.
Figure 1.3: Illustration of the IS/TD channels. The incoming gas-phase particle strikes the surface and deposits energy, and enters into either the IS or TD channels. In the IS channel, the particle immediately scatters back into the gas-phase with a significant fraction of its original energy, whereas in the TD channel, the particle momentarily binds to the surface, and desorbs and scatters back into the gas-phase at a later time with energy close to the thermal energy of the surface.

1.2.1 The IS and TD channels

At high incident energies (> 25 kJ mol$^{-1}$ for a neon atom), TOF spectra for scattered gases are typically bimodal. The interpretation of this result, due to Nathanson and colleagues [108], assumes that the incoming gas particle enters into one of two scattering channels, namely the direct inelastic scattering (IS) and trapping-desorption (TD) channels. In the IS channel, the incoming particle undergoes one or a few impulsive collisions with the surface, scattering back into the vacuum with a significant fraction of its incident energy. These particles quickly reach the mass spectrometer, accounting for the high energy peak of a TOF spectrum. The low energy peak is accounted for by the TD channel, in which the particle loses so much energy upon colliding with the surface that it temporarily adsorbs or dissolves into the bulk, eventually desorbing back into the vacuum with a Maxwell-Boltzmann (MB) distribution of velocities at the temperature of the liquid, and hence taking a longer time to reach the mass spectrometer. The idea comes from an analogous process which occurs in gas-solid collisions [35]. The branching between IS and TD channels is illustrated in Figure 1.3.

The contribution of the IS channel diminishes as the incident energy of the beam decreases [109]. For example, for neon atoms incident upon a room temperature squalane surface at $\theta_i = 45^\circ$ to the surface normal (see Figure 1.2 for a definition of $\theta_i$), $\sim 70\%$ enter into the IS channel when the incident beam energy is 25 kJ mol$^{-1}$, whereas the contribution is only $\sim 15\%$ with an incident energy of 6 kJ mol$^{-1}$ [109]. The relative contributions of the IS and TD channels to the TOF spectra also have some angular dependence. In general, the TD signal increases relative to the IS signal as the incident angle of the beam approaches zero (i.e., as $\theta_i$ in Figure 1.2 approaches zero). That is, particles colliding ‘head on’ with the liquid surface are more likely to undergo trapping-
desorption than particles undergoing ‘grazing’ (large $\theta_i$) collisions. Similarly, the TD contribution increases as the exit angle of the product decreases (i.e., as $\theta_f$ in Figure 1.2 approaches $-90^\circ$), showing that back scattered particles have a larger tendency to emerge from the TD channel.

1.2.2 Collisional energy transfer in the IS channel

Since particles entering into the TD channel scatter without any information on their initial conditions, the dynamics of a gas-liquid collision event are inferred from the IS channel. Invariably, the distribution of energies of scattered gases in the IS channel is broad and are skewed away from the incident energy of the beam, towards lower energies. The former observation hints at the wide range of collision environments that are available at the surface of a liquid, whereas the latter illustrates a crucial point: impulsive energy transfer into a liquid surface is substantial. For example, on average, a 75 kJ mol$^{-1}$ neon atom incident at 45$^\circ$ to the normal of a room temperature squalane surface loses $\sim 60\%$ of its energy to the surface [109]. Moreover, this fraction increases with the mass of the atom. Under the same situation, 80 kJ mol$^{-1}$ argon atoms and 185 kJ mol$^{-1}$ xenon atoms lose $\sim 70\%$ and $\sim 90\%$ of their incident energies, respectively. The latter is predicted by the Baule formula (1.5), which says that the fraction of energy lost by the colliding particle, $\Delta E/E_i$, increases with $m_g$. The Baule formula also accounts for the fact that there has never been a case of an atom gaining energy from the surface upon collision$^1$.

In accord with the dependence of the IS and TD contributions on incident and exit angles, on average, energy loss becomes more substantial as the incidence angle of the beam relative to the surface normal approaches zero. For example, 80 kJ mol$^{-1}$ argon atoms colliding with room temperature squalane and detected at an exit angle of $\theta_f = 45^\circ$ lose an average of $\sim 75\%$ of their energy to the surface when incident at 45$^\circ$ to the surface normal, and an average of $\sim 70\%$ when incident at 65$^\circ$. This dependence appears to weaken as the incidence angle of the beam decreases further to zero. Energy loss decreases as the particles are scattered into larger exit angles [46]. For the case of argon approaching squalane at 45$^\circ$ to the surface normal, atoms scattered at exit angles near 65$^\circ$ to the surface normal on average lose $\sim 5\%$ less energy to the surface than those scattered near 45$^\circ$ to the surface normal [46]. These observations can be predicted by the Baule formula (1.5). For example, smaller incidence angles of the beam might suggest more ‘head on’ collisions between the incoming particle and surface fragments, in which the angle $\phi_i$ in Figure 1.1 is close to 0$^\circ$ and the fractional energy loss of the atom is at its largest. Conversely, larger incident angles might imply more ‘grazing’ collisions, corresponding to $\phi_i$ near 90$^\circ$ and very small energy losses.

An important result to highlight is that, at high incident energies, fractional energy

---

$^1$This is not true when the incoming gas has internal structure. For example, a carbon dioxide molecule becomes rotationally excited upon colliding with squalane and perfluorinated polyether surfaces [88]. This observation will be returned to in Chapter 7.
loss in the IS channel depends very weakly on incident energy [109]. A 32 kJ mol\(^{-1}\) neon atom incident and detected at 45\(^\circ\) to the surface normal of squalane (i.e., \(\theta_i = \theta_f = 45^\circ\) in Figure 1.2) loses an average of \(\sim 50\%\) of its energy to the surface, whereas doubling its energy to 75 kJ mol\(^{-1}\) only leads to a loss of \(\sim 63\%\) [109]. Measurements at lower incident energies have not been reported, due to difficulty of analysing the small IS contributions under these conditions. This weak dependence can be anticipated from the Baule formula (1.5), which shows that fractional energy loss \(\Delta E/E_i\) is independent of \(E_i\), the incident energy of the incoming particle.

1.2.3 Angular distributions of scattered rare gases

By plotting the intensity of the mass spectrometer signal as a function of \(\theta_f\), one obtains an angular distribution of the scattered particles. Since atoms desorbing in the TD channel scatter with only thermal energies, their contribution to the total flux is relatively small, meaning that for a high energy beam, a total angular distribution may be taken as a reasonable approximation to an angular distribution of the IS channel alone [61].

Atoms scattering in the TD channel have cosine-like angular distributions which peak at the surface normal (\(\theta_f = 0^\circ\)), in accord with the expectation that atoms should thermally desorb without any preference for a direction. Angular distributions in the IS channel are usually broad and have a characteristic skew, peaking near the specular angle (where \(\theta_f = \theta_i\)). In principle, angular distributions should give information on the topography of the liquid surface. Discussions along these lines are largely absent in the literature, which is unsurprising because a rigorous explanation of angular distribution data in terms of the conformations of individual surface molecules would be difficult. In place of a detailed explanation, the broadness of the distributions is usually attributed to ‘surface corrugation’. Thus, a PFPE surface is more corrugated than a squalane surface on account of a broader neon angular distribution, and a heavy xenon atom reduces the corrugation of a squalane surface upon collision, because its angular distribution is more narrow [46]. The ‘surface corrugation’ concept will be put on rigorous footing by the theory that we develop in the subsequent chapters. It is not possible to make inferences on the angular distribution through the Baule formula, because it does not say anything about the orientation of the surface fragment or of the motion of the atom during the collision period. However, some extensions of the two-body picture in Figure 1.1, most notably Tully’s washboard model [122], do put an orientation on the surface fragment and can draw qualitative inferences from certain gas-solid angular distributions. In general, direct application of these models to gas-liquid collision data fails to capture the broadness of these distributions or even their essential shape [64].

Overall, there seems to be relatively little interest amongst the gas-liquid scattering community for angular distribution data. An anonymous reviewer of a paper relating to this work [84] criticised our interest in angular distributions on the grounds that they are ‘too subtle’ for theoretical work, and that energy loss should be the center of our attention.
because the concept is better defined. This attitude is not uncommon amongst gas-liquid
scattering researchers, which is unfortunate. Surely, designating angular distributions as
‘subtle’ is just another way of saying that there is no comprehensive theory describing their
origins? Indeed, angular distributions represent nothing more than the motion of the atom
between emerging from the source to arriving at the detector, which is the phenomenon
that this work has in sight.

1.2.4 The role of liquid composition

The Baule formula does a nice job of explaining the dependence of fractional energy loss
in the IS channel on the composition of the liquid. Its essential prediction is that energy
loss should decrease with increasing mass of the surface fragment, which correlates well
with experimental observations. For example, a 60 kJ mol\(^{-1}\) neon atom colliding with
a squalane and a PFPE surface loses \(\sim 60\%\) and \(\sim 40\%\) of its energy, respectively, to
the surface [110]. This corresponds well with the fact that the surface of squalane should
consist of -CH\(_n\) groups, whereas more massive -CF\(_n\) groups should be present at the
surface of PFPE. Meanwhile, energy losses for neon striking glycerol and squalane are
quite similar, which goes well with the fact that the -OH group of glycerol has a similar
mass to the -CH\(_2\)- and -CH\(_3\) groups a squalane molecule [109]. Similarly, 30–70 kJ mol\(^{-1}\)
neon atoms incident and detected at 55\(^\circ\) to the surface normal only lose \(\sim 20\%\) of their
energy upon colliding with the heavy atoms of a liquid indium surface [104]. Hence, the
dependence of energy loss on liquid composition can be explained by the differing masses
of the constituent molecules.

1.2.5 The role of liquid temperature

An extension of the Baule formula which accounts for the thermal oscillations of the sur-
face fragments about their equilibrium positions is discussed in reference [35]. However,
this addition is somewhat superfluous because when the incoming atom is moving fast
enough for the impulsive collision assumption to hold, the thermal motions of the surface
fragments should be too slow to play any role. The essential experimental trend is that the
TD contribution weakly increases relative to the IS contribution as the temperature of the
liquid increases, and with a rate nearly independent of the identity of the gas. For neon,
argon, and xenon scattering from PFPE, the rate spans \(\sim 0.05\) over an 85 K range for
each gas [47]. This increase might be interpreted as meaning that a thermally roughened
surface enhances the number of successive, multiple collisions between the incoming gas
and the surface molecules. Such thermal roughening indeed seems to be apparent to the
incoming atoms, because argon-PFPE angular distributions become slightly more broad
on increasing the liquid temperature from 280 K to 359 K [45]. However, there is room to
doubt the role of multiple collisions, because fractional energy loss of all three gasses are
essentially independent of the liquid’s temperature [47]. If thermal roughening increases
the occurrence of multiple collisions, then the fractional energy loss of the scattered atoms must similarly increase. This interpretation has been severely criticised by the computational community [74], who repeatedly find a significant number of multiple interactions in the IS channel in their molecular dynamics simulations. We will return to this point in the next section.

1.3 Insights from Theoretical and Computational Studies

We distinguish ‘theoretical studies’, which involve the development of new theories, from ‘computational studies’, which simulate the motion of every particle in a system over a short time interval. While the nature of the two approaches are different, they both have the same goal of producing new physical insights into the gas-liquid collision problem. Computational investigations into the gas-liquid collision problem have been via classical molecular dynamics (MD) simulations, and have been pursued far more extensively than theoretical investigations. Indeed, the only piece of theoretical work which makes any significant deviation from the two-body picture in Figure 1.1 is by Manson and colleagues [73, 36]. The main attraction of MD simulations is that they can investigate the actual dynamics of the atom as it approaches, collides with and scatters from the surface. Dynamical insights are beyond the scope of the current two-body collision theories, which are limited to predicting only the final energy and scattering angle of the atom following the collision event.

1.3.1 MD simulations and the role of multiple gas-liquid collisions

The first MD simulation of gas-liquid collision dynamics was performed by Gerber and co-workers in the early ’90s [61]. This study looked at xenon collisions with a squalane surface, which was modelled as a system of Lennard-Jones spheres. Since then, realistic models and force fields have been developed (for example, see reference [51]), and recent simulations have tentatively reproduced the splitting between the IS and TD channels [87]. The major dynamical contribution that MD simulations have made to the gas-liquid collision picture is the occurrence of multiple collisions between the incoming particle and liquid surface in both the IS and TD channels. This is best exemplified by a recent study by Yan, Hase and coworkers [87], who simulated 10,000 neon trajectories over the surface of squalane. Their finding was that \( \sim 75\% \) of the trajectories experienced more than one ‘kick’ (an event where one of the three components of the velocity of neon changes sign) by the surface before scattering back into the gas-phase, with around 10 kicks required for the particle to reach thermal energies and (presumably) enter into the TD channel. The occurrence of multiple collisions was significant for neon atoms scattered in-plane,
with \( \sim 55 \% \) of the trajectories undergoing more than one kick with the surface [128]. Other simulations which find a significant role played by multiple collisions can be found in references [61], [7], [13] and [121]. MD simulations have also given insight into the molecular structure that is probed by the incoming gas. In the neon-squalane study mentioned above, for example, it was found that \( \sim 60 \% \) of collisions involved a methyl group, suggesting that the methyl groups of squalane tend to protrude from the surface into vacuum. MD simulations have also found good support for the two-body collision picture shown in Figure 1.1, having identified discrete impact sites involved in the collision event [61, 87, 7].

1.3.2 The basic tenet of gas-liquid collisions

With support from both experimental and computational work, the two-body collision model introduced in section 1 appears to be a very reasonable way to describe gas-liquid collisions. This model and the IS/TD channels introduced in section 2 are the essential components of the modern picture of gas-liquid collisions. This picture can be supplemented with multiple collisions in the IS channel if desired, although the reader needs to be aware that their occurrence is not as well established by experimental data as the other features of the picture, at least for collisions which occur in-plane. Whatever the case, this picture explicitly involves the molecular structure of the liquid, and experimental data are seldom discussed without reference to surface molecules. This critical point is here referred to as the basic tenet of gas-liquid collisions: the outcome of a gas-liquid collision strongly depends upon the molecular structure of the target surface. While the tenet has never been explicitly stated, its presence will be quickly noticed upon delving into the literature.

In general, the tenet of gas-liquid collisions is rather hard to dispute. Not only can the two-body collision picture account for most experimental trends, but the seemingly authoritative nature of MD simulations makes it difficult to visualise gas-liquid collisions without molecules. But does it hold under all conditions? There is some evidence that for atom-liquid metal collisions it may not.

1.3.3 Classical scattering theory applied to liquid metals

While several extensions of the Baule two-body collision model are available [122, 34, 35], only classical scattering theory makes a large deviation from the basic two-body picture of Figure 1.1. So-called classical scattering theory (CST) is a model of atom-crystalline surface collisions developed by Brako and Newns in 1982 [9]. It earns its name because its chief approximation is that the trajectory of the incoming atom is classical, while the surface is treated as either a classical or quantum phonon bath. Manson and co-workers have extended the model over the last two decades, and have applied their results to the case of rare gas collisions with liquid metal surfaces [73, 36]. Two limiting cases of the
theory are available. The first corresponds to the gas-phase atom colliding with several discrete atomic centers. This involves an effective mass parameter, and gives essentially the same picture as a two-body collision theory (Figure 1.1). The second limit corresponds to an atom collision with a flat, repulsive barrier, beneath which the atoms of the surface reside. The barrier is shaped by vibrational motion of the underlying atoms. While the transfer of energy into the surface is still treated as a two-body collision in this limit, the actual change in the momentum vector is due to an interplay between collisional energy loss and the shape of the barrier. Manson and co-workers show that an intermediate regime between these two limiting cases produces strong quantitative agreement with experimental data for rare gas collisions with liquid indium, gallium and bismuth surfaces [73].

Being a gas-solid theory, it is difficult to understand why CST works so well when applied to liquid metal surfaces, especially in pictorial terms. Nonetheless, the key point from this study is clear. It is not a strict necessity to account for the atomic structure of a liquid metal surface to model atom-liquid metal collision data. In other words, liquid metal surfaces can be treated with some amount of coarse graining. ‘Coarse graining’ is a term which applies generally to the approximation of atomic and molecular detail with a spatially smoothed model. This conclusion is in contrast with the tenet established above. However, since it has not been shown whether CST can model data from non-metallic, molecular surfaces such as squalane, there is no discussion in the literature on whether the tenet is too strong. Rather, liquid metal surfaces are considered to be anomalously smooth, and hence be an exception to the rule [64]. The idea that ‘liquid metal surfaces are different’ is worth keeping in mind over the following chapters, as it will appear again.

1.4 Guide to the Rest of this Work

With experimentalists focusing on increasingly complicated systems and a growing number of molecular beam groups taking an interest in liquid surfaces, the need for a comprehensive theoretical description of a gas-liquid collision event has become more acute. The current theoretical descriptions — the two-body collision theories — do a good job of explaining collisional energy loss, but do not say anything about the actual motion of the incoming particle during the collision period, which should be important in explaining the origins of experimental angular distributions. To accommodate this, we have MD simulations, whose overly detailed output ultimately embellishes the elegant, simple picture given by the two-body collision theories. Thus, what is missing is a simple dynamical theory of a gas-phase atom approaching, colliding with and scattering from a liquid surface.

This work fulfills the need by developing closed equations of motion for the incoming gas-phase particle. By ‘closed’, we mean equations in which the forces are derived from a realistic model of the liquid surface, rather than by simultaneously solving equations of motion for every other degree of freedom in the system. To explain the concept further,
consider a system of \( n \) particles, with particle 1 at position \( r_1 \), particle 2 at position \( r_2 \), ..., particle \( n \) at position \( r_n \). Now introduce another particle \( s \) into the system and consider its motion. The equations of motion for particle \( s \) are

\[
m_s \frac{d^2 r_s}{dt^2} = - \frac{\partial}{\partial r_s} \Omega(r_1, \ldots, r_n),
\]

where \( m_s \) is the mass of particle \( s \) and \( \Omega \) is its potential energy. In order to solve this equation, we need to simultaneously solve equations of motion for particles 1, 2, ..., \( n \) in order to compute \( \Omega \). In our terminology, the equations in (1.6) are open; their solution requires the solution of other equations of motion. Closed equations of motion are obtained by replacing the force term on the right hand side with an expression which does not depend upon the solutions of other equations of motion.

From a model-building perspective, this situation is quite interesting. If progress towards deriving closed equations of motion were to be made, then some degree of coarse graining would be needed so that the innumerable surface degrees of freedom and structural details of the liquid would not render the problem intractable. This fact goes against the tenet established above, but suppose for now that such a model did turn out to exist. Then, impulsive forces would need to be included to account for collisional energy exchange. However, we could not establish such forces on the basis of a two-body energy loss treatment, because this would involve saying something about the molecular structure of the liquid, which is the very thing that needs to be avoided in order to solve the problem! In other words, if we want to succeed in deriving closed equations of motion, we need to ignore both the basic tenet of gas-liquid collisions and the well-established two-body picture shown in Figure 1.1. That is, the model needs to be very different than one developed from the current picture of gas-liquid collisions.

The theory is developed over the course of the next four chapters, which are summarised below.

- Chapter 2 looks for an appropriate coarse grained model of the liquid surface. The hydrodynamical local mode model is suggested and tested numerically, and is shown to do a reasonable job of modelling angular distributions for rare gases. These results suggest that the local mode model provides a good approximation of the topography of a molecular-scale liquid surface.

- In Chapter 3, we consider how the shape of the liquid surface, as described by the local mode model, would appear looking straight down at the surface from the viewpoint of the incoming atom. The reason for making this inquiry will become clear in Chapter 5, where it will be shown to lead directly to an analytic expression for the gas-liquid interaction potential. What is seen from the viewpoint of the incoming atom is given by a mathematical function which we term a random walk on parabolas. The first section of this chapter constructs the random walk on parabolas in a qualitative, pictorial fashion, whereas the (optional) second half rigorously
establishes it as a *stochastic process*.

- Chapter 4 develops a novel model of energy exchange that does not involve structural parameters such as relative mass. The model contrasts greatly with a two-body collision model, both in pictorial terms and in style, yet makes predictions that are in good agreement with experimental energy loss data for the case of a small incoming rare gas atom (namely neon) colliding with squalane and glycerol surfaces. A similar theory is developed for collisions with liquid metal surfaces, and also does a good job of modelling experimental data.

- Chapter 5 uses the random walk on parabolas and the collisional energy exchange impulse developed in Chapter 4 to derive equations of motion for a small incoming rare gas atom passing over a liquid surface. After discussing these equations in detail, numerical methods for solving them are described. They are put to work in Chapter 6.

We find that the theory makes predictions which are in good agreement with experimental angular distributions, energy losses and trapping probabilities for the case of a *small rare gas atom*. Suggestions for extending the theory to the general case are given in Chapter 7. While the applicability of the theory is limited, it still delivers several important insights that are not obvious from the ‘current’ picture of gas-liquid collisions. Indeed, since every step that is taken to develop the theory is quite removed from the basic tenet described above, the reader is encouraged to return to this introductory chapter at regular intervals to appreciate the state of the game.
Chapter 2

The Local Mode Model of a Liquid Surface

Chapter 1 outlined the goal of deriving closed equations of motion for a gas-phase atom approaching, colliding with and scattering from a liquid surface. By ‘closed’, it is meant that their force terms are derived from a model for the liquid surface, rather than by simultaneously solving equations of motion for every liquid particle in the system. There is little hope of finding a tractable model that is rich in molecular detail, so we will have to be content in working at a coarse-grained level. Despite what the ‘basic tenet’ introduced in the previous chapter would lead us to believe, such an approach will turn out to be very fruitful in tackling the gas-liquid collision problem.

A natural candidate for a coarse-grained description of a molecular-scale liquid surface is one based on the fluid dynamics of surface waves. The purpose of this chapter is to introduce local modes, a limiting kind of surface wave which could be a good approximation to what an incoming particle sees as it approaches a molecular-scale liquid surface. Section 1 briefly overviews the fluid dynamics of surface waves. This section does not assume any knowledge of fluid dynamics, and some equations are given without justification. In such cases the reader is referred to any standard fluid dynamics text (Levich’s Physicochemical Hydrodynamics is highly recommended [55]). This section is only included to ensure that the reader is familiar with the language of fluid dynamics. Hence, while viscous fluids are more relevant to the gas-liquid scattering problem, this section only gives a detailed account of the simpler case of low viscosity fluids. Local modes are studied in some detail in the second part of this section. Following this, we describe a simplistic numerical simulation which tests the utility of the local mode model on the scale of a gas-phase atom approaching a liquid surface. The local mode model is shown to make some reasonable predictions, motivating its use in closing the equations of motion in the next chapters.
2.1 Fluid Dynamics of Surface Waves

On the macroscopic scale, a liquid surface undergoes wave-like deformations from its flat equilibrium shape as a result of disturbances from the bulk fluid (such as non-uniform convection of fluid elements) and environment (such as an impact of another body on the surface). These deformations are accompanied by an increase in surface free energy (both Gibbs and Helmholtz), which leads to capillary forces which work to restore the surface to its equilibrium shape. However, due to the fluid’s inertia, the fluid will overshoot the equilibrium position, which again sets up capillary forces which work to restore the surface to its equilibrium shape. And so on. In addition, for waves with sufficiently large wavelengths and amplitudes, gravity also works to restore the surface to its equilibrium shape. Surface waves are called gravity waves if the dominant restoring force is gravity. As the amplitude and wavelength of these disturbances decreases, capillary forces eventually become the dominant restoring force and the waves are referred to as capillary waves. Beyond this, the viscosity of the fluid damps the waves over a distance much less than a wavelength, limiting their spatial extent. Such localised disturbances are called local modes.

2.1.1 Gravity and capillary waves

Since capillary waves and gravity waves are limiting cases of the same phenomenon, both can be described within the same mathematical framework. Consider a fluid whose density, $\rho$, is constant in time and space. Such a fluid is called incompressible. For simplicity, we consider a two dimensional fluid in the $xy$ plane. A fluid element with velocity $\mathbf{v}$ obeys the continuity equation,

$$\text{div } \mathbf{v} = 0,$$

which expresses the fact that there is no net flux of matter into or out of an element of an incompressible fluid (i.e., that mass is conserved). It is helpful to introduce the velocity potential $\phi$, which relates to the velocity of the element in a similar way that a potential relates to a force,

$$\frac{\partial \phi}{\partial \mathbf{r}} = \mathbf{v},$$

where $\mathbf{r}$ is the position vector of the element. Substitution of (2.2) into (2.1) yields Laplace’s equation,

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = 0.$$

Certain solutions to (2.3) will correspond to wave motions throughout the fluid. If we suppose that the fluid is in contact with another fluid phase (say, a gas phase), and is separated from it by an infinitely thin, hypothetical surface membrane, then some of
these motions will take place right beneath the membrane. The fluid dynamical model for wave motion of a liquid surface is wave motion of the surface membrane due to wave motion of the underlying fluid. Let \( y = 0 \) denote the equilibrium location of the surface membrane, and suppose the fluid of interest occupies the region \( y < 0 \). To describe the motion of the membrane, we therefore need a clear concept of wave motion in the fluid at all depths \( y < 0 \) beneath the membrane. In the case of gravity and capillary waves, everyday experience suggests that the solutions corresponding to such motion are periodic functions of distance and time. Hence, let

\[
\phi = f(y) \cos(kx - \omega t) \quad (2.4)
\]

where \( \omega \) is the frequency of the wave motion and \( k \) is its wave vector, which is related to its wavelength \( \lambda \) by \( k = \frac{2\pi}{\lambda} \). Substituting (2.4) into (2.3) gives an equation for \( f(y) \),

\[
\frac{d^2 f}{dy^2} - k^2 f = 0,
\]

which has the general solution

\[
f(y) = Ae^{ky} + Be^{-ky}.
\]

Therefore, a general expression for \( \phi \) is

\[
\phi = (Ae^{ky} + Be^{-ky}) \cos(kx - \omega t). \quad (2.5)
\]

Having established the velocity potential for wave motion at every depth in the fluid, we can now describe the vertical displacement \( \xi \) of the surface membrane from its equilibrium position \( y = 0 \) due to wave motions near \( y = 0 \). In two dimensions, \( \xi = \xi(x,t) \), and a plot of \( \xi \) as a function of \( x \) at fixed \( t \) will correspond to the surface profile of the liquid at time \( t \). To make progress, we assume that the amplitude of the displacement is much less than its wavelength. This assumption will be used at several points throughout this work. It essentially amounts to supposing that the fluid elements do not undergo nonlinear motion in the \( xy \) plane near the surface of the liquid [55]. While this type of motion may be important in the case of large scale gravity waves, it is unlikely to be significant on the scales where capillary waves dominate surface motion [93]. In these cases, disturbances to the liquid surface would result from the thermal motions of small groups molecules near the surface, which in turn travel almost linearly over distances comparable to the mean free path of the liquid. When dealing with capillary waves, this requires that the viscosity of the fluid is very small, as large viscosities mean large shear forces on the fluid elements. This assumption holds well for the case of long wavelength capillary waves. The short wavelength case is described in section 2.1.2. The vertical component of velocity \( v_y \) of a fluid element near \( y = 0 \) is related to the vertical displacement \( \xi \) of the surface membrane by

16
\[ v_y = \frac{\partial \xi}{\partial t} + \frac{\partial \xi}{\partial x} \frac{dx}{dt} \approx \frac{\partial \xi}{\partial t}, \]

since, on the small amplitude assumption, the curvature of the surface is small, and so the second term is much smaller than the first. Hence by (2.2), \( \frac{\partial \xi}{\partial t} \sim \frac{\partial \phi}{\partial y} \). The velocity of the disturbance relates to the potential \( \phi \) at \( y = 0 \), and so

\[ \xi(x,t) = \int \frac{\partial \phi(x,0,t)}{\partial y} \, dt = -(A-B) \frac{k}{\omega} \sin(kx-\omega t), \quad (2.6) \]

Identifying \( -(A-B)k/\omega \) with the amplitude \( a \) of the wave, the vertical displacement of the surface membrane due to wave motion of fluid immediately beneath is

\[ \xi(x,t) = a \sin(kx-\omega t). \quad (2.7) \]

The wave motion described by (2.7) is the fluid dynamical model of a capillary or gravity wave on a liquid surface. Note that the constant \( B \) can be set to zero on the basis of the boundary condition \( v \rightarrow 0 \) as \( y \rightarrow -\infty \).

So far, we have made no mention of gravity or surface tension, despite the assertion that (2.7) relates to both gravity and capillary waves. To see how these forces are related to the above, we need an expression for the frequency \( \omega \) of the waves in (2.7), which may be found as follows. Under the assumption of linear motion near the surface of a liquid, the equations of motion for a fluid element near the surface of the liquid are

\[ \frac{\partial v}{\partial t} = -\frac{1}{\rho} \text{grad } p + g, \quad (2.8) \]

where \( p \) is the static pressure of the fluid and \( g \) is the gravitational force (per unit volume) acting on the element, which only has a component on the \( y \) axis. The equations in (2.8) are known as the linearised Navier-Stokes equations. Noting that \( v = \text{grad } \phi \), (2.8) becomes

\[ \text{grad } \left( \frac{\rho}{\rho} \frac{\partial \phi}{\partial t} + p - \rho gy \right) = 0. \]

The term in the brackets must be equal to a constant. Without loss of generality, this may be taken as zero. This gives an expression for the pressure,

\[ p = -\rho \frac{\partial \phi}{\partial t} - \rho gy. \quad (2.9) \]

At the surface of the liquid, the fluid will experience an additional pressure \( p_s \) due to capillary forces which work to restore the surface to its flat equilibrium shape. Supposing that the fluid works reversibly against the gas-phase in producing the deformation in (2.7), we have an additional boundary condition that needs to be satisfied at the surface of the liquid,
\[ p + p_s = p_g, \quad (2.10) \]

where \( p_g \) is the pressure of the gas-phase above the surface. There are a variety of ways to derive an expression for \( p_s \), the most direct being to suppose that \( p_s \) is proportional to the curvature of the surface,

\[ p_s = -\gamma \frac{\partial^2 \xi}{\partial x^2}, \quad (2.11) \]

where the proportionality constant \( \gamma \) is the liquid’s surface tension. Substituting (2.11) and (2.10) into (2.9) gives

\[ -\rho \frac{\partial \phi}{\partial t} - \rho g \xi + \gamma \frac{\partial^2 \xi}{\partial x^2} = p_g \text{ at } y = \xi. \quad (2.12) \]

Differentiating this boundary condition with respect to \( t \) and substituting \( \partial \xi / \partial t \) for \( \partial \phi / \partial y \) gives

\[ -\rho \frac{\partial \phi}{\partial t} - \rho g \frac{\partial \phi}{\partial y} + \gamma \frac{\partial^3 \xi}{\partial t \partial x^2} = 0, \quad (2.13) \]

Since the displacement may be very small, (2.13) must be fulfilled for the case \( y = 0 \) as well. Evaluating (2.13) at \( y = 0 \) with (2.5) and (2.7) gives

\[ \rho \omega^2 - \rho g k - \gamma k^3 = 0 \]

and hence the dispersion relation for capillary and gravity waves on an incompressible fluid,

\[ \omega = \sqrt{\frac{8 \pi^3 \gamma}{\rho \lambda^3} + \frac{2 \pi g}{\lambda}} \quad (2.14) \]

From (2.14), it can be seen that at very large wavelengths, the term \( 2 \pi g / \lambda \) makes the dominant contribution to the wave’s frequency, and therefore propagation is mainly a gravitational effect. Conversely, at very short wavelengths, the term \( 8 \pi^3 \gamma / (\rho \lambda^3) \) dominates and wave propagation is mainly a capillary (surface tension) effect. The key point is that long wavelength waves are gravity waves, whereas short wavelength waves are capillary waves.

Before moving on, it should be mentioned that if many waves of various lengths are produced on the liquid surface, the overall motion is determined by the individual waves of the type described here. The resulting surface profile \( \xi = \xi(x) \) at a fixed \( t \) is then a Fourier series, with each separate wave playing a the role of an individual component of the series [10]. It is therefore possible to speak of the individual sine waves described above as basis functions for the surface profile.
### 2.1.2 Damping of short wavelength capillary waves

For the case of short wavelength capillary waves, it is not reasonable to suppose that the viscosity of the fluid is so small that nonlinear shearing motion can be neglected. To see why, consider the Navier-Stokes equations with this nonlinear term included,

\[
\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{\rho} \nabla p + \frac{\eta}{\rho} \nabla^2 \mathbf{v} + \mathbf{g},
\]

(2.15)

where \( \eta \) is the viscosity of the liquid. (2.15) is considerably more complicated than (2.8), so we omit the lengthy details of a solution here. This is essentially a mathematical exercise which does not introduce any new physical ideas. The reader is referred to pages 599 to 605 of reference [55] for details. There, it is shown that the components of velocity of a small wavelength capillary wave are

\[
v_x = a\omega e^{ky} \sin(kx - \omega t)e^{-8\eta\pi^2 t/\rho\lambda^2}
\]

(2.16)

\[
v_y = -a\omega e^{ky} \cos(kx - \omega t)e^{-8\eta\pi^2 t/\rho\lambda^2}
\]

(2.17)

Hence, while sinusoidal capillary waves with arbitrarily small wavelengths do exist, they are rapidly damped by the viscous shear forces in the liquid. This damping occurs both in time and, if we imagining the waves propagating along the \( x \) axis from a point source, in space.

The crucial message in (2.16) and (2.17) is that, at sufficiently small wavelengths, capillary waves will be damped over a distance much shorter than their wavelength. This strongly suggests that such cases could be better treated with a spatially more ‘localised’ solution to Laplace’s equation (2.3) than a cosine function, which is the essential idea behind local mode displacements.

### 2.1.3 Local mode displacements

The definitive local mode paper was published by Phillips in 2001 [94]. We consider short wavelength capillary waves which propagate from a point source. On this scale, these disturbances might correspond to a model in which the displacements are excited by random impacts from molecules or groups of molecules in the liquid beneath the surface membrane. On the basis of what was said in the previous section, the amplitude of these waves will be rapidly damped as we move outward from the source. If we were to fix a point in time shortly after excitation of the capillary wave, then the surface profile would appear as a short, symmetric localised oscillation centered on the source of the wave (Figure 2.1). An intuitive guess as to what kind of mathematical function is appropriate for describing the oscillation is a Bessel function, \( J_0(kx) \), where \( k \) is the wave vector of the disturbance. Applying this idea to (2.5) and considering the exponential damping factors in (2.17) suggests a velocity potential of the form
Figure 2.1: Diagram comparing sinusoidal capillary waves (top picture) to Bessel function-shaped local modes (bottom picture). The circles in the diagram indicate fluid molecules, and the arrows represent their velocity vectors. Only some molecules are drawn in for clarity. The light grey molecule represents the one which initiated the disturbance, and causes nearby molecules to oscillate in a coherent fashion. In the case of the sinusoidal wave, this oscillation perpetuates indefinitely along the horizontal direction. However, in the case of the local mode, the viscosity of the fluid damps this coherent motion, limiting the spatial extent of the disturbance.

\[ \phi = \phi_0 e^{ky + nt} J_0(kx), \]  

(2.18)

where \( \phi_0 \) and \( n \) are constants. When three dimensional local modes are considered on a flat surface, the potential takes the same form as (2.18), but with \( x \) replaced by \( r \), the radial distances from the center of the disturbance. In this case, it can be checked that the potential satisfies Laplace’s equation (2.3) [94]. As in (2.6),

\[ \xi = \int \frac{\partial \phi(x,0,t)}{\partial y} dt = \frac{\phi_0 k}{n} e^{nt} J_0(kx), \]

(2.19)

where the integration constant has been set to zero by the letting the zeroes of \( \xi \) coincide with the zeroes of the Bessel function. In the case of short wavelength capillary waves discussed in the previous section, one can derive a surface boundary condition analogous to (2.12), namely [53]

\[ -\frac{\partial \phi}{\partial t} + \frac{\gamma k^2}{\rho} \xi + \frac{2\eta}{\rho} \frac{\partial \xi}{\partial y} = 0 \text{ at } y = \xi \]

(2.20)

substituting (2.18) and (2.19) into (2.20) gives

\[ 0 = e^{nt} J_0(kx)(n^2 \rho - 2\eta k^2 n + \gamma k^3), \]

which must hold for all \( x \) and \( t \). Hence,

\[ n^2 \rho - 2\eta k^2 n + \gamma k^3 = 0, \]

(2.21)

and therefore

\[ n = \frac{\eta k^2}{\rho} \left( -1 \pm \sqrt{1 - \frac{\rho \gamma}{k^2 \eta^2}} \right), \]

(2.22)
We associate critical damping — the changeover from capillary waves to local modes — with the smallest wave vector \( k_c \) which gives (2.21) real roots. Clearly,

\[
k_c = \frac{\rho \gamma}{\eta^2},
\]

which shows that capillary waves are damped at larger wavelengths on more viscous fluids. For example, for water at room temperature, this works out to be \( 7.5 \times 10^7 \) m\(^{-1}\) (corresponding to a wavelength of 8.6 nm), whereas for the highly viscous squalane, this is \( 1.7 \times 10^4 \) m\(^{-1}\) (wavelength of 3.4 mm). Local modes can be thought of as capillary waves with \( k \gg k_c \). When \( k \gg k_c \), (2.23) gives \( n_1 = -2k^2\eta/\rho \). To find the second solution \( n_2 \) to (2.21) when \( k \gg k_c \), we use the fact that the product \( n_1n_2 \) is equal to term \( \gamma k^3 \) divided by the coefficient of \( n^2 \). This gives \( n_2 = -\gamma k/(2\eta) \). Hence, a general expression for the displacement \( \xi \) of the surface membrane due to a local mode oscillation is

\[
\xi = \phi_0 k J_0(kx) \left( c_1 \frac{e^{n_1t}}{n_1} + c_2 \frac{e^{n_2t}}{n_2} \right) = (d_1 e^{n_1t} + d_2 e^{n_2t}) J_0(kx).
\]

The constants \( d_1 \) and \( d_2 \) can be evaluated from the boundary condition \( \xi \to 0 \) and \( \partial \xi/\partial t \to w \) (a constant) as \( r \to 0 \) and \( t \to 0 \). It can be easily verified that

\[
d_1 = \frac{w}{n_1 - n_2} \quad \text{and} \quad d_2 = -\frac{w}{n_1 - n_2}.
\]

Hence, we finally obtain a general expression for a surface displacement due to a local mode,

\[
\xi(x, t) = A \left( e^{n_1t} - e^{n_2t} \right) J_0(kx),
\]

where the amplitude \( A \) is \( w/(n_1 - n_2) \). The above steps are exactly the same in the case of a local mode on a planar surface of a three dimensional liquid (in which the Bessel function is \( J_0(kr) \), \( r \) being the radial distance from the center of the disturbance).

There are several important remarks which can be made about local modes, although here we only give those which are relevant to this work. The first zero of \( J_0(kx) \) occurs at \( kx = 2.41 \). When \( k \) takes its greatest value \( k_{max} \), the first zero should correspond to \( x \) close to the radius of a liquid molecule. Hence, \( k_{max} \approx 2.41/r \), which is in the order of \( 10^9 \) m\(^{-1}\). The sign of the amplitude \( A \) in (2.24) may be taken as either positive or negative, meaning that both positive going and negative going local modes correspond to velocity potentials which solve Laplace’s equation (2.3). Generally, it is supposed that the overall deformation of the surface membrane is due to both positive- and negative-going modes, although on the scale that will be of interest in the following work, the distinction is not so important (see section 2.2.1). The function
Figure 2.2: Plot of the function $c(t)$ for a local mode with $k = 1.7 \times 10^4$ m$^{-1}$ on a room temperature squalane surface.

\[ c(t) = e^{n_1 t} - e^{n_2 t} \]  

(2.25)

in (2.24) gives the time-dependence of the local mode and is plotted in Figure 2.2 for a local mode on a room temperature squalane surface with $k = k_c$. For large values of $k$, $-n_1 \gg -n_2$, meaning that local modes undergo a rapid rise, followed by a slow decay back to zero displacement. The wave vector $k$ controls the rate of rise and decay of the local mode, which is most rapid for the largest values of $k$, and hence the most narrow local modes. The rise time corresponds to the time of the turning point of (2.25), which works out to be $(n_2 - n_1)^{-1} \ln(n_1/n_2)$. For a local mode with $k = 10^9$ m$^{-1}$ on a room temperature water surface, this works out to be $\sim 2$ ps, whereas on a room temperature squalane surface, the rise time is $\sim 0.2$ ps. The faster rise time of a local mode on a squalane surface could be taken to mean that the more viscous the fluid, the higher the energy required by the fluid particles to break away from the bulk, and hence the more energetic the oscillation.

Finally, if many local modes with various values of $k$ are present along the surface, then the overall surface profile can be represented as a Fourier-Bessel series, with each separate local mode serving as an individual component of the series, just as we had with capillary waves and Fourier series. In this work, the Fourier-Bessel series representation of a liquid surface profile is referred to as the local mode model of a liquid surface. It is this model (or at least, a closely approximating model), that we wish to use as our coarse-grained model for closing the equations of motion for a gas-phase particle approaching a liquid surface.\footnote{In section 4.2 of chapter 4, it will be seen that this approach is useful for the case of a non-metallic liquid surface.}
2.2 The Random Local Mode Model

On its own, the local mode model will not be so fruitful in approaching the gas-liquid collision problem. Not only are there practical issues in dealing with an infinite series, but the result would not give much insight into the underlying local mode structure of the surface profile involved in the collision. Moreover, even if we were successful in closing the equations of motion with the local mode model, the Fourier-Bessel series would lead to rather cumbersome discussions of the resulting theory. We therefore consider a slightly different model, in which the local mode surface profile is approximated by a field of randomly superimposed local mode displacements. This field is constructed by randomly superimposing individual local modes on top of one another, with the surface profile itself represented by the continuous line drawn over the outer edge of the construction (Figure 2.3). The ‘random’ aspect of the model comes about from the fact that there should be no preference for the subsurface molecules to displace any particular part of the surface membrane over any other. The random local mode approximation is inspired by the picture of chemical reactivity that often enters into organic and inorganic chemistry, in which atomic orbitals are explicitly considered rather than the resulting molecular orbitals of the molecule, which themselves are a linear series expansion over a basis of atomic orbitals. To make the distinction between this approximate approach to the local mode model and the exact approach using a Fourier-Bessel series, we will refer to the former as the ‘random local mode model’.

2.2.1 Three approximations

It will be helpful to furnish the random local mode model with the following three approximations.

1. On the scale of a gas-phase particle approaching a liquid surface, the only significant gas-surface interactions will be those involving local modes of the same order of size as the incoming particle, that is, with local modes with $k$ near $k_{max}$. Mathematically, $k$ for a particular local mode should be a random variable, which corresponds to the variety of ways in which an individual molecule or groups of molecules could collectively displace the surface membrane to form the local mode. The probability of a local mode with $k$ between $k$ and $k + dk$ occurring in an area $A$ of the surface is proportional to $Ak^2 dk$ (i.e.,
proportional to the number of modes which could be fit into the region \([94]\)). Absorbing \(A\) into the normaliser, we obtain \(h(k) = \text{constant} \times k^2\) as the probability density function for a local mode with \(k\) between \(k\) and \(k + dk\) appearing in the area \(A\). Evaluating the constant gives

\[
h(k) = \frac{k^2}{k_{\text{max}}^3 - k_c^3} \approx \frac{k^2}{k_{\text{max}}^3}.
\]

For \(k < k_{\text{max}}\), the distribution grows slower than \(1/k_{\text{max}}\), whereas for \(k\) close to \(k_{\text{max}}\), it grows approximately as \(1/k_{\text{max}}\). Thus, the distribution of \(k\)'s is heavily weighted towards the local modes with largest values of \(k\). In terms of the incoming particle, the probability of colliding with a local mode with \(k \sim k_{\text{max}}\) is much more likely than any other outcome. For the gas-liquid collision problem, we can therefore approximate the random local mode model by supposing that all local modes have wave vectors equal to \(k_{\text{max}}\).

2. An interesting issue with the random local mode model is that, if both negative- and positive-going local modes are incorporated, discontinuities will occur in the surface profile. To avoid this unrealistic situation, the present model is restricted to positive-going local mode displacements only. Strictly speaking, there is nothing approximate in doing this, because a complete basis of positive-going modes in (2.24) is possible in the local mode model. Moreover, since the random local mode model serves to describe the topography of the liquid surface, and since local modes are assumed wide and shallow, the surface topography produced by either positive- or negative-going modes will be essentially the same.

3. Assume that the component local modes in the Fourier-Bessel representation of a surface profile are closely clustered together. Then, since the rise time of a local mode is so short and the fall time so long, many of the local modes in the surface profile will be close to full displacement, meaning that only the central peaks of the local modes make a significant contribution to the surface profile (see Figure 2.2 again); the successive peaks of the Bessel functions will be ‘buried’ beneath the surface profile. In this case, instead of working with Bessel functions in (2.24), we should be able to proceed with a polynomial approximation to the central peak, and still be able to reproduce the essential features of the surface profile. Such an approximation is given by Newman (truncate the first entry in Table 1 of reference [76] to second order),

\[
J_0(kx) = 1 - \frac{1}{4}k^2x^2.
\]

The random local mode model uses these parabolic local modes, which has some enormous advantages. In particular, it leads to a relatively simple expression for the isotropy condition, which will be discussed in Chapter 3 when we consider the liquid surface profile described by the random local mode model. In addition, it is clear that the parabolic approximation (2.26) will lead to a much more tractable picture of the local mode surface profile than a Bessel function, and therefore lead to even more lucid discussions.
of the overall theory. Additionally, the parabolic approximation protects us from the likelihood that at \( k \) near \( k_{\text{max}} \), capillary waves are damped so rapidly that they do not survive long enough to propagate beyond the first trough of the wave. Such displacements would be better modelled by parabolic displacements than Bessel functions, however one should note that substituting (2.26) into (2.18) does not lead to a potential which solves Laplace’s equation. Thus, it must be the case that parabolas are close approximations to yet another function more suited to capillary waves displacements at \( k \) near \( k_{\text{max}} \) than Bessel functions.

Encouragingly, a recent MD simulation of water by Willard and Chandler found ‘undulating height fluctuations’ at the surface of liquid water upon fitting a smooth curve through the surface molecules [126]. Their result could well have been interpreted in terms of parabolic local modes (see Figure 1a of their paper), although they described the situation more generally in terms of capillary waves.

### 2.3 Test of the Random Local Mode Model

Having introduced the random local mode model of the liquid surface, we now wish to perform a simple test to check whether it is worth using as a means to close the equations of motion for a gas-phase particle approaching a liquid surface. The idea is that, if the key features of an experimental angular distribution can be reproduced by the shape of the random local mode surface profile alone, then it is likely that a more sophisticated treatment involving the actual motion of a gas-phase atom (i.e., closed equations of motion) should do at least as good a job of modelling the data. Figure 2.4 presents the essential model, which treats the entire rare gas beam as a ray which undergoes reflection at the surface of the local modes. The individual local modes on the surface independently rise and fall, intersecting the beam in different places for different lengths of time, which in turn causes the beam to scatter into a variety of directions. The entire model is restricted to two dimensions (the \( xy \) plane), which is adequate for modelling experimental in-plane angular distribution data (see Chapter 1). In particular, the local modes which are responsible for in-plane scattering must be centered on the plane containing the beam, the point of impact on the surface, and the detector. If a local mode were centered slightly out of this plane, then reflection would occur on either side of the \( xy \) plane and would not be seen by the detector. Note that in reality it could be possible for an incoming atom to be scattered slightly out of plane, and then scattered back into the plane \( via \) a second collision, although here we consider the likelihood of such an event to be negligible.

As well as neglecting the influence of the gas-liquid potential on the incoming atoms, the model also treats the collision as an elastic event. This appears rather severe, especially since rare gas atoms undergo extensive energy loss upon colliding with the surface (see Chapter 1). However, it is also known from simulation studies that the shape of an angular distribution for a high energy beam essentially stems from the geometry of the surface itself
Figure 2.4: Scattering model used to test the random local mode model. The incident particle beam is treated as a ray, and undergoes reflection at the surface of the local modes. The local modes rise in fall independently of each other, and with random, uncorrelated phases. Possible phases are indicated in the figure by arrows. In the case shown in A, the local mode marked 1 intersects the beam. This local mode is in a falling phase. Hence, as B shows, a short time later local mode 1 will fall below the path of the beam and the beam will be intersected by a new local mode on the surface, in this case, the local mode marked 2. The successive intersection of the beam by various local modes causes reflection into a variety of directions, which is the basis of the calculation of an angular distribution.
Hence, the results of the test will be meaningful only if the beam is assumed to be of sufficiently high energy.

### 2.3.1 Formulation of the model

In accord with the first approximation in the previous section, we approximate the wave vector of every local mode on the surface with the value $k = k_{\text{max}} \sim 10^9 \text{ m}^{-1}$. By the third, each local mode on the surface has the form

$$\xi(x, t) = Ac(t) \left(1 - \frac{1}{4}k^2x^2\right), \quad (2.27)$$

where, following the second approximation, the sign of $A$ is such that all local modes have positive displacements. To estimate $A$, let $\beta$ be the width of an ‘interfacial region’, which extends from $y = 0$ to the largest height that a local mode with $k = 10^9 \text{ m}^{-1}$ can reach. Let $c_{\text{max}}$ be the value of $c(t)$ at its turning point (i.e., when the local mode is at its maximum height). Then, the relevant boundary condition is that, as $x \to 0$ and $c(t) \to c_{\text{max}}$, $\xi \to \beta$. By (2.27), we then obtain

$$A = \beta/c_{\text{max}}. \quad (2.28)$$

$\beta$ can be estimated from interfacial density profile widths reported in the MD simulation literature. This is because the small system sizes and short time scales that MD simulations are restricted to (typically $\sim 100 - 800$ molecules and for $\sim 3 - 4$ ns [61, 51, 121, 7]) means that height fluctuations corresponding to large local mode displacements (those with small $k$) do not occur; simulated profiles are necessarily averaged over molecular motions corresponding only to the largest $k$ values. Since the distribution of $k$’s is heavily weighted towards $k_{\text{max}}$ (section 2.2.1), this average will be heavily weighted towards $k_{\text{max}}$.

Since we are considering many local modes sitting on a liquid surface, ‘$t$’ in (2.27) is not the same time that is measured in the laboratory. Consider any particular local mode on the surface. Then, $t$ in (2.27) is the time since the start of that local mode’s rise from zero displacement. Since each local mode on the surface rises and falls independently of the others, this parameter will have a different zero for each local mode. To make the distinction clear, the symbol $t$ in (2.27) is replaced by $s$, and by $t$ we now mean laboratory time. In addition, the local mode in (2.27) is centered at point $x = 0$, whereas our formulation needs to allow for the local modes to be centered at different points along the horizontal axis. Let the local mode be centered at point $a$ along the surface. Since each local mode will have a different value of $a$, it is possible to identify each local mode with its value of $a$. Hence, we can unambiguously speak of ‘local mode $a$’. Therefore, the displacement of the surface profile due to local mode $a$ at time $s$ since the start of its rise is
\[
\epsilon_a(x, s) = \beta \frac{c(s)}{c_{max}} \left( 1 - \frac{1}{4} k^2(x - a)^2 \right). \tag{2.29}
\]

The crux of our analysis involves the following two questions. Which local mode on the surface intersects the particle beam at time \( t \)? What is the height of that local mode at time \( t \)? An answer to both questions is provided by the stochastic process \((A_t, C_t)\), which gives the local mode \( a \) which intersects the particle beam at time \( t \) as its first component, and the value of the function \( c(s) \) for that mode as its second component. A stochastic process is a mathematical function which evolves through time following a probability law, rather than a well-defined formula that accompanies a deterministic function. The idea here is that, once the probability law for \((A_t, C_t)\) is fully specified, we can calculate the slope of the surface profile that is encountered by the incoming particle beam (by differentiating (2.29)), and use it to reflect the beam across a tangent to the surface and calculate a scattering angle at time \( t \). In fact, the use of the term ‘stochastic process’ in this chapter is rather loose. However, the concept of a probability law is worth becoming acquainted with before we lay down a more formal definition in the next chapter.

We now put a probability law on \((A_t, C_t)\). Rigorously, the parameter \( t \) should be on the half-line \([0, \infty)\), but for simplicity we suppose it takes on values from a discrete set of indices \( \{0, 1, \ldots \} \) and assume the time step to be very small. Let \((A_0, C_0)\) be a given initial condition. Then, at time \( t = 1 \), one of two events will occur. Either a new local mode will rise up and intersect the beam (Outcome 1), or no new local mode will intersect the beam and the beam will continue to be intersected by the same mode that intersected it at time \( t = 0 \) (Outcome 2). Outcome 1 occurs with a probability \( p \), whereas Outcome 2 occurs with probability \( q = 1 - p \). Suppose that Outcome 1 occurs. Then, it must be that \( A_1 > A_0 \) (Figure 2.5a), since the local mode \( A_0 \) blocks access to modes lying behind it. Owing to the random nature of the local modes in the random local mode model, \( A_1 \) will be a uniformly distributed random variable on \([A_0, a_{max}]\), where \( a_{max} \) corresponds to the largest value of \( a \) which allows for a local mode to intersect the beam. Furthermore, \( C_1 \) must be such that the top of the local mode at \( A_1 \) has just intersected the beam at time \( t = 1 \). The probability law continues in this fashion from \( t = 2 \) onwards.

Note that a type of boundary condition is also required, for if the beam continues to intersect a single local mode, there will come a point where that local mode slips below the beam (Figure 2.5b). At this point, the beam will proceed behind that local mode, and will be intersected by another local mode with \( A_k < A_{k-1} \), which will be at a random point into its oscillation (i.e., \( C_k \) is a uniform random variable). The possible values of \( C_k \) are restricted to the segment that allows for the local mode \( A_k \) to intersect the beam.

The simplicity of this probability law demonstrates an advantage of working with parabolic local modes rather than Bessel function local modes, namely that it leads to a single parameter probability law for \((A_t, C_t)\). If Bessel functions were used, then intersection of the beam by local mode peaks beyond the central peak would also need to be accounted for, requiring several parameters, as well as an awkward long memory stochas-
tic process. For the purposes of testing the random local mode model in the gas-liquid scattering problem, it will be sufficient to leave $p$ as an adjustable parameter. As will be discussed, the sensitivity of the calculated results to variations in $p$ does not suggest that this results in any serious ill-definition of the model. Moreover, it will turn out to be possible to justify the values of $p$ for the liquids investigated here.

A representative segment of a sample path of $(A_t, C_t)$ is shown in Figure 2.5, using parameters for squalane at 298 K (see Table 2.1), $p = 0.04$, and the simulation conditions described at the end of this section. A sample path is one of an ensemble of possible curves that could be realised by a stochastic process. The $A_t$ component, which identifies the local mode intersecting the beam at time $t$, is seen to undergo step-like fluctuations. When the beam is intersected by a new local mode on the surface, $A_t$ undergoes a step increase to a local mode lying in front of the previous one, and when the current local mode slips below the beam, $A_t$ makes a step decrease to a local mode lying behind the previous one. The time evolution of the intersecting local mode is described by the $C_t$ component, which also undergoes step-like fluctuations, although during each step it follows the course of the deterministic function $c(s)$. Accordingly, when $A_t$ undergoes a step increase, $C_t$ takes on the first value of $c(s)$ which permits that local mode to intersect the beam. In this case, this value is always $\sim c_{\text{max}}$, as the rise time of $c(s)$ is faster than the time step used in these calculations. Similarly, when $A_t$ undergoes a step decrease, the next value taken on by $C_t$ is a random value of $c(s)$, subject to the condition that the local mode at $A_t$ still intersects the beam.

### 2.3.2 Calculation of an angular distribution

Having specified the process $(A_t, C_t)$, we need a means to extract an angular distribution from its sample paths. Let the beam be aiming for the origin of the $xy$ plane, making an angle $\theta_i$ to the surface normal. The first task is to work out the range of local modes (that is, the range of $a$'s along the $x$ axis) which could possibly intersect the beam. Since $kx = \pm 2$ at the intersection of the $x$ axis for all values of $c(s)$, the local modes have a
Figure 2.6: A representative segment of a sample path of the process \((A_t, C_t)\), simulated with parameters for squalane at room temperature (see Table 2.1) and \(p = 0.04\). Graph A plots the \(A_t\) component and graph B plots the \(C_t\) component. The \(C_t\) component has been divided through by \(c_{\text{max}}\) for clarity.
half width along the x axis of $2/k$. Hence, the most negative value of $a$ must be $-2/k$, which corresponds to a local mode whose width just touches the origin. Values of $a$ more negative than this correspond to local modes too far from the origin to intersect the beam.

Suppose that the local mode at $a_{\text{max}}$ can only intersect the beam at the instant when it is at maximum displacement (when $c(s) = c_{\text{max}}$). Let $r$ be the distance from the origin to the top of this local mode when it is fully displaced. Then, $\beta = r \sin(\pi/2 - \theta_i) = r \cos \theta_i$ and $a_{\text{max}} = r \cos(\pi/2 - \theta_i) = r \sin \theta_i$, which gives $a_{\text{max}} = \beta \tan \theta_i$. Hence, all and only all local modes lying in the interval $[-2/k, \beta \tan \theta_i]$ can intersect the beam.

The following is algebraically more simple if we shift the origin of the x axis by $2/k$ units, such that the beam is now aiming for point $(2/k,0)$ in the $xy$ plane and all local modes lying on the interval $[0, \beta \tan \theta_i + 2/k]$ intersect the beam. Let $X_t$ denote the distance along the x axis from 0 to the point where the beam is intersected by a local mode, $E_t$ denote the height of the local mode at that point (that is, the y coordinate of that point), and $Z_t$ the distance from $(2/k,0)$ to $(X_t, E_t)$ (Figure 2.7). It is evident that

$$E_t = Z_t \sin(\pi/2 - \theta_i) = Z_t \cos \theta_i$$

$$X_t = Z_t \cos(\pi/2 - \theta_i) + 2/k = Z_t \sin \theta_i + 2/k$$

Furthermore, by substituting $X_t$ and $(A_t, C_t)$ in (2.29) for $x$ and $(a,c)$, respectively, we have

$$E_t = \frac{C_t}{c_{\text{max}}} \left( 1 - \frac{1}{4} k^2 (X_t - A_t)^2 \right).$$

Substituting (2.30) and (2.31) into (2.32) gives

$$0 = Z_t^2 \sin^2 \theta_i + Z_t \left( 2 \frac{2}{k} - A_t \right) \sin \theta_i + \frac{4C_{\text{max}} \cos \theta_i}{\beta k^2 C_t} - \frac{4A_t}{k}$$

When $A_t = 2/k$, the acceptable solution must go to zero as $C_t \to 0$, which is satisfied by the positive solution to (2.33). Because of its length, this solution is not quoted here. With this expression for $Z_t$ in terms of $A_t$ and $C_t$, (2.30) and (2.31) may be used to obtain $X_t$ and $E_t$. Moreover, from (2.32), we can obtain the slope at the point on the local mode that intersects the beam at time $t$. 
Figure 2.8: Diagram used to calculate the scattering angle $\theta_f$ from the slope of the local mode (see text).

$$G_t = -\frac{\beta k^2 C_t}{2c_{\text{max}}} (X_t - A_t).$$

(2.34)

The process $G_t$ will either be zero or negative, since the sides of the local modes where $G_t$ is positive are inaccessible to the particle beam in this model (i.e., $X_t$ is always greater than $A_t$; see Figure 2.7). We use the process $G_t$ to reflect a unit vector coincident to the particle beam across a tangent to the surface. Since the distance between the surface and the detector is so much greater than the height or width of a local mode, the region $[0, \beta] \times [-2/k, \beta \tan \theta_i]$ where the beam is intersected by local modes is essentially a single point. Hence, we can take the point where the beam is intersected by a local mode as the origin $(0, 0)$ of the $xy$ plane (since it is contained in this region), regardless of which local mode is intersecting the beam or how large its displacement is.\(^2\) Hence, let $\mathbf{u}$ be a unit vector coincident to the particle beam whose tip is touching the origin of $(x, y)$. We have

$$\mathbf{u} = -(i \cos(\pi/2 - \theta_i) + j \sin(\pi/2 - \theta_i)), \quad (2.35)$$

where the negative sign on $\mathbf{u}$, which is taken to mean that the vector is aiming at the surface, may be ignored, as it will cancel in the following calculations. To reflect $\mathbf{u}$ across a tangent to the local mode surface, switch to the coordinate system $(\hat{x}, \hat{y})$, which is a rotation of $(x, y)$ such that $\hat{x}$ lies on the tangent to the point on the local mode that intersects the beam (Figure 2.8). Let the angle $xO\hat{x}$ be equal to $\alpha$. Then, by Figure 2.8, $\mathbf{a} \cdot \mathbf{b} = \cos(\pi/2 + \alpha) = -\sin \alpha$, since $\mathbf{a}$ and $\mathbf{b}$ are unit vectors. However, we can also write

$$\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y = a_y = G_t a_x = G_t \cos \alpha.$$ 

The second equality in this equation follows since $b_x = 0$ and $b_y = 1$. In the third equality, we have used the fact that $G_t = a_y / a_x$, whereas the fourth equality is evident from Figure 2.8. Combining these two results gives

--

\(^2\)In our original paper detailing this investigation [83] this approximation was not made. However, the effect of this approximation is so minimal that the extra effort in accounting for the local mode positions and heights does not pay off.
\[ \alpha = \tan^{-1}(-G_t), \quad (2.36) \]

where \( G_t \leq 0 \). With (2.36), we can write \( u \) in the coordinate system \((\hat{x}, \hat{y})\) by premultiplying (2.35) by a rotation matrix,

\[ \hat{u} = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} u = \begin{pmatrix} \sin(\theta_i - \alpha) \\ \cos(\theta_i - \alpha) \end{pmatrix}. \quad (2.37) \]

Reflecting \( u \) across a tangent to the surface is achieved by reflecting \( \hat{u} \) about the \( \hat{y} \) axis, that is,

\[ \hat{v} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \hat{u} = \begin{pmatrix} -\sin(\theta_i - \alpha) \\ \cos(\theta_i - \alpha) \end{pmatrix}, \quad (2.38) \]

where \( \hat{v} \) is \( \hat{u} \) after reflection about the \( \hat{y} \) axis. This vector can be expressed in the \((x, y)\) coordinate system by premultiplying \( \hat{v} \) by the inverse of the rotation matrix in (2.37),

\[ v = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix} \hat{v} = \begin{pmatrix} \sin(2\alpha - \theta_i) \\ \cos(2\alpha - \theta_i) \end{pmatrix}. \quad (2.39) \]

Hence, the angle between the particle beam and the horizontal axis after reflection by the local mode \( A_t \) with displacement \( C_t \) at time \( t \) (the scattering angle) is

\[ \theta_f = \tan^{-1}(v_y/v_x) - \pi/2. \quad (2.40) \]

To summarise, the calculation of the scattering angle starts at \((A_t, C_t)\), which gives \( Z_t \) (via the positive solution to (2.33)), which gives \( X_t \) (via (2.31)), which gives \( G_t \) (via (2.34)), which gives \( \alpha \) (via (2.36)), which gives \( v \) (via (2.39)), which finally gives \( \theta_f \) via (2.40). Since \((A_t, C_t)\) is a stochastic process, \( \theta_f \) is also a stochastic process. The angular distribution itself is calculated by simulating the process \((A_t, C_t)\) over a very large number of time steps, computing the corresponding sample path of \( \theta_f \) by the above scheme, and then plotting its sample path as a histogram. All calculations discussed here simulated \((A_t, C_t)\) for \( 10^6 \) time steps of 0.1 ns length, with each local mode on the surface separated by a distance \( a_{max}/500 \) and initial conditions \( A_0 = -2/k \) and \( C_0 = c_{max} \). The large number of time steps ensured that the computed angular distributions were not significantly affected by the variance of the \((A_t, C_t)\) sample paths, which was found to have a noticeable effect for simulations using fewer than \( \sim 10^3 \) time steps. Larger numbers of time steps and more closely spaced local modes did not notably change the results presented in the next section. In every case, the first 100 time steps were removed to ensure that the process \((A_t, C_t)\) was essentially ergodic (independent of the initial condition) in computing an angular distribution. All calculations were coded and executed in \textit{R} 2.4.1 [117]. Code is available upon request.

In this treatment, \( \theta_f \) will never exceed the specular angle (where \( \theta_f = \theta_i \)). This occurs
because, in putting a probability law on \((A_t, C_t)\), it was assumed that the very top of a rising local mode is the first segment to intersect the beam, and that the beam can only ever intersect the very top of the local mode or the side closer to the beam. This restricts \(G_t\) to zero or negative values (i.e., in (2.34), \(X_t - A_t > 0\)), which in turn only allows reflection at or below the specular angle. This is an approximation because, for all \(a > 2/k\), the first part of the rising local mode to intersect the beam will be a small segment on the side further from the beam, even in the absence of an attractive potential. For a beam striking a glycerol surface, the most negative slope that could be encountered would occur on a fully displaced local mode centered at 0, which gives a lower-bound slope and scattering angle of -0.4 and 6.4\(^\circ\) for all incident angles. This lower-bound to the scattering angle is representative of all systems studied here. In addition, our neglect of a gas-liquid potential interaction prevents the beam from diverting into the back side of the local mode at close range, as is the normal occurrence with scattering from the point source of an interaction potential, which would produce more scattering beyond the specular angle. We also neglect the possibility of the beam undergoing multiple reflections across the surface. Although the MD simulation community has found multiple gas-liquid collisions to play an important role in producing an angular distribution (see Chapter 1), the reader is asked to have faith that this is approximation is a good one; we explain why in Chapter 6. Experimental angular distributions of high energy beams do rapidly decrease beyond the specular angle [46], which leaves plenty of data to assess the quality of the random local mode model in approaching the gas-liquid scattering problem, at least at lower scattering angles.

### 2.3.3 Results and Discussion

Figure 2.8 shows calculated angular distributions for a 185 kJ mol\(^{-1}\) xenon beam incident upon a squalane surface at 290 K and a PFPE (DuPont Krytox 1625 perfluorinated polyether) surface at 290 K, with experimental points corresponding to measurements by King et al [46]. Table 1 lists the parameter values used in each calculation. The values of \(p\) were chosen by manual adjustment until the predicted distribution most closely matched the experimental distribution.\(^3\)

In each case, the model does a reasonable job of tracking the data with an optimal value of \(p\). Discrepancies occur when trying to estimate the broadness of the distributions, although this does not imply serious inaccuracies with the random local mode model. For example, both calculations predict very little density at scattering angles less than 20\(^\circ\). However, this could be expected because the experimental data also includes a large TD component (\(\sim 60\%\) for Xe striking squalane, and \(\sim 20\%\) for Xe striking PFPE [108]),

\(^3\)The original paper on this study also presented results for a 43 kJ mol\(^{-1}\) argon beam scattering from a 298 K glycerol surface. The comparison to experimental data was very poor, and we now believe that this result is meaningless; the beam was of low energy and the experimental data was not flux-weighted [114], meaning that much of the experimental distribution would be in the form of a TD cosine distribution.
Figure 2.9: Angular distributions predicted by the test model (histograms) compared to experimental measurements overlaid as points for 185 kJ mol\(^{-1}\) Xe beams incident upon a 290 K squalane surface, as computed with \(p = 0.04\) (graph A), and a 290 K PFPE surface, as computed with \(p = 0.0026\) (graph B). Although not shown, experimental measurements have been reported beyond the specular angle in each case (see text).
which is not included in our elastic model. Similarly, the predicted distributions peak sharply at the specular angle, underestimating density between 40° and 60°. Muir and Manson [73], who successfully modelled rare gas scattering from molten metal surfaces with a gas-solid surface scattering model (Chapter 1), required account of the gas-surface potential to broaden their predicted distributions and match experimental data, so one might anticipate such discrepancies to be apparent with the assumptions made here. Whatever the case, the key result is that the essential features of high energy angular distributions, namely a long tail leading to a peak at the specular angle, are qualitatively reproduced by the simplified model, suggesting that the random local mode model of the liquid surface holds on the scale of a gas-liquid collision event. Therefore, there is plenty of motivation for going ahead and trying to close the equations of motion for a gas-phase atom passing over a liquid surface with the random local mode model of the liquid surface.

Before moving on, it is worth examining these results further to extract some insights on the liquid surface. The squalane and PFPE data were fitted with \( p \) values of 0.04 and 0.0026, respectively, which is straightforward to justify because \( p \) essentially measures the frequency at which the beam is intersected by new local modes on the surface. PFPE is a highly viscous fluid (viscosity of 490 mPa s), so we would expect most thermal motions from the bulk to be damped well before reaching the interface, which would reduce the frequency of new local modes and hence give a very small \( p \). Squalane is considerably less viscous than PFPE (viscosity of 34 mPa s), permitting more thermal motions to reach the interface and hence increasing the value of \( p \). Since the correlation between \( p \) and viscosity is not perfect, it is likely that \( p \) is also a function of other fluid parameters.

Figure 2.9 shows representative sample paths of \( E_t \), the height of the surface intersected by the incident beam at time \( t \), for squalane and PFPE, as computed with these values of \( p \). For PFPE, the beam spends considerable time scanning the falling phases of the local modes. However, for the squalane case, the beam is frequently intersected by new local modes. In other words, a squalane surface is more dynamic than a PFPE surface. In terms of surface molecules, this result can be interpreted to mean that the frequency of new molecules arriving at a unit area of a squalane surface is larger than at a unit area

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_i ) (degrees)</td>
<td>65(^a)</td>
</tr>
<tr>
<td>( \beta ) (Å)</td>
<td>6.0(^b)</td>
</tr>
<tr>
<td>( \rho ) (Å)</td>
<td>0.81(^d)</td>
</tr>
<tr>
<td>( \eta ) (mPa s)</td>
<td>34(^f)</td>
</tr>
<tr>
<td>( \gamma ) (mN m(^{-1}))</td>
<td>26(^g)</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters used to test the random local mode model via angular distribution calculations. \(^a\) Value from reference [46]. \(^b\) Value at 298 K from reference [51]. \(^c\) Average of squalane and glycerol values. Glycerol value (4 Å) from reference [75]. \(^d\) Value from reference [109]. \(^e\) Value at 293 K from reference [8]. \(^f\) Estimated at 0 external pressure from three measurements at different external pressures (see Table 4, listing \( x = 0 \) in reference [120]). \(^g\) Value from reference [52]. \(^h\) Value for DuPont Krytox 1525 at 293 K from reference [24].
of a PFPE surface.

A possible criticism of this work is that leaving $p$ as an adjustable parameter permits too much lee-way in producing an angular distribution. The nature of the sensitivity of the distributions towards $p$ does not suggest that this is an issue. As $p$ tends toward unity, the beam is rapidly intersected by new local modes with successively larger displacements, and spends almost all of its time reflecting from the flat, top parts of the local mode. This causes the angular distributions to cluster very tightly about the specular angle at large $p$. As $p$ decreases from unity, the amount of specular reflection decreases and the distributions adopt a wide, bell shape centered at approximately 20 degrees below the specular angle. As $p$ is decreased further to a critical angle, the distributions rapidly take on the distinctly left skewed shape of an experimental distribution. As $p$ approaches zero, the beam spends considerable time scanning the top of a flat, decaying local mode ($C_t \sim 0$), and the distributions narrow tightly about the specular angle once again. The observation that $p$ induces only two distinct scattering regimes which converge to the same result suggest that the surface tension, density and viscosity carry the essential information of the model and that by leaving $p$ as an adjustable parameter the model does not become ill-defined and overly dependent on $p$. This result is not unexpected, because these three parameters implicitly account for the temperature of the fluid and the mass of the surface molecules, two features which are not explicitly accounted for in the above formulation but are known to affect experimental scattering angle distributions [109, 45].

### 2.3.4 Final remarks

Having found good motivation for using the random local mode model to close the equations of motion for a gas-phase particle passing over a liquid surface, it is important to have a clear interpretation of a molecular-scale (high $k$) local mode. In this work, a molecular-scale local mode displacement is interpreted as a *coarse grained representation of a surface molecule*, with the surface profile drawn by the random local mode model interpreted as a *coarse grained representation of the molecular topography of a liquid surface*. The surface membrane is not regarded as a material object, but rather as an attractive force field which keeps the surface molecules in close association. The interpretation of a local mode displacement as a coarse grained surface molecule makes sense, because in order for a liquid surface to smoothly go from the continuous picture offered by surface waves to the discrete molecular picture, it must be the case that the continuous picture becomes a coarse grained picture of the surface in the molecular limit. In other words, the continuous description cannot suddenly become meaningless in approaching the molecular scale, or else it would imply that beyond a certain critical resolution there is a dramatic change in the physical nature of the liquid surface.

Despite this reasoning, the reader may remain unconvinced that a hydrodynamic model is meaningful on the scale of a gas-liquid collision. In fact, it is a misconception that hydrodynamic fluid motion does not operate near the molecular scale. For example, simulations
Figure 2.10: Representative sample paths for the process $E_t$ for squalane at $p = 0.04$ (graph A) and for PFPE at $p = 0.0026$ (graph B).
of hard sphere atomic liquids have shown that the hydrodynamic equations quantitatively predict the fluid velocity field down to a distance of about three inter-particle diameters [2]. While an individual local mode might appear to correspond to the motion of an individual surface molecule, its actual appearance on the surface would be the net result of the coherent motion of several liquid molecules over several inter-molecular distances. In light of this, it is unsurprising that the molecular-scale liquid surface should bear resemblance to a surface of local mode displacements. What remains to be seen is whether it is the molecular structure of the local modes or the local modes themselves that the incoming atoms are sensitive to. The results in the previous section hint at the latter, but not in a definitive way.

Figure 2.11 presents the local mode picture of a gas-liquid collision. It shows a gas-phase atom approaching a liquid surface which is composed of randomly superimposed local mode displacements. At the moment, it is uninteresting. However, as the theory is developed over the next few chapters we will add features to this picture as a means to keep track of where we are. By the time we reach Chapter 6, the picture will be ready for an experimental test.
Chapter 3

The Random Walk on Parabolas

The previous chapter introduced the random local mode model of the liquid surface, and finished with preliminary results which suggested that it would be a good model for closing the equations of motion for a gas-phase atom passing over a liquid surface. Closing the equations of motion amounts to using the random local mode model to derive an analytic expression for the force acting on the incoming atom (see Chapter 1 section 4). There are many ways in which the random local mode model could be used to derive an expression for the force. Each of these approaches involves various approximations and each will lead to expressions of different complexity. Our task is to find an approach that leads to a very simple expression, but yet involves reasonably conservative approximations. For this, we consider a guiding principle that was used by Einstein in his formulation of general relativity: physics is only simple when analysed locally [70]. In the case of an atom passing over a liquid surface, ‘locally’ means from the viewpoint of the incoming atom. The purpose of this chapter is to consider what is seen looking straight down at the surface from the viewpoint of the incoming atom. In particular, we wish to know the displacement of the surface directly beneath the incoming atom at time $t$ since emerging from the source. The way in which this concept will be useful will seem vague at this stage, however it will be seen in Chapter 5 that it leads to an expression for the force with very little effort. Indeed, much of the grunt work of the theory is contained in this chapter, and it is important that the reader is at least comfortable with the concepts presented in the first section before proceeding.

What is seen from the viewpoint of the incoming atom is given by the random walk on parabolas, a stochastic process that is developed from the random local mode model. The physical reason for the random walk on parabolas being a stochastic process is that the random, uncorrelated nature of the surface local modes should limit us to only making probabilistic, rather than precise, statements about the displacement of the surface beneath the incoming atom at time $t$. This chapter is divided into three parts. The first section, which is compulsory reading, introduces the random walk on parabolas in a pictorial way. This section emphasises the physical picture over mathematical details, and
puts the random walk on parabolas together in an heuristic fashion. The second section, which is optional reading and does not introduce any new physical concepts, puts the ideas of the previous section on rigorous mathematical footing. Curious readers who lack the necessary background will find this material accessible after taking the Crash Course on Stochastic Analysis, which is presented as an appendix to this work.

While the construction presented in section 2 is adequate for the subsequent chapters, its complicated nature makes it difficult to look at its limiting mathematical properties. While such properties are largely irrelevant to the gas-liquid collision problem, they are still satisfying to pursue. The third section therefore introduces the random walk on polynomials, a process which has similar paths to the random walk on parabolas but with a more simple construction. After appropriate renormalisation, we identify an interesting limit in which the random walk on polynomials converges to a Wiener process, a crude model of the Brownian motion. This section is also optional reading.

The division between ‘pictorial’ and ‘mathematical’ is often encountered in theoretical science. For example, one can obtain a working understanding of Feynman’s path integral formula in quantum mechanics without ever knowing the mathematically rigorous Feynman-Kac formula.

3.1 Pictorial Construction

3.1.1 Improvements on the random local mode model

Before going any further, we take the opportunity to make some improvements in the random local mode model. Since the wave vector in (2.29) is not such a meaningful concept for a parabolic local mode, we write the parabolic local modes in the form

\[ f(x) = b(1 - (x - a)^2/h^2) \]  \hspace{1cm} (3.1)

where \( b \) is the amplitude of the local mode (\( = \beta c(s)/c_{\text{max}} \) in (2.29)), \( a \) is the center of the local mode, and \( h \) the half width of the local mode along the \( x \) axis. It is straightforward to see that both representations are equivalent (substitute the local mode half width 2/\( k \) from the wave vector representation into (3.1)). For the case of a single fast incoming particle, we can assume that the local modes are essentially static during the time interval in which an incoming particle passes overhead. While this may appear to be a poor assumption due to the fast rise time of a local mode (for instance, a 29 kJ mol\(^{-1}\) neon atom takes \( \sim 0.6 \) ps to travel a nanometer distance along the \( x \) axis, whereas the rise time of a local mode on squalane is \( \sim \) only 0.2 ps), the local mode is much more likely to be in its long, slow falling phase when the particle passes overhead. Hence, we may take the amplitude \( b \) as a constant during this time period. This assumption was not included in the random local mode model test in the last section of the previous chapter, because there we were considering the scattering of an entire beam of particles over a longer time.
period, rather than the motion of a single particle passing over the surface. To determine
the value of the amplitude $b$, consider the excess area $A$ of a local mode displacement (3.1)
over a flat surface. In three dimensions,

$$A = 2\pi \int_0^h r \left( \sqrt{1 + \left( \frac{df}{dr} \right)^2} - 1 \right) dr$$

(3.2)

where we have replaced $x$ in (3.1) with $r$ to emphasise that we are considering the area
of the corresponding three dimensional paraboloid. Supposing that the amplitude of the
local mode is much smaller than the diameter $2h$, (3.2) is approximately [59]

$$A \approx 2\pi \int_0^h r (df/dr)^2 dr$$

(3.3)

Evaluating (3.3) using (3.1) gives $A \approx \pi b^2$. Next we consider the average height of
a local mode at the maximum of its oscillation. Here, the energy of the mode will be
approximately $k_B T$, the average thermal energy of the molecule which gave rise to the
mode, where $k_B$ is Boltzmann’s constant and $T$ the temperature of the liquid. In producing
the local mode, the molecule would have been resisted by a ‘surface force’, which arises
from the attractive interactions between molecules within the liquid and serves to prevent
a liquid molecule from evaporating into the gas-phase. By analogy with the macroscopic
surface tension, we consider this force to be a constant per unit area and denote it by $\gamma$.
The average excess area of a local mode at the maximum of its oscillation will therefore
be $A = k_B T / \gamma$, which gives

$$\langle b \rangle = \sqrt{\frac{k_B T}{\pi \gamma}},$$

(3.4)

as the average height of a local mode at the maximum of its oscillation. In accord
with experimental data, formulations of the capillary wave model of the liquid surface
usually assume that the vertical coordinate of the surface membrane at a particular point
is normally distributed with mean zero [10]. Accordingly, we suppose that $b$ is an element
of a collection of normal random variables with mean zero and standard deviation $\langle b \rangle$. To
accommodate the need for only positive-going local modes (see approximation 2 of section
2.2.1), this collection of normal random variables is restricted to zero or positive numbers.
In this work, $\gamma$ is approximated by the macroscopic surface tension. The accuracy of this
approximation is discussed in Chapter 6. The assumption that the amplitudes of the local
modes are much smaller than $2h$ is good for the liquids studied here. For instance, for
a squalane surface at 290 K, the root-mean-square displacement due to the local mode
amplitudes is only 2.22 Å ($= \sqrt{\frac{k_B T}{\pi \gamma}}$), whereas the full width of a mode is of the order
of a molecular diameter, i.e. about 10.2 Å [61].
3.1.2 Construction of the random walk on parabolas

We now ask what is the displacement of the liquid surface profile immediately beneath the incoming atom at time $t$ since emerging from the molecular beam source. The random local mode model provides an answer to this question in the form of the stochastic process $Q_t$, which we term the random walk on parabolas. The construction of the random walk on parabolas is natural. We suppose that the incoming atom moves an infinitesimal distance along the horizontal axis, and then consider all of the possible surface displacements beneath the atom at its new position, as allowed by the random local mode model. We then narrow this list of possibilities by selecting only those that maintain a continuous and isotropic surface profile, and assign the remaining possibilities an equal probability of occurring.

Since we have assumed the individual local modes to be essentially static on the time scale of their interaction with an incoming gas-phase atom, we can simplify the construction by supposing that $Q_t$ will change only when the horizontal coordinate of the particle changes, that is, $Q_t = Q_t(X_t)$, where $X_t$ is the horizontal coordinate of the incoming atom at time $t$. A plot of $Q_t$ against $X_t$ will correspond to the profile of the liquid surface as seen from the point of view of the incoming atom. Let an incoming atom with horizontal coordinate $x$ shift an infinitesimal distance $\delta x$ in the horizontal direction. The various possible results of this translation give rise to one or the other of two major outcomes. The first is that the particle will continue to observe the same local mode displacement as was observed before the infinitesimal shift along the $x$ direction. Identifying this local mode with a subscript $i$, $Q_t$ will therefore go from having the value $b_i(1 - (X_t - a_i)/h^2)$ to $b_i(1 - (X_t + \delta x - a_i)/h^2)$. The second possibility is that, owing to randomly superimposed nature of the local modes, the particle will see a different local mode after shifting along the $x$ axis. In this case, the value of $Q_t$ will change from $b_i(1 - (X_t - a_i)/h^2)$ to $b_j(1 - (X_t + \delta x - a_j)/h^2)$, where $i \neq j$. Note that the value of $h$ is kept constant, in accord with the first approximation in section 2.2.1. Mathematically, the evolution of $Q_t$ with respect to $X_t$ would be a kind of random walk where, for each infinitesimal change in $X_t$, $Q_t$ will either involve the same parabola as before or will shift to a different one. The walk is on a set of parabolas (rather than on the real numbers, as it is in the diffusion literature), with the actual value of the stochastic process being that of the current parabola evaluated at the $x$ coordinate of the incoming particle.

To put this concept on quantitative footing, let $F = \{f_1, f_2, \ldots\}$ be a collection of parabolas of the form (3.1), with each element having a particular value of the position $a$ and displacement $b$. In accord with the previous section, each $b$ needs to be an element of a sequence of positive normal random variables with mean zero and standard deviation $\sqrt{k_B T/\pi \gamma}$. Let $Z_t$ be a random walk process which takes on values corresponding to an index in the set $F$, and suppose that transitions in the random walk correspond to the particle going from local mode $i$ to local mode $j$ as a result of moving an infinitesimal distance $\delta x$ along the horizontal axis. Then by the preceding description, the random walk
on parabolas is

\[ Q_t = f_{Z_t}(X_t). \]  

(3.5)

In order that \( Q_t \) evolves in a way which is consistent with the random local mode model, certain requirements need to be placed on the transition events of the random walk \( Z_t \). Let \( p_{ij}(t) \) be the transition probability of the random walk \( Z_t \) when the particle has horizontal coordinate \( X_t \) (corresponding to the probability that, on moving from point \( X_t \) to \( X_t + \delta x \) along the horizontal axis, the incoming particle will go from seeing local mode \( i \) to local mode \( j \)), and suppose that there is a set of conditions \( C \) that must be fulfilled in order for the transition to occur. Then we have

\[ p_{ij}(t) = \begin{cases} 
\rho & \text{if } C \text{ occurs} \\
0 & \text{otherwise} 
\end{cases} \]  

(3.6)

The reason for the transition probability taking on the same constant value for all possible transitions is that, since the local modes are randomly superimposed across the surface, there should be no preference for \( Z_t \) to make any particular transition, as long as the transition satisfies the requirements of \( C \).\(^1\) As pre-empted above, the conditions in \( C \) are that the random walk \( Z_t \) leaves the surface profile continuous, as well as isotropic (i.e., does not show different features when viewed from left-to-right or right-to-left). For continuity, we evidently require that \( Q_t = Q_{t-} \), where \( t- = \lim_{s \to t, s < t} s \) is the time immediately before the transition. For isotropy, let \( A_{ij}^- \) denote the event where \( a_j \leq X_t \leq a_i \) when that the particle is travelling from right-to-left across the surface \( (dX_t/dt < 0) \), and \( A_{ij}^+ \) the event where \( a_j \geq X_t \geq a_i \) when the particle is travelling from left-to-right across the surface \( (dX_t/dt > 0) \). The condition that one of \( A_{ij}^- \) or \( A_{ij}^+ \) must occur when a transition in \( Z_t \) occurs ensures that the surface profile remains isotropic when viewed

\(^1\)Throughout chapters 3 to 7, the symbol \( \rho \) will denote the transition probability defined in equation (3.6), rather than a density.
from either direction. To see how this works, refer to Figure 3.1, which considers a case where the particle is travelling from right-to-left across the surface \((dX_t/dt < 0)\) and this condition has been dropped. Say that at time \(t\) the particle is over a local mode with \(a_i < X_t\), such that the surface profile produced by the process \(Q_t\) is increasing at that instant. When the particle shifts a short distance \(-\delta x\) along the horizontal axis, then, if \(\rho\) is sufficiently large, there is a correspondingly large probability that the particle will see a new local mode beneath itself in the superposition, with \(a_j < a_i\). The particle will probably continue to see new local modes each time it shifts a short distance \(-\delta x\), so that, over a long distance, the surface profile produced by the process \(Q_t\) would be non-decreasing when viewed from right to left. In the unlikely event that the particle flies over the top of a local mode and observes its decreasing side, then the next transition in \(Z_t\) could result in either the decreasing or increasing side of a new local mode. By (3.6), both events are equally likely, which means that the particle will soon go back to observing a non-decreasing surface profile. Thus, for large \(\rho\), the surface profile generated by \(Q_t\) would be anisotropic, tending to increase more when viewed from right-to-left than from left-to-right. This anisotropic behaviour can be eliminated by ensuring that \(Z_t\) only makes transitions when the particle is over the decreasing side of a local mode (i.e., \(X_t < a_i\)) and that the particle goes on to see the increasing side of the next local mode upon making the shift \(-\delta x\) along the \(x\)-axis (i.e., \(a_j < X_t\)). Similar arguments apply for when the particle moves from left to right across the surface. Note that other isotropy conditions could be derived in which the peaks do not need to be kept separated, however these would require an awkward long-memory random walk process instead of \(Z_t\). The condition \(C\) is therefore

\[
C = \{Q_t = Q_{t-}\} \cap \{A^+_{ij} \cup A^-_{ij}\} 
\tag{3.7}
\]

(this can be read as ‘the event where \(Q_t = Q_{t-}\) occurs and where either \(A^+_{ij}\) or \(A^-_{ij}\) occurs’). The major reason for making the parabola approximation in section 2.2.1 lies in the simplicity of the isotropy condition that it requires; if Bessel functions were used, then their oscillations at large \(x\) would require an impractical number of other conditions to ensure that the remaining surface profile was isotropic. The final requirement relates to the case where the horizontal coordinate of the incoming particle is such that the parabola in (3.1) takes on a negative value. In this case, it is required that a transition in \(Z_t\) occurs with unit probability and fulfils the continuity condition \(\{Q_t = Q_{t-}\}\).

In summary, the random walk on parabolas process \(Q_t\) involves a collection of parabolas of form (3.1) (each corresponding to a particular local mode with a particular displacement) the transition probability (3.6) and the condition (3.7), and gives the displacement of the surface as seen looking straight down at the surface from the viewpoint of the incoming atom at time \(t\). The actual value of the stochastic process at time \(t\) corresponds to that of the parabola specified by the random walk evaluated at the \(x\) coordinate of the incoming particle ((3.5)). Sample paths of the random walk on parabolas cannot be computed without knowing the state of the incoming atom, which in turn is produced by
Figure 3.2: Random walk on parabolas process simulated for a particle travelling right-to-left above a 290 K squalane surface and parallel to the horizontal axis with velocity 1700 m s\(^{-1}\) using A. \(\rho = 0.000\), B. \(\rho = 0.0025\), C. \(\rho = 0.005\) and D. \(\rho = 0.01\). The curves can be interpreted as the surface displacement that might be observed if one was looking straight down at the liquid surface from the point of view of the passing particle. It can be seen that the larger the value of \(\rho\), the more closely clustered the local modes are in the surface profile.

46
equations of motion for the incoming atom. However, we can simulate them without the equations of motion if we assume that the atom moves without accelerating along the \( x \) axis. Such paths are shown in Figure 3.2 for a 290 K squalane surface, using various values of \( \rho \) and a horizontal component of velocity of 1700 m s\(^{-1}\), which roughly corresponds to a 29 kJ mol\(^{-1}\) neon atom passing over the surface at a very large incident angle \( \theta_i \). The paths were coded and executed in \( R \) 2.9.2. [118], and code is available upon request.

That is essentially all that needs to be known about the random walk on parabolas in order to understand the theory developed in the following chapters. Figure 3.3 presents the local mode picture of a gas-liquid collision, which was introduced at the end of the last chapter (Figure 2.11), but has here been modified to accommodate the assumptions introduced by the random walk on parabolas model. It shows a dotted vertical line beneath the particle, which is divided into a segment labelled \( Q_t \) and a segment labelled \( R_t \). In this diagram, \( R_t = Y_t - Q_t \), where \( Y_t \) is the vertical coordinate of the incoming atom at time \( t \). The diagram hints at the way in which the random walk on parabolas might be used to obtain the force term, namely by approximating the distance between the incoming particle and the surface by \( R_t \) and using this as the argument of the gas-liquid potential. The region of the liquid lying ahead of the particle has been erased, which represents the idea that, looking straight down at the surface from the viewpoint of the incoming particle, an observer would not know exactly what surface topography lies ahead, due to the intrinsic disorder of the random local mode surface profile.

Readers may now move on to Chapter 4 if they wish. Mathematically inclined readers may be unsettled by some aspects of this construction, so they are encouraged to read the next section, which puts the random walk on parabolas on rigorous mathematical footing.
3.2 Rigorous Construction of the Random Walk on Parabolas

The above construction lost its rigour after we said ‘let \( F = \{ f_1, f_2, \ldots \} \) be a collection of parabolas of the form (3.1), with each element having a particular value of the position \( a \) and displacement \( b \).’ The problem is that the position parameters \( a \) and displacement parameters \( b \) must themselves be elements of some other set, but these sets were never defined. The collection \( F \) is therefore poorly defined. Consequently, it is unclear how the value of the random walk process \( Z \) corresponds to a parabola in \( F \), and so the notation ‘\( f_Z(t)(X_t) \)’ is not meaningful. Indeed, it may be that \( F \) contains no local modes which fulfil the conditions in \( C \), and hence that \( Z \) may not exist. The remedy for this situation is to give \( F \) a more precise definition, and then define the random walk on parabolas in such a way that the role of \( Z \) is obvious.

In the following two sections, the stochastic process \( \{ A_q \}_{q \in \mathbb{R}^+} \) is denoted by \( A \), and \( A_t \) is the value of \( A \) at time \( t \). Assume a filtered probability space \((\Omega, \mathcal{F}, \mathbb{F}, P)\) and that the horizontal and vertical coordinates of the incoming atom are \( \mathcal{F}_t \) adapted, continuous stochastic processes, which are denoted as \( X \) and \( Y \), respectively. Furthermore, we assume that \( X \) and \( Y \) are sufficiently smooth for the velocity processes \( dX_t/\ dt \) and \( dY_t/\ dt \) to exist at all \( t \), are of finite variation on compacts, and that the initial conditions \( X_0 \) and \( Y_0 \) are given. All of these are obvious from a physical point-of-view. For mathematical convenience, we suppose that the atom moves in the bounded hemisphere \( H = \{ (x, y) \in \mathbb{R}^2 : \sqrt{x^2 + y^2} \leq \sqrt{X_0^2 + Y_0^2} \} \). This assumption is of little physical limitation, because we may make \( X_0 \) and \( Y_0 \) as large as desired.

3.2.1 Basic definitions

The following provides a meaningful definition of ‘a collection of local modes’.

**Definition 3.1.** Let \( N_0 \) be a given countable finite collection of \( N(0, k_B T/\pi \gamma) \) and take the subset \( B = \{ n : n \in N_0, 0 \leq n \leq Y_0 \} \). Let \( C = [-\sqrt{X_0^2 + Y_0^2} - h, \sqrt{X_0^2 + Y_0^2} + h] \). The collection \( F \) of all functions from \( \mathbb{R} \) to \( \mathbb{R} \) with representation

\[
f(x) = b \left( 1 - (x - a)^2 / h^2 \right)
\]

where \( a \in C \), \( b \in B \) and \( h \) is a fixed positive real constant, is the local mode collection.

Unlike the collection in section 3.1.2, it is clear which local modes are contained in the local mode collection. Namely, those with amplitudes in \( B \) and origins in \( C \). Each function in the local mode collection corresponds to a possible local mode that the atom may pass over during its motion in \( H \). By taking the set \( N_0 \) as given, we can be sure that the amplitudes of the local modes are not correlated with the motion of the particle. Since it is not possible to assign numbers to an uncountable number of points, assuming that
$N_0$ is countable ensures its existence. The finiteness of this collection poses no physical limitation as we can make it as large as we wish.

With this definition for the local mode collection $F$, it is now easy to set up a random walk process $Z$ which can identify parabolas from $F$. Writing $f(x;\alpha,\beta)$ as shorthand for the function $f(x) = \beta(1-(x-a)^2/h^2)$ in $F$, it follows from the definition that

$$ C \times B = \{(a,b) : f(x;a,b) \in F \text{ for all fixed } x \in \mathbb{R}\}, \quad (3.9) $$

which means that each element of $C \times B$ corresponds to a unique element of $F$. We can therefore assign $C \times B$ as the state space of $Z$. This provides an unambiguous connection between the value of $Z$ and a local mode in $F$. We can now define the random walk on parabolas as the process $\{f(X;Z)\}$.

**Definition 3.2.** The process

$$ Q = \{f(X;Z)\} $$

where $f \in F$ and $Z \mapsto C \times B$ is an adapted pure jump process is a random walk on parabolas.

### 3.2.2 Isotropy and continuity conditions

Before going on to define the process $Z$, it will be useful to make some comments about the isotropy and continuity conditions. These conditions must be satisfied when $Z$ makes a jump to another region of $C \times B$. In the pictorial construction, we defined $A_{ij}^+$ as the event where $a_j \geq X_t \geq a_i$ when the atom is travelling from left-to-right across the surface, $dX_t/dt > 0$. We required either this condition or $A_{ij}^-$ to be fulfilled when the random walk $Z$ made a transition from local mode $i$ to local mode $j$ at time $t$. Since the local mode collection $F$ is uncountable in the present construction, it is not so meaningful to speak of ‘local mode $i$’ or ‘local mode $j$’. However, we can still describe the situation by considering the value of the $C$ component of the process $Z$ at transition time $U$. If the value of the $C$ component of $Z$ at time $U^- = \lim_{u \to U, u < U} u$ is $c_1$, then we require the event

$$ A_0(c_1) = \left\{X_{U^-} < c_1 \cap \dot{X}_{U^-} < 0\right\} \cup \left\{X_{U^-} > c_1 \cap \dot{X}_{U^-} > 0\right\}, \quad (3.11) $$

where $\dot{X}_{U^-} = dX_t/dt|_{t=U^-}$, to occur for a transition to occur at time $U$. To formulate the second part of the isotropy condition, we suppose that at the transition time $U$ the second component of the process $Z$ takes on the value $c_2$. Following the pictorial construction, it must be that the event

$$ A_1(c_2) = \left\{X_{U} > c_2 \cap \dot{X}_{U} < 0\right\} \cup \left\{X_{U} < c_2 \cap \dot{X}_{U} > 0\right\} \quad (3.12) $$

A set is countable if its elements can be individually counted. One way to ensure that a mathematical construction is sensible is to show how it is related to a countable set.
occurs with the transition. Events $A_0(c_1)$ and $A_1(c_2)$ collectively define the isotropy condition, although not in terms of their intersection. For reasons that will become clear in the next section, it is helpful to speak of them separately. The continuity condition is obviously $\{Q_U = Q_U\}$, and so the condition that must occur with probability 1 at the transition time $U$ is

$$A(c_2, b) = A_1(c_2) \cap \{Q_U = Q_U\}, \quad (3.13)$$

where $b$ is the value of the amplitude component $b \in B$ of $Z$ after completing the transition.

It is worth pointing out that we can think of the isotropy conditions $A_0(c_1)$ and $A_1(c_2)$ in terms of a symmetry operation on the sample space. To see this, note that events of the form $\{G \cap H^C\} \cup \{H \cap G^C\}$ are usually written the symmetric differences [124],

$$G \triangle H = \{G \cap H^C\} \cup \{G \cap H^C\}. $$

While the events $\{X_{U_-} < c_1\}$ and $\{X_{U_-} > c_1\}$, and $\{\dot{X}_{U_-} < 0\}$ and $\{\dot{X}_{U_-} > 0\}$ are not quite complementary, it is still very tempting to write (3.11) as a symmetric difference,

$$A_0(c_1) = V_{U_-} \triangle C_{U_-} \quad (3.14)$$

where $V_{U_-} = \{\dot{X}_{U_-} < 0\}$ and $C_{U_-} = \{X_{U_-} < c_1\}$. Similarly, $A_1(c_2)$ is approximately in the form $\{G^C \cap H^C\} \cup \{G \cap H\}$. It can be shown via a Venn diagram or other means that such an event can be written as the compliment of a symmetric difference, namely $\{G \triangle H\}^C$. We can therefore rewrite $A_1(c_2)$ as

$$A_1(c_2) = \{V_{U} \triangle C_U\}^C. \quad (3.15)$$

The representations of $A_0(c_1)$ and $A_1(c_2)$ in terms of symmetric differences are illustrated in Figure 3.4. As can be seen, the isotropy condition means that the region of the sample space available at time $U$ is an inversion of the region available at time $U_-$. While the association of isotropy with inversion symmetry is indeed very nice, it needs to be regarded with some caution because the representation of $A_0(c_1)$ and $A_1(c_2)$ as symmetric differences and their compliments is not exact.

### 3.2.3 The pure jump process $Z$

The construction will be complete once we define the process $Z$. This needs to be done in several steps, and the isotropy and continuity condition described above also needs to be considered. It is required that $Z$ makes a jump when either the incoming atom goes on to see a new local mode beneath itself or when the local mode that the atom is currently over begins to take on negative values. We therefore consider two sets of random times $T_1, T_2, \ldots$ and $S_1, S_2, \ldots$, and let $U_i = T_i \wedge S_i$. Now, let $J_1 = T_1, J_2 = T_2 - U_1, \ldots$ be
Figure 3.4: Venn diagrams illustrating the events $A_0(c_1)$ and $A_1(c_2)$. A Venn diagram represents a sample space by a square and depicts events contained in a sample space by partitioning the square. The left hand diagram shows events defined at time $U_-$ (i.e., just before $Z$ makes a transition to a new local mode), and the right hand diagram shows events defined at the transition time $U$. In the left hand diagram, the event $\{\dot{X}_{U-} < 0\}$ occupies the region of the sample space to the left of the dotted line and $\{\dot{X}_{U-} > 0\}$ occupies the region to the right. Similarly, the event $\{X_{U-} < c_1\}$ occupies the region above the dotted line and $\{X_{U-} > c_1\}$ occupies the region below. The construction of the right hand diagram is similar. The shaded regions represent events that are allowed by the isotropy conditions $A_0(c_1)$ and $A_1(c_2)$. It can be seen that the regions of the sample space allowed at time $U$ can be obtained by inverting the regions allowed at time $U_-$, and in this sense we can associate the isotropy conditions with inversion symmetry. These interpretations need to be regarded with some caution, because these diagrams ignore events such as $\{X_{U-} = c_1\}$ and $\{\dot{X}_{U-} = 0\}$.

exponentially distributed iid random variables, that is

$$P(J_i < j) = 1 - e^{-\lambda j} \quad (3.16)$$

for some constant $\lambda > 0$. The intervals $J_i$ are the waiting periods between new local modes appearing beneath the incoming atom. The connection between the parameter $\lambda$ in (3.16) and $\rho$ in (3.6) will be explained shortly. Next, define

$$S_1 = \inf (0 < t \leq T_1 : Q_t < 0)$$

$$S_2 = \inf (U_1 < t \leq T_2 : Q_t < 0)$$

and so on. If for a particular $S_i$ such a time does not exist, set it to $T_i$. The times $S_i$ correspond to times at which the surface profile of the liquid surface begins to take on negative values. For $U_i < t \leq U_{i+1}$, $Z$ is defined as

$$Z_t = \begin{cases} W_{i+1} & t = U_{i+1} \text{ and } A_0(c_1) \text{ occurs} \\ Z_{U_i} & \text{otherwise} \end{cases} \quad (3.17)$$

where $W_{i+1}$ is a random variable with probability distribution that incorporates the condition $A(c_2,b)$, as will be described shortly. Note that $A_0(c_1)$ will always occur if
$U_{i+1} = S_{i+1}$. Thus, the process $Z$ jumps when the particle goes on to see a new local mode beneath itself (an event which occurs after an exponential waiting time and when the isotropy condition is satisfied), or when the local mode begins to take on negative values, whichever occurs first.

To define the probability distribution of the random variable $W_{i+1}$ in (3.17), recall that there in the random local mode model there is no preference to make any particular transition, as long as the transition satisfies the condition $A(c_2, b)$. We therefore have

$$P(W_{i+1} \in (dc, b)) = \begin{cases} \text{constant} & \text{if } A(c, b) \text{ occurs} \\ 0 & \text{otherwise} \end{cases} \tag{3.18}$$

where $dc$ is the smallest open interval centered on point $c$ in $C$. The constant in (3.18) can, in principle, be evaluated by ensuring that the distribution is normalised over $C \times B$. In this work, we assume that this is the case. Note that the transition probability (3.18) is defined for a region of $C$ and an individual point in $B$, rather than for individual local modes like in the transition probability in (3.6).

From (3.18) alone, it might not be obvious that the measure $P(W \in dw)$ is mathematically well-defined. This is clarified by the following theorem.

**Theorem 3.1.** The probability measure $P(W \in (dc, b))$ is well-defined.

**Proof.** Let $E = \{(c, b) \in C \times B : A(c, b) \text{ is satisfied}\}$. $E$ is the collection of all regions where $W$ may lie with nonzero probability. For $P(W \in (dc, b))$ to be well-defined, it is sufficient for the collection $E$ to correspond to a countable union of disjoint regions in $C \times B$ (see the third point in Definition 10.3 in the Appendix). We can then define $P(W \in E^C)$ as $1 - P(W \in E) = 0$. By the continuity condition in $A((c, b))$, we have

$$f(X_{U_{i+1}}; Z_{U_i}) = f(X_{U_{i+1}}; Z_{U_{i+1}}) = b \left(1 - (X_{U_{i+1}} - c)^2/h^2\right),$$

and hence

$$c = X_{U_{i+1}} - h \sqrt{1 - f(X_{U_{i+1}}; Z_{U_i})/b},$$

which implies $b \in \{\beta : \beta \in B, \beta \geq f(X_{U_{i+1}}; Z_{U_i})\}$. By Definition 1, this collection is countable, and by (3.9) each element corresponds to a unique point $c \in C$. Hence, $E$ corresponds to a countable union of disjoint regions $(dc, b) \in C \times B$.

Going further from Theorem 1 and constructing the distribution of $Z$ (and hence of $Q$) is far from trivial, because the random variables $W_i$ depend on $X_{U_1}, X_{U_2}, \ldots$. Since we will only be interested in simulating paths of the random walk on parabolas, the above construction is satisfactory.

---

3The smallest open interval centered on point $c$ is $(c - \epsilon, c + \epsilon)$, $\epsilon \to 0$. 

52
The final remark is that the parameter of the random walk process $Z$ is the Poisson parameter $\lambda$, and that the parameter $\rho$ which featured in the pictorial construction of section 1 is seemingly absent. The latter is used as it is more natural from the point of view of numerical integration of the equations of motion. It is straightforward to show that the pictorial construction closely approximates the proceeding mathematical construction. Suppose that the interval $[U_i, U_{i+1}]$ is partitioned into smaller intervals of length $l$. If there is a probability $\rho$ during each interval of the walk making a jump, then the probability that the interval has the length of at least $L$ intervals is $(1 - \rho)^L$, and therefore the probability that the jump will occur before time $j = lL$ since the start of the interval is $P(J_{i+1} < j) = 1 - (1 - \rho)^L$. Let $L \to \infty$ and $\rho \to 0$, while $L\rho$ is kept at a constant value $\lambda j$. In this limit

$$P(J_{i+1} < j) = 1 - \lim_{L \to \infty} \left(1 - \frac{\lambda j}{L}\right)^L = 1 - e^{-\lambda j},$$

which is the same as (3.16). Hence, the transition probability in the pictorial construction of section 1 holds well for small time steps and small $\rho$. As well as its advantage in numerical algorithms, the approximate approach involving $\rho$ will be more lucid than the Poisson parameter in physically motivated discussions of our work.

### 3.2.4 Integration w.r.t a random walk on parabolas

When the equations of motion are finally obtained in Chapter 5, we will need a clear interpretation of the integral $\int_{t_0}^{t} f(Q_s) \, dQ_s$, where $f$ is a continuous function, in order to solve them. In general, special precautions need to be taken when computing integrals with respect to stochastic processes, and it is not usually the case that the results are the same as those of a classical Riemann-Stieltjes integral from ordinary calculus [98]. Such cases arise when the process has paths of infinite variation, as well as when the paths are discontinuous. The paths of the random walk on parabolas process are clearly continuous, so the latter is not an issue. To see that they are of finite variation on compacts,\footnote{This fact would be regarded as ‘trivial’ by most mathematicians. A detailed explanation is given here as we do not expect the reader to be familiar with path variation.} recall that the variation of $Q$ on path $\omega$ on the interval $[t_a, t_b]$ is

$$V_{[t_a, t_b]}(\omega) = \int_{Q_{t_a}}^{Q_{t_b}} |dQ_t(\omega)|.$$  

(3.19)

**Theorem 3.2.** The random walk on parabolas process has paths of finite variation. 

**Proof.** It will be sufficient to prove the claim on the finite interval $[u_i, u_{i+1}] \subseteq [U_i, U_{i+1}]$, since an arbitrary time interval is covered by a finite union of such intervals. On this interval,
\[ Q_t = f(X_t; Z_{U_i}) \]

by path continuity, and hence \( dQ_t = (df(X_t; Z_{U_i})/dX_t) dX_t \). Writing the components of \( Z_{U_i} \) as \((\alpha, \beta)\), (3.8) gives

\[ df(X_t; Z_{U_i})/dX_t = -2\beta(X_t - \alpha)/h^2 \leq 2\beta/h \]

The inequality follows from Definition 2 (\(|X_t - \alpha| \leq h\), or else \( f < 0 \) and \( f \notin F \)). This gives

\[ V_{[U_i, U_{i+1}]}(\omega) = \int_{Q_{U_i}}^{Q_{U_{i+1}}} |dQ_t(\omega)| \leq (2\beta/h) \int_{X_{U_i}}^{X_{U_{i+1}}} |dX_t(\omega)|. \]

Let \( \beta \to \max_{b \in B} b \). Since all \( b \in B \) are finite normal random variables, this quantity will be finite for all paths. The finiteness of the right hand side follows from the assumptions on \( X_t \) given at the beginning of this section.

The crucial consequence of Theorem 3.2 is that we can integrate the equations of motion with the familiar methods of classical calculus. See reference [98] for details.

### 3.3 The Random Walk on Polynomials

As defined above, the random walk on parabolas is adequate for the gas-liquid collision problem. However, its construction renders certain mathematical questions difficult to answer. Features which complicate the random walk on parabolas are that it depends upon another stochastic process \( X \), that the isotropy conditions in (3.14) and (3.15) are very strong, and that the specialised structure of \( C \times B \) leaves the local mode collection awkward to work with. Moreover, the process is overly elaborate for its central mathematical feature: that it follows a parabolic curve up to a random time \( U_1 \), then another parabolic curve up to \( U_2 \), and so on. The purpose of this section is to define the random walk on polynomials, a process which follows a polynomial curve up to a random time \( U_1 \), then another polynomial curve up to a random time \( U_2 \), and so on, but without the same complications as the random walk on parabolas. It is shown that, as the lengths of the time intervals \( U_i - U_{i+1} \) converge to zero, the random walk on polynomials weakly converges to a Wiener process (see the Appendix for a definition of weak convergence and the Wiener process). This task will not help us understand gas-liquid collisions in any more detail, but is interesting enough to include here.

Before delving into the mathematics, it is worth asking why a random walk on polynomials should converge to a Wiener process at all. A representative sample path of a Wiener process is plotted in the Appendix. Recall that a Wiener process serves as a
mathematical model of the trajectory of a particle executing a Brownian motion.\footnote{The model can be cast in terms of Newton’s second law supposing that the Wiener process is the impulse of the force on the Brownian particle, rather than the particle’s trajectory. This gives Ornstein-Uhlenbeck equation \cite{123}. Also see reference \cite{82}. The Ornstein-Uhlenbeck equation is a specific representation of the Langevin equation, which is probably more familiar to readers of a physical background. Note that, as far as probability distributions are concerned, the physical Brownian motion and Wiener process are essentially the same thing; it only takes a rescaling of time by a factor of twice the diffusion coefficient to convert the Wiener process to a Brownian motion.} We can therefore think of it as representing the trajectory of a large, massive body through a medium, subject to successive, rapid interactions with other particles in a medium. The paths of a random walk on polynomials can be interpreted in a similar way. Namely, as the trajectory of a particle subject to successive interactions with other particles, with each interaction resulting in a polynomial displacement on the particle’s position. Thus, as the duration of these interactions become vanishingly small, we might expect the trajectory to resemble one of a particle undergoing Brownian motion. It needs to be emphasised that the particles and motion described here is purely conceptual, and does not have any direct relationship with the physical motion that is described by Newton’s second law. However, owing to their frequent appearance in statistical physics, it is natural (and standard) to think of stochastic processes in terms of a particle interacting with many other particles.

### 3.3.1 Construction of the process

The random walk on polynomials is constructed in much the same way as the random walk on parabolas, although now we consider polynomials that are functions of time, rather than parabolas that are functions of another process $X$. As before, we assume a filtered probability space $(\Omega, \mathcal{F}, \mathcal{F}, P)$. We begin by introducing an increasing sequence of random times $U_1, U_2, \ldots$. In terms of a particle undergoing successive interactions, we can interpret $U_1$ as the time when the first interaction finishes, and $U_2$ as the time when the second interaction finishes, and so on.

**Definition 3.3.** Let $g : \mathbb{R}_+ \to \mathbb{R}$ be a polynomial of $n^{th}$ degree in $t - U_p \in \mathbb{R}_+$, where $p = \max(k : U_k \leq t)$, with real coefficients bounded by the same constant $C$,

$$g(t - U_p) = \sum_{i=1}^{n} a_i(t - U_p)^i. \tag{3.20}$$

The collection of all polynomials with representation (3.20) is the $n$ collection (denoted $G_n$).

For example, if $g(t) = a_1(t - U_p) + a_2(t - U_p)^2$, where $a_1$ and $a_2$ are in $[-C, C]$, then every element of $[-C, C]^2$ corresponds to a possible doublet $(a_1, a_2)$, and $G_n \ (= G_2$ in this case) is the collection of $g(t) = a_1(t - U_p) + a_2(t - U_p)^2$ obtained from every point $[-C, C]^2$. We write $g(t; a_1, \ldots, a_n)$ as shorthand for a polynomial in $G_n$. Letting
we have, in general,

\[ [-C,C]^n = \{ v_n : g(t - U_p; v_n) \in G_n \text{ for all fixed } t - U_p \in \mathbb{R}_+ \} \]  \hspace{1cm} (3.21)

meaning that every element of \([-C,C]^n\) corresponds to a unique polynomial in \(G_n\). The \(n\) collection can be interpreted as a collection of all possible polynomial displacements that a particle may experience as it travels through a medium and undergoes successive interactions with other particles.

**Definition 3.4.** Let \(Z \mapsto \mathbb{R}^n\) be an adapted pure jump process with jump times \(U_0, U_1, \ldots\). The process \(\{g(t - U_p; Z_t)\}\), where \(g \in G_n\) for a given \(n\), is a discontinuous random walk on polynomials process (DRWP process for short).

In terms of the particle interpretation, the random variable \(g(t - U_p; Z_t)\) can be thought of as the displacement of a particle at time \(t\) due to the interaction that it is currently involved in. The displacement is measured relative to the position of the particle at the start of the interaction. The role of the process \(Z\) is to 'pick' which interaction the particle will experience at each point in time, similar to how \(Z\) in the random walk on parabolas picked local modes from the local mode collection to be directly beneath the incoming particle at time \(t\).

So far, the developments have been analogous to the random walk on parabolas described above. So that the DRWP process is mathematically more simple than the random walk on parabolas, we now take a slightly different course of development in defining the process \(Z\). Let \(\{g(t - U_p; Z_t)\}\) be bounded in terms of a finite constant \(M\) with probability 1. This can be thought of as the maximum distance that the particle can be displaced before it is too far away from the other particle for the interaction to continue. As before, we introduce two increasing sets of random times \(T_0, T_1, \ldots\) and \(S_0, S_1, \ldots\), with \(T_0 = 0\) and \(S_0 = 0\) a.s, and let \(U_i = T_i \wedge S_i\). Let

\[
S_1 = \inf (0 < t \leq T_1 : |g(t; Z_t)| > M)
\]

\[
S_2 = \inf (U_1 < t \leq T_2 : |g(t; Z_t)| > M)
\]

and so on. If for a particular \(S_i\) such a time does not exist, set it to \(T_i\). Let \(J_1 = T_1, J_2 = T_2 - U_1, \ldots\) be exponentially distributed iid random variables. That is,

\[
P(J_i < j) = 1 - e^{-\lambda j}
\]

for some constant \(\lambda > 0\) for all \(i\). \(Z_t\) is then defined for \(U_i < t \leq U_{i+1}\) as
\[ Z_t = \begin{cases} 
Z_{U_i} & U_i < t < U_{i+1} \\
W_{i+1} & t = U_{i+1} 
\end{cases} \quad (3.23) \]

where \( W_{i+1} \) is a random variable with uniform probability density on \([-C, C]^n\) (and zero elsewhere else). Note that the distribution \( P(g(t - U_p; Z_t) \in \Lambda) \), where \( \Lambda \) is a Borel set in \( \mathbb{R} \), is well-defined for each of the random variables \( \{g(t - U_p; Z_t)\} \). This can be seen by letting \( \Lambda \) be an open (closed) set in \( \mathbb{R} \), fixing \( t \) and considering \( g \) as a function its coefficients (i.e., \( g = g(v_n; t - U_p) \)). Since polynomials are continuous in their coefficients, there is an open (closed) set \( S \in [-B, B]^n \) such that \( g(t - U_p; Z_t) \in \Lambda \) implies \( Z_t \in S \).

Hence,

\[ P(g(t - U_p; Z_t) \in \Lambda) = P(Z_t \in S) \quad (3.24) \]

In passing, note that, while the paths of the process \( Z \) involve discontinuous jumps, the paths are càdlàg, that is, they are right continuous with left limits. A function \( f(x) \) is right continuous if \( \lim_{x \to x_0, x > x_0} f(x) = f(x_0) \), and has a left limit if \( \lim_{x \to x_0, x < x_0} f(x) \) is well-defined. In the case of the paths of \( Z \), \( \lim_{t \to U_i, t > U_i} Z_t = Z_{U_i} \) and \( \lim_{t \to U_i, t < U_i} Z_t = Z_{U_i-} \).

The word càdlàg is a nonsensical French abbreviation that has become popular in the stochastic analysis literature.

We can now define the random walk on polynomials process.

**Definition 3.5.** Let \( \{g(t; Z_t)\} \) be a discontinuous random walk on polynomials process with \( Z \) constructed as above. The process defined by the random variables

\[ Q_t = Q_{U_p-} + g(t - U_p; Z_t) \quad (3.25) \]

is the random walk on polynomials (RWP process for short).

Figure 3.5 plots a sample path of the RWP process for the case of \( G_n = G_2, \lambda \sim 0.015, C = 5 \) and \( B = 5000 \) (units have been left unspecified). The path was simulated in \( R 2.9.2 \) [118] and code is available upon request. The paths RWP process \( Q \) can be interpreted as the trajectories of the particle. Each of the periods \( [U_i, U_{i+1}) \) corresponds to an interval during which the particle interacts with one other particle from the surrounding medium and experiences a polynomial displacement on its path. These displacements are bounded by a constant \( M \), beyond which the particle is pushed away from the source to such an extent that the interaction is over. Thus, the interaction ends when either a different external particle goes on to interact with the particle (i.e., \( U_{i+1} = T_{i+1} \), an event which occurs after an exponentially distributed waiting time), or when the displacement is too large to continue occurring \( (U_{i+1} = S_{i+1}) \). While the bound \( M \) is mathematically convenient, we are going to use it in such a way that we can draw insights into the trajectories of a particle subject to interactions of extremely short duration. \( C \) poses no limitation on our interpretation, as it can be as large (but finite) as desired.
3.3.2 Convergence to a Wiener Process

Let $K_i = U_i - U_{i-1}$. $K_1, K_2, \ldots$ are iid random variables. $K_i$ is interpreted as the duration of the $i^{th}$ interaction. We are interested in the limit in which the random variables $J_1, J_2, \ldots \to 0$ a.s. This might be interpreted as an extreme situation in which the particles of the medium travel with such great velocities that the test particle-particle interactions are interrupted almost as soon as they begin. Since $K_i < J_i$ for all $i$, this limit implies $K_1, K_2, \ldots \to 0$. Since $J_1, J_2, \ldots (K_1, K_2, \ldots)$ are iid random variables, we can consider an arbitrary random variable $J$ from this sequence and use $E(J) (E(K))$ to denote the joint convergence $E(J_1), E(J_2), \ldots \to 0 \ (E(K_1), E(K_2), \ldots \to 0)$. Indeed, there is no great difficulty imposed by working with the weaker limit $E(J) \to 0$ rather than the limit $J_1, J_2, \ldots \to 0$, and the result obtained can easily be extended to the latter case.

The goal of this section is to show that as $E(J) \to 0$, $Q \Rightarrow W$, where $\Rightarrow$ denotes weak convergence. In order to achieve this convergence, we need to set $M = \sqrt{3E(K)}$. Adjusting a mathematical model so that it has sensible limiting behaviour is known as renormalisation, and is in fact very common. A famous example is a classical random walk, in which a particle jumps either left or right along the $x$ axis by a distance $\delta x$ with equal probability after a fixed length of time $\delta t$. A classical random walk only converges to a Wiener process in the limit $\delta t \to 0$ when $\delta x$ is set to $\sqrt{\delta t}$ [106]. While renormalisation may appear somewhat arbitrary at first, it usually leads to interesting insights into the limiting behaviour of the system.

**Theorem 3.3.** Let $\{Q^k\}, k = 1, 2, \ldots$ be a sequence of RWP processes with $E(J^k) \to 0$. If $M_k = \sqrt{3E(K^k)}$, $Q^k \Rightarrow W$.

**Proof.** By $E(J^k) \to 0$ we mean $\lambda_k \to \infty$, since $E(J^k) = 1/\lambda_k$. By equation (3.22),
\[ P(J^k > \epsilon) = e^{-\lambda_k \epsilon} \to 0 \text{ for all } \epsilon > 0, \] and so \( E(J^k) \to 0 \) implies \( J^k \to 0 \) a.s. Since \( J^k > K^k \) a.s., we also have that \( K^k \to 0 \).

Choose \( 0 = t_0 < t_1 < \cdots < t_v < \infty \) such that for each \( j = 1, \ldots, v \) we can write

\[
Q^k_{t_j} - Q^k_{t_{j-1}} = (Q^k_{t_j} - Q^k_{U_p}) + \sum_{i=m+1}^p (Q^k_{t_j} - Q^k_{U_{i-1}}) + (Q^k_{U_m} - Q^k_{t_{j-1}})
\]

(3.26)

where \( p = \max(h : U_h \leq t_j) \), \( m = \max(h : U_h \geq t_{j-1}) \), and the \( U_i \) are understood as functions of \( k \). The random variables \( \{Q^k_{t_j} - Q^k_{t_{j-1}}\} \) are independent. Consider the \( j \)th member of this collection. By the a.s. continuous paths of the process \( Q^k \), we have \( Q^k_{U_p} = Q^k_{U_{p-1}} \), and so by (3.25) in Definition 3.5 and the càdlàg paths of \( Z^k \),

\[
P \left( \left| Q^k_{t_j} - Q^k_{U_p} \right| > \epsilon \right) = P \left( \left| g(t_j - U_p; Z^k_{U_p}) \right| > \epsilon \right)
\]

for all \( \epsilon > 0 \). Since \( t_j - U_p < U_{p+1} - U_p = K^k_{p+1} \to 0 \) a.s., this probability goes to zero for all \( \epsilon > 0 \). To obtain the same result for the third term in (3.26), note that \( Q^k_{U_m} = Q^k_{U_{m-1}} + g(U_m - U_{m-1}; Z^k_{U_{m-1}}) \) and \( Q^k_{t_j} = Q^k_{U_{m-1}} + g(t_{j-1} - U_{m-1}; Z^k_{U_{m-1}}) \) by the càdlàg of \( Z^k \), and so

\[
P \left( \left| Q^k_{t_j} - Q^k_{t_{j-1}} \right| \right) = P \left( \left| g(U_m - U_{m-1}; Z^k_{U_{m-1}}) - g(t_{j-1} - U_{m-1}; Z^k_{U_{m-1}}) \right| \right)
\]

which also goes to zero in the limit. We have therefore established that

\[
Q^k_{t_j} - Q^k_{t_{j-1}} \to \sum_{i=m+1}^p (Q^k_{U_i} - Q^k_{U_{i-1}}) \text{ a.s.} \quad (3.27)
\]

We now obtain the distribution of the iid random variables \( \{Q^k_{U_i} - Q^k_{U_{i-1}}\} \) and apply the central limit theorem to (3.27). Since \( Q^k_{U_{i-1}} = Q^k_{U_{i-1}} \) we have that

\[
P \left( Q^k_{U_i} - Q^k_{U_{i-1}} \in (q_1, q_2) \right) = P \left( g(U_i - U_{i-1}; Z^k_{U_{i-1}}) \in (q_1, q_2) \right)
\]

(3.28)

By (3.24), there is a Borel set \( \Lambda_{q_1 q_2} \) of \([-B, B]^n\) such that

\[
P \left( g(U_i - U_{i-1}; Z^k_{U_{i-1}}) \in (q_1, q_2) \right) = P \left( Z^k_{U_{i-1}} \in \Lambda_{q_1 q_2} \right)
\]

and so, since \( Z^k_{U_{i-1}} \) is a uniform random variable on \([-B, B]^n\),

\[
P \left( Q^k_{U_i} - Q^k_{U_{i-1}} \in (q_1, q_2) \right) = \frac{D(\Lambda_{q_1 q_2})}{D([-B, B]^n)}
\]

(3.29)

where
\[
D(\Lambda_{q_1 q_2}) = \int_{\Lambda_{q_1 q_2}} dv_n
\]

\[
D([-B, B]^n) = \int_{[-B, B]^n} dv_n
\]

Consider all polynomials which fall within \((q_1, q_2)\) at time \(U_i\) and construct a subset of these polynomials by fixing various values of the coefficients \(a_2, \ldots, a_n\) and varying the value of \(a_1\). Let \(a_2, \ldots, a_n\) be fixed at the values \(\alpha_1, \ldots, \alpha_n\). In terms of events, it can be seen that

\[
\left\{ g(U_i - U_{i-1}; Z_{U_{i-1}}^k) \right\} \supseteq \left\{ q_1 < a_1(U_i - U_{i-1}) + \sum_{j=2}^{n} \alpha_j(U_i - U_{i-1})^j < q_2 \right\}
\]

\[
= \left\{ \frac{q_1 - \sum_{j=2}^{n} \alpha_j(U_i - U_{i-1})^j}{U_i - U_{i-1}} < a_1 < \frac{q_2 - \sum_{j=2}^{n} \alpha_j(U_i - U_{i-1})^j}{U_i - U_{i-1}} \right\}
\]

Hence, by varying the possible values of \(a_2, \ldots, a_n\), it follows that all points between the surfaces

\[
a_{1q_1} = \frac{1}{U_i - U_{i-1}} \left( q_1 - \sum_{j=2}^{n} a_j(U_i - U_{i-1})^j \right)
\]

\[
a_{1q_2} = \frac{1}{U_i - U_{i-1}} \left( q_2 - \sum_{j=2}^{n} a_j(U_i - U_{i-1})^j \right)
\]

(3.30)

correspond to a polynomial such that \(g(U_i - U_{i-1}; Z_{U_{i-1}}^k) \in (q_1, q_2)\). It can be verified that fixing \(a_1, \ldots, a_{i-1}, a_{i+1}, \ldots, a_n\) and varying \(a_i\) also leads to the same surfaces as in (3.30). Thus, every polynomial falling within \((q_1, q_2)\) at time \(U_i\) corresponds to a point in the volume between the surfaces in (3.30). Let \(v_{n1} = (a_2, \ldots, a_n)\). We therefore have

\[
D(\Lambda_{q_1 q_2}) = \int_{[-B, B]^{n-1}} (a_{1q_2}(v_{n1}) - a_{1q_1}(v_{n1})) dv_{n1}
\]

\[
= (q_2 - q_1) \frac{D([-B, B]^{n-1})}{U_i - U_{i-1}}
\]

(3.31)

(3.29) and (3.32) then give

\[
P\left( Q_{U_i}^k - Q_{U_{i-1}}^k \right) = \frac{q_2 - q_1}{U_i - U_{i-1}} \frac{D([-B, B]^{n-1})}{D([-B, B]^n)}
\]

Since \(D([-B, B]^{n-1}) / ((U_i - U_{i-1}) D([-B, B]^n))\) is independent of \(q_1, q_2\) and \(q_2 - q_1\),
the distribution of $Q^k_{U_{i}} - Q^k_{U_{i-1}}$ depends only linearly on $q_2 - q_1$. Hence $Q^k_{U_{i}} - Q^k_{U_{i-1}}$ is uniformly distributed on $[-M_k, M_k]$ and

$$E(Q^k_{U_{i}} - Q^k_{U_{i-1}}) = 0$$

$$V(Q^k_{U_{i}} - Q^k_{U_{i-1}}) = M_k^2/3$$  \hspace{1cm} (3.32)

It is clear that $k \to \infty$ implies $p - m \to \infty$. It then follows from the central limit theorem and (3.27) that

$$Q^k_{t_j} - Q^k_{t_{j-1}} \Rightarrow N(0, (p - m)M_k^2/3)$$

Substituting the formula $M_k = \sqrt{3E(K^k)}$ gives $(p - m)E(K^k)$ as the variance of the limiting random variable. Since $E(pK^k) = E(K^k_1 + \cdots + K^k_p) = E(U_p)$, $E(t_j - K^k_{p+1}) < E(U_p) < E(t_j + K^k_{p+1})$ and $E(K^k_{p+1}) \to t_j$, $E(pK^k) \to t_j$. Similar arguments can be used to show that $E(mK^k) \to t_{j-1}$. We therefore have $Q^k_{t_j} - Q^k_{t_{j-1}} \Rightarrow N(0, t_j - t_{j-1})$. Recalling that $W_{t_j} - W_{t_{j-1}} N(0, t_j - t_{j-1})$ shows that $Q^k_{t_j} - Q^k_{t_{j-1}} \Rightarrow W_{t_j} - W_{t_{j-1}}$. Since its components are independent, we have obtained weak convergence of the vector,

$$(Q^k_{t_1}, Q^k_{t_2} - Q^k_{t_1}, \ldots, Q^k_{t_v} - Q^k_{t_{v-1}}) \Rightarrow (W_{t_1}, W_{t_2} - W_{t_1}, \ldots, W_{t_v} - W_{t_{v-1}}).$$

By the continuous mapping theorem (see page 273 of reference [26]), this implies convergence of finite dimensional distributions,

$$(Q^k_{t_1}, \ldots, Q^k_{t_v}) \Rightarrow (W_{t_1}, \ldots, W_{t_v}).$$

For convergence of finite dimensional distributions to imply $Q^k \Rightarrow W$, we need to show that the probability measures of $Q^k$ are tight.\footnote{An anonymous reviewer of reference [82] is thanked for pointing out the need to prove tightness.} We therefore need numbers $N_\epsilon$ and $\delta > 0$ such that, for every $t_i - t_{i-1} < \delta$

$$P\left(\left|Q^k_{t_i} - Q^k_{t_{i-1}}\right| \leq N_\epsilon\right) \geq 1 - \epsilon$$  \hspace{1cm} (3.33)

for every $\epsilon > 0$ and all $k$. Let

$$N_\epsilon = M_1 = \sqrt{3E(K^1)}$$  \hspace{1cm} (3.34)

for every $\epsilon$. Since $M_k$ and $K^k \to 0$, the process $Q^1$ is the only one which may exceed the bound $M_1$ during any of the periods $K^1_1, K^2_2, \ldots$ with nonzero probability. The shortest time in which $Q^1$ may exceed this bound is $T$, where $T$ is the smallest positive solution of $M_1 = Bt + Bt^2 + \cdots + Bt^n$. We therefore take

61
\[
\delta = \lim_{m \to \infty} \frac{T}{2^m}
\] (3.35)

The inequality in (3.33) holds for all \(\epsilon > 0\) with \(\delta\) given by (3.35) and \(N_\epsilon\) given by (3.34).

To interpret the formula

\[
M_k = \sqrt{3E(K^k)}
\] (3.36)

recall our interpretation of \(Q^k\) as the trajectory of a particle which is subject to successive interactions with external particles, with each interaction resulting in a polynomial displacement on the particle’s trajectory. \(M_k\) is the maximum size of a displacement, beyond which the interaction cannot be sustained because the particles move too far apart. While \(M_k\) decreases as \(k \to \infty\) (and the duration of the interactions go to zero), equation (3.36) shows that the rate of decrease is slower than the rate of decrease of \(E(K^k)\). Thus, in approaching the limit, the size of the displacements never vanish and hence maintain a definitive size. To understand what happens to the shape of the interactions, let \(a_m\) be the \(m^{th}\) coefficient of the polynomial in (3.20) and consider the range of possible values of \(a_m\) which cause the polynomial to exit the interval \((-M, M)\) during an interval of duration \(E(K)\). To compute this range, subtract the second equation in (3.30) from the first and set \(q_1 = -M\), \(q_2 = M\), and \(U_i - U_{i-1} = E(K)\). Substituting (3.36) into the result gives

\[
a_m M - a_m (-M) = \frac{2M}{E^m(K)} = \frac{2\sqrt{3}}{E^{m-1/2}(K)} \to \infty
\]

since \(m \geq 1\). The range of values therefore becomes very large (but still bound by \(2B\)). The renormalisation used to secure the result therefore leads to a limiting picture of a particle undergoing successive, rapid interactions with other particles, with each interaction resulting in a \textit{sharp} deviation in the particle’s trajectory from its starting position.

Qualitatively, these limiting trajectories are what we might expect of a physical particle undergoing Brownian motion, and so the renormalisation appears to be sensible. In fact, we can show that the renormalisation is sensible from a mechanical point of view by supposing that the random walk on polynomials process corresponds to the impulse of the force on the particle, rather than its trajectory. Its derivative is then equal to the force on the particle, and we are interested in the convergence of the velocity of the particle to the solution of a Langevin equation. We omit the details here, as the arguments require some understanding of the stability of stochastic differential equations; see reference [82] for details. In this case, it turns out that the renormalisation (3.36) implies that the mass of the test particle grows relative to the mass of the other particles of the medium in approaching the limit. This is consistent with the assumption that a particle undergoing
Brownian motion is of a relatively large mass, and it is reassuring to see a large mass appear naturally in the convergence of the random walk on polynomials process.
Chapter 4

Impulsive Energy Loss Constraints

Chapters 2 and 3 have provided us with tools for developing closed equations of motion for an atom passing over a liquid surface. We began by investigating the random local mode model, and found it to be a promising coarse grained model for a molecular-scale liquid surface. Then, we took the random local mode model and considered what would be seen looking straight down at the surface from the viewpoint of the incoming atom. This resulted in a stochastic process called the random walk on parabolas (RWP process). While it may not be obvious at the moment, the RWP process will play a crucial role in closing the equations of motion for the incoming atom.

Despite its importance, the RWP process is unable to close the equations of motion on its own. Indeed, the RWP process will only be helpful for describing the forces acting on the atom as it approaches and scatters away from the surface. It does not have anything useful to say about the *impulsive forces* which remove energy from the atom when it collides with the surface. To state the situation in mechanical terms, our tool kit lacks means of placing *impulsive constraints* on the atom’s motion. As described in Chapter 1, experimental data shows that atoms incident upon a liquid surface undergo extensive energy loss upon collision. No theory can ignore such an important result, so it must be accounted for. Moreover, this needs to be done in a way which is consistent with the picture of a gas-phase atom passing over a surface of superimposed local mode displacements.

We have therefore reached a formidable obstacle. While the literature provides plenty of models of collisional energy exchange, all relate in some way to the two-body model presented in Chapter 1, and hence to the molecular structure of the liquid surface. Moreover, the success of these theories in accounting for experimental data suggests that collisional energy loss has a sensitive dependence on the molecular structure of the liquid surface, which is the essential content of ‘the tenet of gas-liquid collisions’ introduced in Chapter 1. How can we use a structurally rich model of collisional energy loss to put an impulsive constraint on the motion of an atom passing over a coarse grained model liquid surface?

This is not the kind of question that we want to answer. Instead of compromising our coarse grained picture with molecular details, we attempt the counter-intuitive task of
Figure 4.1: An atom (large, dark circle) colliding with a liquid surface. The surface degrees of freedom (small circles) retract, approximately producing a parabolic local mode at the maximum of the retraction. The diagram shows a two dimensional cross section through the surface. The parabola is not necessarily to scale, as unknown constants prevent the parameters $\alpha$ and $\beta$ from being computed (see text). The distance $r$ runs from the center of the parabola outward along the line marked by $b$.

creating a new theory of energy loss which does not have any dependence on the molecular structure of the liquid surface. Despite what the tenet of gas-liquid collisions would lead us to believe, such a treatment is possible and turns out to be successful for the case of a small, fast rare (noble) gas atom, such as neon. It is at this point that we have to significantly narrow the range of systems that the theory can investigate, although the results will be fruitful nonetheless. The first section of this chapter presents an energy loss constraint which is appropriate for viscous molecular liquids such as squalane. In the second section, these concepts are extended to the case of a non-viscous, metallic liquid surface.

### 4.1 A Statistical Treatment of Energy Loss

Molecular details inevitably enter into energy loss theories when the mechanics of energy transfer into the surface are explicitly considered. This is exemplified by the two-body collision theories described in Chapter 1, in which energy loss is deduced from the mechanics of energy exchange between two colliding bodies (see equations (1.1) to (1.5)). An alternative approach might be to infer the energy loss of the atom from the eventual outcome of the surface’s response to collisional energy dispersal into the liquid. Thus, instead of starting at the collision event, we begin at the aftermath of the collision and work backwards to the collision event itself.

The starting point for this theory is an assumption on the outcome of collisional energy dispersion into the liquid surface. Our assumption is summarised in Figure 4.1, according to which it is supposed that the impact of the collision causes the surface to retract downward, approximately generating the shape of a parabola at the maximum of the retraction, before recovering to its unperturbed position. The parabola is more than a convenient coarse grained description of the collision outcome, as it can also be regarded as an approximation to a negative-going local mode displacement, excited by the
colliding atom. This does not necessarily imply that we are working within the continuum regime; the role of the parabola is simply to approximate the excess surface area due to the retraction relative to the unperturbed surface. Intuitively, the parabola assumption should hold best for when the incoming atom strikes perpendicular to the surface, although the results of this theory perform well against experimental data for a variety of incidence angles and are not very sensitive to the shape of the depression in the surface. There are two other key assumptions.

1. The collision period of the atom is much less than the retraction time of the surface degrees of freedom.

2. The amplitude of the parabola is small enough not to have a significant effect on the gas-liquid interaction potential.

The first assumption is analogous to the ‘sudden’ collision assumption used to study gas-gas collisions [56]. A few lesser assumptions will be introduced as required.

### 4.1.1 Derivation of a collisional energy loss distribution

Consider parabolic displacements of the form $$\xi = \alpha \left( \frac{r^2}{b^2} - 1 \right)$$, where \( r \) is the horizontal distance measured outwards from the center of the parabola, \( b \) the half width of the parabola and \( \alpha \) its amplitude (Figure 4.1). The parameters in this parabola have been given different symbols from their counterparts in previous chapters (such as in equation (3.1)) to distinguish them from the local modes that appear in the random local mode model. By assumptions 1 and 2, the energy lost to the surface by the colliding atom is equal to the excess potential energy of the surface at the maximum of the retraction (the turning point) relative to the unperturbed surface. In turn, this will equal the work done by the surface degrees of freedom against an opposing force during the retraction. Such a force will arise when the covalent bonds within the surface molecules and the van der Waals interactions between molecules are disturbed and deformed during the dispersal of energy from the collision point. Since there is little to be said about such a force at this level of inquiry, it is treated as a constant per unit area. By analogy with the macroscopic surface tension, the constant is denoted by \( \gamma \), but its value depends on the scale of the surface deformation [71]. The situation is similar to the appearance of \( \gamma \) in the random local mode model (equation (3.4)), although we allow for the possibility that the constants are different. When the retraction has reached its maximum, the excess area of the resulting parabola will be (cf. equation (3.2))

$$A = 2\pi \int_{0}^{b} r \left( \sqrt{1 + \left(\frac{d\xi}{dr}\right)^2} - 1 \right) dr.$$  

Since we are supposing that the parabola corresponds to a local mode displacement, its amplitude will be small relative to its width, and we can employ the approximation
\[ \sqrt{1 + \left(\frac{d\xi}{dr}\right)^2} - 1 \approx \left(\frac{d\xi}{dr}\right)^2/2, \] which gives \( A \approx \pi \alpha^2 = \text{constant} \times b^2. \) The work performed is \( \int_0^A \gamma da = \gamma A, \) which gives

\[ e(b) = \text{constant} \times b^2 \gamma \quad (4.1) \]

as the energy lost by the colliding atom in producing a parabola with half width \( b. \) Since the atom may lose anywhere from zero to all of its incident kinetic energy \( e_k, \) \( b \) will be distributed from \( b = 0 \) to \( b = b_{\max}, \) where \( b_{\max} \) is the half width of the parabola with energy \( e_k. \)

We define the random variable \( B \) as the half width of the parabola generated by the colliding atom. The task is now to find a probability density function for \( B, f(b), \) which will be used to find a probability density \( g(e) \) for the random variable \( E, \) the energy lost by the atom upon collision. The problem amounts to counting microscopic states, and the standard way to do this would be to create a physical model for the states. However, as well as introducing more assumptions, this approach would go against our philosophy of avoiding molecular detail. As counter-intuitive as it may seem, a detailed physical model is not necessary. Instead, it is possible to proceed in a general way with the kind of logic that appears in mathematical existence theorems.

**Step 1. Relate the probability density function of \( B \) to the number of corresponding microstates.** Consider all parabolas with a half width between 0 and \( b. \) For each of the parabolas in this collection, there is a collection of microscopic configurations of the surface degrees of freedom which correspond to that parabola. Each possible microscopic configuration is called a microstate. Let the collection of all microstates corresponding to a parabola with half width between 0 and \( b \) be denoted by \( M_b. \) These microstates include all degrees of freedom contained within the volume under the parabola down to an arbitrarily large but finite depth of the liquid. The probability density function of \( B \) is therefore equal to the probability that the collision will produce a microstate in \( M_b. \)

The collision model in Fig. 4.1 starts out at a particular microstate and does not give us any information on how that microstate resulted from the initial Boltzmann distribution of microstates of the equilibrium surface. The lack of such information requires to assign every microstate of every parabola with energy between 0 and \( e_k \) equal a priori probabilities of occurring. The probability that \( B \) is less than or equal to \( b \) is proportional to the number of microstates in \( M_b, N_b, \) and the probability density function of \( B \) is

\[ f(b) = \text{constant} \times \frac{dN_b}{db}. \quad (4.2) \]

While the assumption of equal a priori probabilities is always used when we have no information on the state of a system, its appearance in this theory is bound to cause some discomfort amongst certain readers. If the reader is happier with Boltzmann-type weightings, then note that the microstates are probably all within a few \( k_B T \) of each other,
leaving the weightings roughly uniform.\(^1\) This is plausible, because the maximum amount of energy that could be supplied to the surface, \(e_k\), would be much smaller than the total thermal energy of all surface molecules involved in generating the retraction (only about 8 surface molecules with energies close to \(3k_B T/2\) are needed for a room temperature surface to have comparable energy to a 30 kJ mol\(^{-1}\) neon atom, for instance).

**Step 2. Partition \(M_b\) into subsets.** We shall obtain a general expression for the function \(N_b\) by bounding it from above and below and inferring its behaviour at arbitrarily large \(b\). In order to do this, we partition the set \(M_b\) into \(c\pi b^3\) subsets, where \(c\) is a constant. To understand the physical meaning of such a partition, consider dividing the volume beneath every parabola with half width between 0 and \(b\) into smaller tubular volumes, extending down to the depth of the volume. If these tubular volumes are sufficiently narrow, then the number of volumes for an individual parabola will be very nearly equal to the circular basal area of the parabola times a proportionality constant. Hence, the total number of volumes for every parabola with half width between 0 and \(b\) is close to \(c\pi b^3\). Let these volumes be indexed from \(i = 1\) to \(c\pi b^3\). We can therefore partition the set \(M_b\) into \(c\pi b^3\) subsets by assigning each of the microstates in \(M_b\) to a particular tubular volume according to some classification rule. A simple rule would associate a microstate with the volume within which the largest number of its degrees of freedom fall. If more than one such volume existed for a microstate, then the rule would be modified to assign the microstate to the volume with the lowest index. This construction can be taken as ‘proof of existence’ for a partition of \(M_b\). In fact, the mere existence of such a partition is all that is needed to continue; nothing needs to be established on the outcome of the partition.

**Step 3. Use the partition to bound the function \(N_b\).** Let \(M^i_b\) be the set of microstates of \(M_b\) assigned to volume \(i\) by the classification rule. The \(M^i_b\) constitute the partition of \(M_b\), and therefore

\[
N_b = \sum_{i=1}^{c\pi b^3} |M^i_b| \leq c\pi b^3 \max_i |M^i_b| \leq c\pi b^3 \max_{i,b} |M^i_b| = \text{constant} \times b^3,
\]

where \(\max_i |M^i_b|\) is the largest number of microstates assigned to a particular tubular volume from parabolas between 0 and \(b\), and \(\max_{i,b} |M^i_b|\) is the largest number assigned to a particular tubular volume from parabolas between 0 and \(b_{max}\). The reason for the second inequality is that \(\max_i |M^i_b|\) will depend on \(b\). To obtain a lower bound, simply adjust the widths and depths of the volumes until there are more microstates than volumes. This action does not invalidate the above upper bound. Hence we can write

\[
N_b \geq c\pi b^3 = \text{constant} \times b^3.
\]

Thus, \(N_b\) is bounded above and below by a quantity proportional to \(b^3\).

---

\(^1\)This point was raised by an anonymous reviewer of reference [85].
Before moving on, it is helpful to make some comments on the continuity of these bounds and of the function $N_b$. Since we have approximated the number of tubular volumes with the quantity $c\pi b^3$, these bounds will change continuously with $b$. This amounts to supposing that the discontinuous jumps in the number of tubular volumes with increasing $b$ is so small that, over the range of $b$, this number essentially grows as a continuous function. Strictly speaking, the function $N_b$ is an increasing step function of $b$. However, as the following arguments show, the continuity of the upper and lower bounds implies that the function $N_b$ must itself be treated as a continuous function.

**Step 4. Deduce an expression for $N_b$ by examining its behaviour at large $b$.** Since the parameter $b_{\text{max}}$ may take arbitrarily large (but finite) values, a given functional form for $N_b$ must hold for all $b$ up to an arbitrarily large $b$. Observe that $N_b$ is an increasing function. Unless this function could be written in the form $N_b = \text{constant} \times b^3$, there would be a $b$ beyond which $N_b$ would exceed the upper bound ($N_b$ would grow too fast) or would be exceeded by the lower bound ($N_b$ would not grow fast enough). As pre-empted above, $N_b$ turns out to be a continuous function with the approximations we have made so far. Substituting this result into (4.2) gives

$$f(b) = \text{constant} \times b^2.$$  

(4.3)

Having established a functional form for $f(b)$, we can obtain an expression for $g(e)$ from some simple calculus.

Let the constants in (4.1) and (4.2) be denoted by $c_1$ and $c_2$, respectively. By rearranging (4.1) to give $b(e) = \sqrt{e/\gamma c_2}$ and using (4.2), the probability density function for $E$ can be computed by the integral transform $g(e) = f(b(e)) |db(e)/de|$ [67]. This gives $g(e) = C\sqrt{e/\gamma^3}$ where $C = c_1/2c_2^{3/2}$. Since $g(e)$ must be normalised, $1 = C \int_0^{e_k} \sqrt{e/\gamma^3}$ and hence $C = 3(\gamma/e_k)^{3/2}/2$. We finally obtain the expression

$$g(e) = \frac{3}{2\sqrt{e_k^3}} \sqrt{e/\gamma^3}$$

(4.4)

for the probability density function for the amount of energy lost by the atom upon colliding with the liquid surface.

### 4.1.2 Comparison with experimental data

Before using (4.4) as an impulsive energy loss constraint for a gas-phase atom passing over a liquid surface, we test its predictions against experimental data. The shapes of experimental energy loss distributions are reasonably sensitive to the exit angle of the scattered species [46], which we have neglected, and there are no published distributions measured over a range of exit angles. We therefore consider average energy losses and trapping probabilities of the colliding atom instead. It is useful to study the latter first. Suppose that the particle becomes ‘trapped’ if the collision removes so much energy that
Figure 4.2: A. Predicted trapping probabilities (curve) from (4.4) and experimental trapping-desorption measurements (points) for a neon atom striking a glycerol surface, as a function of incident kinetic energy. B. \((1 - P_{\text{trap}})^{2/3}\) plotted against \(1/e_k\) using experimental data for neon striking a squalane surface. The line is a linear least-squares fit to all points, the slope of which gives an estimate of the neon-squalane well depth (3.86 kJ mol\(^{-1}\) in this case). Experimental data from reference [109].

the particle cannot escape the potential well at the liquid surface. If the well has depth \(\epsilon\), this requires an energy loss of at least \(e_k - \epsilon\), the probability of which is \(\int_{e_k-\epsilon}^{e_k} g(e) \, de\). Using (4.4) gives

\[
P_{\text{trap}} = 1 - \left(1 - \frac{\epsilon}{e_k}\right)^{3/2} \tag{4.5}
\]

as the trapping probability of the particle. Since absolute trapping probabilities have not yet been reported, we compare (4.5) to trapping-desorption fractions measured in molecular beam experiments. This will work if the probability that a trapped atom will be taken up by the bulk liquid is significantly smaller than the probability of desorption, which is an excellent approximation for neon striking a hydrocarbon surface [74]. Moreover, neon is a suitable candidate for the ‘small and fast’ criterion of assumptions 1 and 2, at least compared to heavier atoms such as argon and xenon. The left graph in Figure 4.2 compares equation (4.5) with neon trapping-desorption fractions measured from glycerol by Saecker and Nathanson [109]. The well depth is taken as the estimate (2.9 kJ mol\(^{-1}\)) given by Benjamin et al [7]. Although (4.5) overestimates the trapping-desorption fraction by a small amount, the comparison is reasonably good. In passing, note that the data in Figure 4.2 is actually the trapping fraction measured at a fixed exit angle of the particles (45\(^{\circ}\) to the surface normal), and will vary with exit angle due to variation in the trapping desorption fraction. The agreement in Figure 4.2 is likely due to 45\(^{\circ}\) being close to the peak of the direct inelastic scattering distribution for neon striking a squalane surface [46], where the dependence of the trapping-desorption fraction on incidence energy should be
The greatest and possibly most representative of the overall trapping-desorption fraction. It would be useful to investigate this idea in future experimental and theoretical work.

The result (4.5) can be rearranged to give

\[(1 - P_{\text{trap}})^{2/3} = 1 - \frac{\epsilon}{\epsilon_k}\]  

(4.6)

showing that, if the theory works well for a particular system, a plot of \((1 - P_{\text{trap}})\) against \(1/\epsilon_k\) using experimental data should yield a straight line with an intercept of 1 and slope \(-\epsilon\). The bottom graph in Figure 4.2 shows such a plot using trapping-desorption fraction measurements for neon colliding with squalane [109], a system for which the literature gives no specific estimate of \(\epsilon\). Least-squares regression on this data gives an intercept of 0.96 and \(\epsilon = 3.86\ \text{kJ mol}^{-1}\) (standard error = 0.07). The fit is very good \((R^2 = 0.999)\), although the point lying on the far-right appears to have too much influence on the regression. Neglecting this point and using only the four points on the left yields an intercept of 0.94, \(\epsilon = 3.23\ \text{kJ mol}^{-1}\) (standard error = 0.38), and a slightly poorer fit \((R^2 = 0.97)\). The large difference in estimated well depth demonstrates the need for a larger number of points across the range of measured \(1/\epsilon_k\) when using such a plot. Neglecting the far-right point causes a larger deviation of the intercept from unity, so we prefer the estimate \(\epsilon = 3.86\ \text{kJ mol}^{-1}\) for neon interacting with squalane. It is important to note that plotting (4.5) with these two values of \(\epsilon\) gives two quite different fits to the data; this demonstrates the sensitivity of the curve to \(\epsilon\) and therefore the need for more data to get a better estimate of this parameter.

To estimate an average energy loss from (4.4), note that the inelastically scattered flux (IS channel) will exclude the portion of atoms trapped at the liquid surface. Thus, the average measured energy loss is \(\langle E \rangle = \int_0^{\epsilon_k} \epsilon \chi(\epsilon) \text{d}\epsilon\), which gives

\[
\langle E \rangle_{\text{IS}} = 3 \frac{5}{5} \left(1 - \frac{\epsilon}{\epsilon_k}\right)^{5/2}
\]  

(4.7)

as the average fractional energy loss measured from the inelastically scattered flux. The top and bottom graphs in Figure 4.3 compare (4.7) to fractional energy losses of neon following collision with glycerol and squalane surfaces, respectively, as measured by Saecker and Nathanson [109] with a beam incident and detected at 45° to the surface normal and with the liquids at 290 K. These calculations used the neon-glycerol well depth estimated by Benjamin et al [7] and the neon-squalane well depth estimated above. While the agreement is not perfect, (4.7) follows the essential experimental trend for both systems, namely a fractional energy loss that increases slowly with incident energy for fast \((> 20\ \text{kJ mol}^{-1})\) atoms. At high collision energies \((\epsilon_k \gg \epsilon)\), (4.7) reduces to

\[
\frac{\langle E \rangle}{\epsilon_k} = \frac{3}{5}
\]  

(4.8)

Thus, the prediction is that fast, small incoming gas-phase atoms colliding with a
liquid surface and detected in the IS channel will have lost an average of 60% of their incident energy. Indeed, for 75 kJ mol\(^{-1}\) neon atoms incident at 45° and detected at 45° to the surface normal, Saecker and Nathanson report average fractional energy loses of 63% and 56% upon collision with 290 K squalane and glycerol surfaces, respectively [109]. Using the same incidence and detection angles, Behr et al. measure an average fractional energy loss of 57% for 85 kJ mol\(^{-1}\) Ne atoms striking a sulphuric acid surface (averaged over the liquid temperature range of 213 K to 243 K) [6]. Other average energy losses in the neighbourhood of 60% include 69% and 50%, respectively, for 118 kJ mol\(^{-1}\) chlorine atoms and 47 kJ mol\(^{-1}\) oxygen atoms striking a room temperature squalane surface at 60° to the surface normal, as measured by Garton et al. (averaged over all exit angles) [33]. The result (4.8) can also be obtained directly by averaging (4.4) over all energies (from 0 to \(e_k\)), implying that the average energy loss of a small, fast gas-phase particle upon colliding with a liquid surface should be near 60%. This prediction is distinct from (4.8), which only pertains to atoms detected in the IS channel.

This model has not considered variations in the incidence angle of the incoming atom, or of the liquid temperature. Both energy transfer and the trapping probability of a small atom are known to increase as the incidence angle decreases, although the increase is not dramatic. For example, on going from a 65° incidence angle to a 45° incidence angle, experimental energy loss curves for neon striking squalane only increase by about 7%, with the increase appearing to become smaller as the incidence angle decreases further [46]. The performance of (4.4) to (4.8) against experimental data suggests that a parabolic local mode picture is a good coarse grained description of the dominant collision outcome over a range of incidence angles. However, the results obtained here are quite insensitive to the shape of the retraction in Figure 4.1, suggesting that the parabolic assumption is
reasonably robust to minor non-ideal features of the real system. For instance, choosing a triangular (conical)-shaped retraction $\alpha (|r|/b - 1)$ in place of the parabola $\alpha (r^2/b^2 - 1)$ also leads to (4.4). In fact, the same results can be obtained for any retractions of the form $\alpha (c_1(|r|/b)^n + c_2(|r|/b)^m + \cdots )$, where $n, m, \ldots$ are positive integers and $c_1, c_2, \ldots$ are constants, which include all shapes derived from rotating a polynomial about the vertical axis. Note that these observations mean that Bessel functions would also lead to the results presented here, although, as discussed in section 2.2.1, parabolas are probably a better description of a local mode on the molecular scale. Dependence of energy loss and trapping on surface temperature is also very weak [45], and is not expected to play a role in the theory derived here because a sufficiently fast incoming atom would not be perturbed by the thermal motions of the liquid molecules.

The results obtained from this ‘backwards’ non-ballistic approach to collisional energy loss lack any dependence on the molecular properties of the liquid surface, as encapsulated in the surface force $\gamma$. This is consistent with experimental results. For example, Saecker and Nathanson observed very little change in fractional energy loss on going from squalane to glycerol, and Behr et al. observed only a weak dependence on the concentration of sulfuric acid in their aqueous liquid [109, 6]. Our derivations involved enumerating the microscopic states of the surface after collision, during which we did not have to specify the ‘surface degrees of freedom’ as being associated with particular atoms or parts of a molecule. Physically, this suggests that the final outcome of the collision does not have a strong dependence on the microscopic details of the energy dispersal. Thus, the disordered and dynamic molecular environment of the liquid surface must provide so many mechanisms for energy dispersal that there are many distinct ways to achieve essentially the same outcome. While different liquids would involve different molecules, the available mechanisms of energy dispersal would be similar. Experimentally, the average over all available mechanisms would be observed, leading to a lack of dependence on the trapping probability and energy loss on the nature of the surface. A more direct, yet less revealing explanation lies in the fact that all of the information on how much energy the surface has gained upon collision is encapsulated by the parabolic assumption of the outcome of energy exchange. This lack of dependence on structural details makes this approach a natural means of incorporating impulsive constraints into dynamical theories of the gas-liquid scattering process involving a coarse grained model of the liquid surface.

4.2 Extension to Liquid Metal Surfaces

A key prediction from the above model is that a small, fast atom will lose around 60% of its initial energy on average upon colliding with the liquid surface. While this conclusion holds well for neon collisions with a variety of viscous, molecular fluids, it evidently does not apply to neon-liquid metal collisions. Neon collisions with liquid indium, bismuth and gallium surfaces result in average energy losses of around 20% [104, 64], which is much
Figure 4.4: Model of a rare gas atom colliding with a liquid metal surface. After colliding with the surface (A), the atom (dark grey circle) recoils back into the gas phase, generating a circular wave that propagates away from the point of impact (B). The diagram is drawn in the $xz$ plane, with the wave propagating in the $xy$ plane.

less than the 60 % prediction given above. The goal of this section is to try and explain the difference without retreating to the two-body collision picture.

The critical damping wave vector for the changeover from sinusoidal capillary waves to damped local modes provides a clue to the discrepancy. Recall from Chapter 2 that for sinusoidal capillary waves on a liquid surface, critical damping to local modes by viscous shear forces occurs for wave vectors much greater that $k_c = \rho \gamma / \eta^2$, where $\gamma$ is the surface tension of the liquid (which should be distinguished from the surface force $\gamma$ presented above), $\rho$ is its density and $\eta$ is its viscosity. Liquid metal surfaces have relatively large surface tensions and densities and relatively small viscosities, which tends to result in unreasonably large values of $k_c$. For instance, near their melting points, capillary waves on gallium, indium and bismuth have critical damping wave vectors in the order of $10^9$ m$^{-1}$, which corresponds to wavelengths of around 6 nm. This is only an order of magnitude larger than the diameters of surface atoms, and so we cannot expect waves with wave vectors ‘much greater’ than $k_c$ to be meaningful. Is is therefore reasonable to suppose that sinusoidal capillary waves on a liquid metal surface persist right down to wavelengths comparable to inter-atomic distances. In other words, we propose that coherent, atomic-scale motions are stable on a liquid metal surface.

By this reasoning, it seems more appropriate to assume that the collision excites a coherent, wave-like motion on the surface which propagates a large distance from the point of impact. When the atom strikes a liquid surface and scatters back into the gas-phase, it might be imagined that it causes a surface atom or a small group of surface atoms to oscillate about their equilibrium positions. For a viscous, non-metallic liquid, shear forces would damp this motion before it could be transferred to surface atoms a substantial distances from the point of impact, resulting in a local mode displacement like the one in Figure 4.1. However, for a non-viscous liquid metal surface, dissipation of

\footnote{Fluid parameters for these three liquids are tabulated in reference [104].}
energy into the bulk would be relatively slow, and the oscillating atom could efficiently transfer some energy to its neighbours, causing them to oscillate as well. Energy would be transferred to surface atoms a large distance from the point of collision, resulting in a wave-like motion which propagates from the point of impact. Our new model is presented in Figure 4.4, which supposes the collision excites an under-damped sinusoidal capillary wave that extends over a large but finite area of the surface. The wave is circular, propagating in the $xy$ plane from the point of impact. Following assumptions 1 and 2, we suppose that the amplitude of the disturbance is small enough and sufficiently delayed to have no effect on the potential energy of the outgoing atom. The model should be appropriate for an atom approaching parallel to the $z$ axis. The 20% energy loss for neon atoms striking liquid metal that was mentioned above was measured with the neon beam at an incident angle of 55° to the surface normal [104]. Energy transfer for neon-hydrocarbon collisions slowly increases as the incident angle approaches 0° [46], so our model should predict an average energy transfer slightly greater than 20%.

4.2.1 Energy loss distribution for capillary wave excitation

With the previous model, we began the analysis at the time when the local mode reached its maximum depth. Here, we begin at the time when the initial disturbance is past and the circular wave covers an arbitrary area of radius $R$, which is still small enough for the damping by viscosity to be slight. We represent this circular wave as a superposition of plane capillary waves which propagate as a series of parallel crests in the $xy$ plane,

$$z(r) = \sum_j c_j e^{ik_j \cdot r},$$  \hspace{1cm} (4.9)

where $k_j$ is the wave vector of component wave $j$ and the vector $r$ lies in the $xy$ plane. From the theory of capillary waves [59], the energy of component wave $j$ in (4.9) is

$$e_j(k_j) = \pi k_j^2 \gamma \xi_j^2 R^2 / 2,$$  \hspace{1cm} (4.10)

where $\xi_j^2$ is the root-mean-square (rms) displacement of the wave, $k_j$ the magnitude of its wave vector, and $\gamma$ the surface tension of the liquid. On the scale of interest, the surface tension $\gamma$ can be considered as being the ‘surface force’ introduced in equation (4.1), however its exact nature is unimportant as it will again cancel when we go to renormalise the energy loss probability density function. Note that

$$\frac{d e_j(k_j)}{d k_j} \propto R^2 \frac{d(k_j^2 \xi_j^2)}{d k_j}.$$  \hspace{1cm} (4.11)

Thus, by choosing a value of $R$ that is not too small, we can reach a situation where a small change in the wave vector of a component wave leads to a large change in its energy. It follows that, because the collision supplies a fixed amount of energy to the surface, the range of wave vectors that correspond to a given circular displacement must
be quite small. We therefore make the assumption that, for a particular circular wave, the components have wave vectors with magnitudes clustered around an average value \( k \) and that, within the range of \( k \) values \( \delta k \), the rms displacement \( \xi_j^2 \) is a slowly varying function of \( k \). The circular wave is now characterised by the value of \( k \) for its components, and we can speak of the collision as exciting a circular wave packet with a suitably averaged wave vector \( \vec{k} \). The problem therefore involves two parts, namely finding the energy of a circular wave with a given wave vector \( \vec{k} \), and finding the probability that the collision generates a circular wave with wave vector \( \vec{k} \).

The total energy of a circular wave with wave vector \( \vec{k} \) is equal to \( e(\vec{k}) \) multiplied by the number of component waves in the circular wave. We will compute this number in a way similar to the calculation of the degeneracy of photons in a black body. Since the component sine waves must have zero amplitude at the edge of the circular wave, the wave vector \( \vec{k} = (k_x, k_y) \) must satisfy

\[
2Rk_x = n_x \pi \\
2Rk_y = n_y \pi 
\]  

(4.12)

where \( n_x \) and \( n_y \) are positive integers. Squaring the equations in (4.12) and adding them together gives an equation for a circle with radius \( 2Rk/\pi \) in the space of the integers \( n_x \) and \( n_y \). The number of pairs \((n_x, n_y)\) corresponding to a component wave with wave vector less than or equal to \( \vec{k} \) is the area of the positive quadrant of this circle, namely \( A_k = R^2k^2/\pi^2 \). The component waves of the circular capillary wave all have wave vectors close to \( \vec{k} \), so the pairs \((n_x, n_y)\) of interest are clustered along the outer edge of the circle. To good approximation, the number of component waves in the circular wave is therefore

\[
N_k \approx \frac{dA_k}{dk} \delta k = \frac{2R^2k}{\pi^2} \delta k 
\]  

(4.13)

Multiplying (4.10) by (4.13) and denoting the quantity \( R^2\gamma \xi^2 \delta k / \pi^2 \) by \( c_1 \), we obtain

\[
e(\vec{k}) = c_1 \vec{k}^3 
\]  

(4.14)

as the total energy of the circular wave. This energy, which is dissipated gradually as the radius \( R \) increases, must equal the energy transferred to the surface by the colliding atom.

With the model discussed in section 4.1, a significant part of the problem involved obtaining the probability that the collision would generate a local mode with a particular half width. The analogous situation with the current model is finding the probability that the collision will generate a circular wave with component waves that have a wave vector close to \( \vec{k} \). However, we have already established that the range of wave vectors that survive to contribute to the circular wave at \( R \) is small. Thus it is not unreasonable
to suppose that all the wave vectors that contribute to the circular wave have the same probability of being excited by the initial impact, and the probability density function for exciting a wave vector in this range is therefore

\[ f(\vec{k}(e)) = c_2 \] (4.15)

where \( c_2 = 1/\delta k \). The density function (4.15) is understood as being zero outside the range \( \delta k \).

We now use (4.14) and (4.15) to find the density function \( g(e) \) for the random variable \( E \), the energy lost by the particle upon colliding with the surface. By rewriting (4.14) as \( \vec{k}(e) = (e/c_1)^{1/3} \) and employing the probability integral transform \( g(e) = f(\vec{k}(e))d\vec{k}(e)/de \), we obtain \( g(e) = (c_2/3c_1^{1/3})e^{-2/3} \). The maximum amount of energy that the colliding particle can lose is \( e_k \), the kinetic energy of the atom when it collides with the surface. Treating \( c_2/3c_1^{1/3} \) as a normaliser, we then have \( 1 = (c_2/3c_1^{1/3}) \int_0^{e_k} e^{-2/3} de \), and hence \( c_2/3c_1^{1/3} = 1/3e_k^{1/3} \). We therefore obtain

\[ g(e) = \frac{1}{3e_k^{1/3} e^{2/3}} \] (4.16)

as the probability density function for the collisional energy loss of a fast, light atom colliding perpendicularly with a liquid metal surface.

### 4.2.2 Comparison with experimental data

As with the density function in (4.4), the density function in (4.16) is difficult to compare with experimental data because it applies across all exit angles of the scattered product. Hence, we again focus on average energy losses and trapping probabilities for the colliding atom. The average energy loss of the atom to the surface is \( \langle E \rangle = \int_0^{e_k} eg(e) de = e_k/4 \), and hence the average fraction of energy lost is

\[ \frac{\langle E \rangle}{e_k} = \frac{1}{4} \] (4.17)

so the model predicts an energy loss slightly greater than 20 %, as we had anticipated above. Neon atoms incident upon 553 K bismuth, 410 K indium and 436 K gallium surfaces at 55° to the surface normal, and detected at 55° to the surface normal, lose an average of ~ 17 %, 20 % and 23 % of their energy, respectively, to the surface upon collision, as measured over a range of \( e_k \) [104]. Our prediction is that neon atoms incident at 0° to the surface normal should lose an average of around 25 % of their energy upon collision.

The result (9) applies to all atoms that collide with the surface. Therefore to compare it with experimental data we have to assume that trapping events are rare and that almost all scattered product enters into the inelastic channel. We can avoid this assumption by excluding trapped atoms from the average, which gives
Figure 4.5: Fractional energy loss curves (equation (4.18)) for $\epsilon = 2 \text{ kJ mol}^{-1}$ (curve A), $4 \text{ kJ mol}^{-1}$ (curve B) and $6 \text{ kJ mol}^{-1}$ (curve C). Curve D is the fractional energy loss curve for neon striking a 290 K squalane surface (from Figure 4.3).

\[
\langle E \rangle_{IS} = \frac{1}{4} \left( 1 - \frac{\epsilon}{e_k} \right)^{4/3}
\]  

(4.18)

where $\epsilon$ is the depth of the gas-liquid potential well at the surface. (4.18) is plotted in Figure 4.5 for three reasonable values of $\epsilon$, with the curve for neon striking a squalane surface from Figure 4.4 overlaid for comparison. It can be seen that the fractional energy loss curve in (4.18) rises much more sharply than the squalane curve, reaching a plateau at lower incidence energies. Thus, notable deviations from the 25 % result in (4.17) are only expected for low incidence energies ($< 25 \text{ kJ mol}^{-1}$). Note that, like the expression for the trapping probability that is about to be derived, (4.17) can be rearranged into a linear equation in $1/e_k$ which can be used to estimate $\epsilon$. The data in Figure 4 of reference [104] would be appropriate for this purpose, however it consists of only three points which occur in the plateau region of (4.18). Consequently, the fit is dominated by random scatter, which leads to unreliable estimates of $\epsilon$. The best estimates of $\epsilon$ would require data collected in the step region before the plateau, however this might be difficult to obtain because of the increased likelihood of trapping in this region.

The probability that the atom becomes trapped at the surface can be calculated by integrating (4.16) from $e_k - \epsilon$ to $e_k$;

\[
P_{trap} = 1 - \left( 1 - \frac{\epsilon}{e_k} \right)^{1/3}
\]  

(4.19)

The literature contains little data for trapping probabilities of neon colliding with liquid metal surfaces as measured across a range of $e_k$, so we instead plot (4.19) for
three reasonable values of $\epsilon$ and compare them to the trapping curve for neon striking a squalane surface from Figure 4.2 (Figure 4.5). At low energy the liquid metal curves rise much more steeply than the squalane curve. At higher energy the liquid metal curves reach low probability plateaus at around 30 kJ mol$^{-1}$. Ronk et al. estimate that the trapping-desorption fraction for a 64 kJ mol$^{-1}$ neon beam incident upon a 536 K indium surface is less than 0.03 \cite{104}. For comparison, (4.19) predicts trapping probabilities of 0.01, 0.02 and 0.03 for $\epsilon = 2$ kJ mol$^{-1}$, 4 kJ mol$^{-1}$ and 6 kJ mol$^{-1}$, respectively.

The present model provides an explanation of the ‘low energy shoulder’ that is seen in the final energy distributions of rare gases scattered from liquid metal surfaces \cite{104, 64}. This is of particular interest because in the past this shoulder has been considered a signature of multiple gas-liquid collisions \cite{121, 13}. A plot of the distribution (4.16) for an incident energy of 20 kJ mol$^{-1}$ is given in Figure 4.6; the essential shape does not depend on the incident energy of the particle. The distribution quickly falls from large values down to a plateau region. Energy losses beyond $e_k - \epsilon$ correspond to trapping of the neon atom at the surface, and would not be observed in the inelastically scattered flux. The result is a prominent shoulder at high energy losses in the distribution, and therefore a low energy shoulder in the final energy distribution of inelastically scattered neon atoms. Mathematically, the relative prominence of the shoulder for the case of liquid metals is because the energy loss distribution in (4.16) is a decreasing function of the incident kinetic energy of the incoming particle and has a long tail, whereas the distribution in (4.4) is an increasing function. We will not say anything more about multiple collisions until Chapter 6, and instead leave the reader with certain reservations about the concept.

An interesting question is why the circular capillary wave displacement leads to a...
much smaller fractional energy loss than a local mode displacement. This is probably a consequence of the difference between a circular wave, which spreads over a large area of surface, and a local mode which is concentrated at a point. The circular wave involves motion of atoms that are in or close to the surface, whereas the local mode involves the motion of molecules at a greater depth in the liquid and provides more immediate and, because of the slow rate of recovery of the local mode, more efficient energy dissipation. The idea that capillary waves on a liquid metal surface are of very small amplitude and only involve atoms very close to the surface is supported by the findings of Morgan and Nathanson, who showed that argon energy exchange with a bismuth-gallium solution was directly related to the surface coverage of Bi atoms [72].

We have therefore shown that the disagreement between the statistical energy loss model presented in the previous section and experimental data can indeed by explained in terms of surface capillary waves. Not only do the two approaches show that collisional energy loss can be treated without considering molecular surface structure, but they also demonstrate a certain consistency with the hydrodynamic approach to gas-liquid collisions. As well as being a satisfying in its own right, this observation reassures us that the coarse grained hydrodynamic approach that we have decided to take in this work leads to a rigorous description of the surface.
Final Remarks

This chapter has achieved the goal of creating an impulsive energy loss constraint from a model which is devoid of molecular detail. This model is entirely compatible with the coarse grained picture of a gas-phase particle passing over a surface of superimposed local mode displacements. Along with the random walk on parabolas process, we now have everything that is needed to close the equations of motion for the incoming atom.

In employing this model, however, we need to restrict attention to neon atoms, which are light enough to meet the ‘small and fast’ criteria of assumptions 1 and 2. Fast heavy atoms such as argon and xenon, which respectively lose around 70 % and 90 % of their energy upon colliding with a squalane surface [109], are inappropriate for the model. This is probably due to a break down in assumption 1, such that the atom actually enters the cavity created by the collision due to its longer collision period. Furthermore, the approach does not work well for a fast neon atom colliding with a PFPE surface, in which a 60 kJ mol$^{-1}$ atom loses only around 43 % of its incident energy to the surface [110]. The fact that gas scattering from a PFPE surface is well-modelled by scattering from a perfluorinated alkanethiol self assembled monolayer [91, 79] suggests that the molecular features of the PFPE surface are rather prominent and cleanly separated from collective modes, which results in rather poor transfer of energy into the collective modes of the surface molecules. This suggests that the extent of agreement or disagreement with the present model might be used to draw useful qualitative inferences about the nature of the processes by which collisional energy is dissipated into a bulk liquid. Our restriction to neon obviously prevents general conclusions regarding gas-liquid collision dynamics, but
will nonetheless lead to some useful insights in the following chapters. We will also put liquid metal surfaces aside in the following, as their surfaces are dominated by sinusoidal capillary waves and so are not appropriate for the random local mode model. A possible way to create a ‘random capillary wave model’ will be discussed in Chapter 7.

Figure 4.4 shows the local mode picture of a gas-liquid collision, which has been updated to accommodate the impulsive energy loss constraint derived here. With this constraint, the picture now assumes that the incoming projectile is a light rare gas atom, such as neon. The only detail missing from this picture are the equations of motion for the atom in the gas-liquid potential, which are derived in the next chapter.
Chapter 5

Motion of an Atom Over a Liquid Surface

Chapter 1 outlined our goal of deriving closed equations of motion for a gas-phase particle approaching, colliding with and scattering away from a liquid surface. By ‘closed’, we meant equations derived from a realistic model of the liquid surface, rather than by simultaneously solving equations of motion for every other degree of freedom of the system. The motivation is that such equations would serve as a comprehensive dynamical theory of a gas-liquid collision event. The random local mode model of a liquid surface was presented in Chapter 2. On the basis of some simple exploratory calculations, it was shown to provide a promising liquid surface model for the gas-liquid scattering problem. Chapter 3 introduced the random walk on parabolas, a stochastic process which was constructed by considering what would be the displacement of the liquid surface immediately beneath the incoming atom at time \( t \). The random walk on parabolas was developed from the random local mode model, and was claimed to provide a simple means of closing the equations of motion for the incoming atom. At the start of Chapter 4, we mentioned that the random walk on parabolas would not be able to close the equations on its own, because it did not account for energy loss constraints which remove energy from the atom when it collides with the surface. To fulfil this need, a new model of gas-liquid collisional energy loss was created. The model made no reference to the molecular structure of the liquid surface, making it compatible with the coarse grained picture of the liquid surface provided by the random local mode model. The model only worked well for the case of a fast incoming light atom such as neon, and so we restrict attention to this case in what follows.

Having developed the necessary tools, we can finally derive closed equations of motion for an atom passing over a liquid surface. With all the work that we have done, this turns out to be a straightforward task. Therefore, most of this chapter discusses the application of the Runge-Kutta algorithm for obtaining accurate solutions to these equations.

For convenience, we list the key assumptions that have been utilised so far.

1. The incoming particle is a structureless rare gas atom of mass \( m \).
2. The molecular topography of the liquid surface can be approximated by a field of randomly superimposed local mode displacements (Chapter 2).

3. The atom is moving fast enough for the thermal motions of the local modes to appear static (Chapter 3).

4. Energy exchange with the surface is impulsive, and the collective response of the surface to energy gain by the colliding atom occurs over a period much longer than the collision period of the atom (Chapter 4).

5. The Equations of Motion

5.1 Derivation

As in Chapter 3, the horizontal and vertical coordinates of the particle at time \( t \) are denoted by \( X_t \) and \( Y_t \), respectively. Let \( \Omega(X_t, Y_t) \) be the gas-liquid interaction potential when an atom is at point \( (X_t, Y_t) \) above the surface. Since we are considering a potential that is averaged over many surface atom-atom potentials, this expression will depend upon the shortest distance between the particle and the surface. However, a reasonable analytic expression for this distance will not be available in the general case. For example, for a particle passing over a parabolic-shaped surface displacement, it is possible to show that this distance is a solution to a formidable cubic equation.\(^1\) However, local modes have widths that are large relative to their amplitudes, and so are reasonably flat. To good approximation, the shortest distance between the incoming atom and the liquid surface is the vertical distance between the atom and the liquid surface. Call this distance \( R_t \). Now, recall that the displacement of the liquid surface immediately beneath the incoming atom at time \( t \) is \( Q_t \), the random walk on parabolas at time \( t \). Therefore, \( R_t = Y_t - Q_t \), and

\[
\Omega(X_t, Y_t) \sim \Omega(R_t). \tag{5.1}
\]

We can finally see how the random walk on parabolas helps close the equations of motion. It leads to an analytic expression for the gas-liquid interaction potential.

The derivative of (5.1) gives the force acting on the particle as it passes over the liquid surface. However, this force is conservative, and so we need to incorporate impulsive forces for when the atom collides with the surface and loses energy. For these purposes, we assume a hard-sphere potential (one which abruptly jumps to infinity at a distance \( \sigma \) from the surface, where \( \sigma \) is the radius of the incoming atom), which allows us to define a collision time as any \( t \) such that \( Y_t = \sigma + Q_t \). The usual form of Newton’s second law is

\[ \text{(Equation unnumbered)} \]

\(^1\)Indeed, let \((x, y)\) be the position of the particle. The distance between this point and a point \((x_l, f(x_l))\) on the surface of a parabolic local mode is \( r = \sqrt{(x - x_l)^2 + (y - f(x_l))^2} \). Minimising \( r \) with respect to \( x_l \) gives an expression \( 0 = x - x_l + (y - f(x_l)) \frac{df(x_l)}{dx_l} \). Attempting to solve this for \( x_l \) leads to a cubic equation.
inappropriate for handling impulsive forces, so we consider its integral representation [14]. For the horizontal component of velocity \( U_t = dX_t/dt \), we have

\[
U_t = U_0 + \frac{1}{m} \int_0^t F(s) \, ds
\]  
(5.2)

where \( F(s) \) is the horizontal component of force acting on the incoming particle at time \( s \). This force is the sum of two independent forces, a continuous force, which we can identify as \(-\partial\Omega/\partial X_t\), and the impulsive force \( F_i(s) \), which removes energy from the atom at each collision. Therefore,

\[
\int_0^t F(s) \, ds = -\int_0^t (\partial\Omega/\partial X_s) \, ds + \int_0^t F_i(s) \, ds
\]  
(5.3)

Let \( T = \{\tau_1, \tau_2, \ldots\} \) be the collection of all collision times less than \( t \) and \( \tau^+ = \lim_{t\to\tau, t<\tau} t \). Since \( F_i(s) \) only takes non-zero values during the intervals \((\tau, \tau^+)\), the second term in (5.3) can be rewritten as

\[
\int_0^t F_i(s) \, ds = \sum_{\tau \in T} \int_{\tau}^{\tau^+} F_i(s) \, ds = \sum_{\tau \in T} I^x_{\tau},
\]  
(5.4)

where \( I^x_{\tau} = \int_{\tau}^{\tau^+} F_i(s) \, ds \) is the horizontal component of the impulse of \( F_i(s) \) at the collision time \( \tau \). Hence, substituting (5.4) and (5.3) into (5.2), we obtain

\[
U_t = U_0 + \frac{1}{m} \sum_{\tau \in T} I^x_{\tau} - \frac{1}{m} \int_0^t \frac{\partial\Omega}{\partial X_s} \, ds.
\]  
(5.5)

Note that by having the set \( T \) contain only collision times less than \( t \), momentum is only deducted from the particle after collision with the surface, which will leave the motion of the atom well-defined and physically realistic. The same arguments produce an equation for the vertical component of velocity,

\[
V_t = V_0 + \frac{1}{m} \sum_{\tau \in T} I^y_{\tau} - \frac{1}{m} \int_0^t \frac{\partial\Omega}{\partial Y_s} \, ds.
\]  
(5.6)

By assumption 4, we can suppose that the impulsive constraints can be handled with the collisional energy loss theory developed in the previous chapter. Hence, the amount of energy lost by the particle upon colliding with the surface is a random variable \( E \) with probability density function

\[
g(e) = \frac{3}{2\sqrt{2\pi}} \frac{e}{e_{\tau-}^2}
\]  
(5.7)

where \( e_{\tau-} \) is the energy of the atom at time \( \tau^- = \lim_{t\to\tau, t<\tau} t \). Let \( f_\tau = E/e_{\tau-} \), the fractional energy loss following collision at time \( \tau \). The effect of the impulse \( I_\tau \) is to take a fraction \( \sqrt{f_\tau} \) of the particle’s momentum at time \( \tau^- \) and subtract it at time \( \tau^+ \). In order for the impulse to preserve the direction of the momentum vector following collision (so that the outgoing direction of the particle is decided only by the orientation of the
hard-sphere wall), we subtract the fraction $\sqrt{f_\tau}$ of the particle’s momentum at time $\tau$—equally from both components of momentum. This gives

$$
I_x^\tau = -m\sqrt{f_\tau}U_-^\tau
$$
$$
I_y^\tau = -m\sqrt{f_\tau}V_-^\tau
$$

(5.8)

The negative signs in (5.8) should not be taken too literally; they merely signify that the impulses should be such that they reduce the components of momentum immediately following a collision.

To obtain the final form of the equations of motion, we differentiate the random walk on parabolas process to give $dQ_t/dt = (\partial Q_t/\partial X_t)dX_t/dt$, which leads to a change of variables formula,

$$
\frac{\partial Q_t}{\partial X_t} dt = \frac{dQ_t}{U_t}
$$

(5.9)

Thus, the integral in (5.7) can be rewritten as

$$
-\int_0^t \frac{\partial}{\partial Y_s} \Omega(Y_s - Q_s) ds = \int_0^t \frac{d\Omega}{dR_s} \frac{\partial Q_s}{\partial X_s} ds = \int_0^t \frac{d\Omega}{dR_s} \frac{dQ_s}{U_s}
$$

(5.10)

The first equality is an application of the chain rule, whereas the second follows from the change of variables formula (5.9), which saves us from having to specify the derivative process $\partial Q_t/\partial X_t$. For the vertical component of velocity, we obtain

$$
-\int_0^t \frac{\partial}{\partial Y_s} \Omega(Y_s - Q_s) ds = -\int_0^t \frac{d\Omega}{dR_s} ds
$$

(5.11)

Substituting (5.11), (5.10) and (5.8) into (5.5) and (5.6) finally gives equations of motion for a fast rare gas atom passing over a surface of randomly superimposed local mode displacements,

$$
U_t = U_0 - \sum_{\tau \in T} \sqrt{f_\tau}U_-^\tau + \frac{1}{m} \int_0^t \frac{d\Omega}{dR_s} \frac{dQ_s}{U_s}
$$
$$
V_t = V_0 - \sum_{\tau \in T} \sqrt{f_\tau}V_-^\tau - \frac{1}{m} \int_0^t \frac{d\Omega}{dR_s} ds.
$$

(5.12)

These equations are indeed closed; their solution does not require simultaneous solution of equations of motion for any the degrees of freedom of the liquid.

While the equations in (5.12) are the most complete description of the particle’s motion, their differential forms, which hold only when the particle is moving freely through the gas-liquid potential and is not colliding with the surface, are more compact and easier to discuss:
\[
\begin{align*}
U_t \frac{dU_t}{dt} &= \frac{1}{m} \frac{d\Omega}{dR_t} \frac{dQ_t}{dt} \\
\frac{dV_t}{dt} &= -\frac{1}{m} \frac{d\Omega}{dR_t}.
\end{align*}
\] (5.13)

5.1.2 Interpretation

The reason why the equations have a relatively simple form is that they were derived entirely from the viewpoint of the incoming atom. To repeat the guiding principle used in Chapter 3 to construct the random walk on parabolas: \textit{physics is simple only when analysed locally.} In this context, ‘locally’ means from the viewpoint of the incoming atom. The equations in (5.12) and (5.13) describe the motion that would occur if the displacement of the surface directly beneath the atom had the appearance of a sample path of the random walk on parabolas process \(Q_t\).

The key feature of (5.12) is that, since \(Q_t\) is a stochastic process, the solutions \(U_t\) and \(V_t\) are also stochastic processes. Hence, (5.12) is a system of \textit{stochastic differential equations} (written in integral form). What this amounts to is that each time the integrals in (5.12) are evaluated, we will obtain one of an ensemble of possible trajectories for the gas-phase atom. Physically, each trajectory corresponds to a different local mode topography (i.e., different path of the process \(Q_t\)) that could be observed from the viewpoint of the incoming atom as the atom passes over the surface. Hence, by independently solving (5.12) a large number of times, we should be able to study the range of collision dynamics and liquid surface topographies that are involved in experimental molecular beam data. The equations of motion in (5.12) are therefore a means to an end rather than an end in themselves, and have the principal use of extracting useful information from experimental data. In this sense, we have tried to follow the style of the two-body collision models described in Chapter 1.

A key parameter of the theory is the parameter of the random walk on parabolas process, \(\rho\) (see (3.6)). \(\rho\) is the probability that, on moving an infinitesimal distance \(\delta x\) along the horizontal axis, the incoming atom would go from being above a particular local mode on the surface to being above another one. It is here that we pay the price for working from the point-of-view of the incoming atom. It is not possible to obtain \textit{a priori} estimates of \(\rho\) from surface structure information. As was described in section 3.2, \(\rho\) is closely related to the average frequency (in time) at which new local modes appear directly beneath the incoming atom as it passes over the liquid surface. Surface structure information would be required in the form of the average spatial distances between local modes, and using this to calculate \(\rho\) would require knowing the horizontal component of velocity of the particle during its entire trajectory over the surface, which in turn can only be calculated if \(\rho\) is given. That is, \(\rho\) is a \textit{local parameter} (relating to the motion of the incoming atom itself), rather than a surface parameter such as \(\gamma\) (the surface tension).
or $h$ (the half width of a local mode), which could, in principle, be obtained from direct measurements on the surface itself. This work treats $\rho$ as a fitting parameter. However, this should not diminish its significance as a quantity relating to what is observed from the viewpoint of the incoming atom as it passes over the liquid surface. It is by adjusting $\rho$ that we extract information on the local mode topography of the liquid surface and the dynamics of the incoming atom. This is similar to how the two-body models adjust $\mu$, the relative mass parameter, in order to extract information on the molecular topography of the liquid surface (see Chapter 1).

The form of the equations is straightforward to interpret. When the particle is not colliding with the surface, the second term in (5.12) is constant and only the continuous force works on the particle. It is straightforward to show that continuous force in the equations of motion is projected perpendicular to a tangent to the surface profile drawn directly beneath the incoming particle$^2$. In this case, the motion can be accurately described by (5.13), and the horizontal component of force can be written as $(d\Omega/dR_t)\partial Q_t/\partial X_t$ (apply the change of variables formula (5.9)). Since the vertical component is $-d\Omega/dR_t$, we have

$$F_y/F_x = \tan \theta = -1/(\partial Q_t/\partial X_t) = -1/G_t \quad (5.14)$$

where $\theta$ is defined in Figure 5.1 and $G_t$ is the slope of the surface beneath the particle at time $t$. Now, consider the construction in Figure 5.1, in which the angle $\phi_1$ between a vector perpendicular to a tangent to the surface profile and a horizontal axis is shown. Our goal is to show that $\phi_1 = \theta$. By Figure 5.1, $\phi_1 + \phi_2 = \pi/2$ and, since $\mathbf{a}$ and $\mathbf{b}$ are unit vectors, we have that $\mathbf{a} \cdot \mathbf{b} = \cos(\pi/2 + \phi_2) = \cos(\pi - \phi_1) = -\cos \phi_1$. Moreover,

$$\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y = b_y = G_t b_x = G_t \cos(\pi/2 - \phi_1) = G_t \sin \phi_1$$

$^2$D. J. Nesbitt is thanked for pointing this out.
Figure 5.2: An explanation of how the approximation \( \Omega(X_t, Y_t) \sim \Omega(R_t) \) serves to approximately direct the particle along the shortest route to the surface (along the line marked \( r \)) when the curvature of the surface is small. The continuous force \( F \) is projected perpendicular to a tangent to the surface profile and will point between the lines marked \( r \) and \( R_t \). When the curvature of the surface profile is small, these two lines, and therefore the force, are almost coincident.

Combining these results gives \(-1/G_t = \tan \phi_1\), and hence that \( \phi_1 = \theta \), by (5.14). Assuming the curvature of the surface to be small, the effect of this is to approximately direct the particle along the shortest route to the surface (Figure 5.2), which is a consequence of the assumption that the potential is felt along the vertical distance \( R_t \). Since this approximation exaggerates the vertical component of force on the particle, it will lead to inaccuracies at larger incidence angles (relative to the normal to the surface).

By employing (5.7), we ignore the dependence of energy loss on surface temperature and incidence angle. For the case of a small, fast, incoming atom (such as neon), the dependence of energy loss on these variables is not strong [46, 45], and therefore is not expected to have a significant effect on the motion of the atom following collision with the surface. As discussed in Chapter 4, the thermal motions of the liquid surface will appear static to a fast incoming atom (cf. assumption 3). Recall that, on going from a 65° incidence angle to a 45° incidence angle, experimental energy loss curves for neon striking squalane increase by only about 7 %, with the increase appearing to become smaller as the incidence angle decreases further [46]. Equation (5.7) does not lead to a dependence of energy loss on exit angle, and therefore the solutions of (5.12) will not be able to associate various regions of an angular distribution with particular average final energies of the outgoing particle. Nonetheless, this dependence is not dramatic for a small, fast incoming atom [46], and the distribution (5.7) is very broad, so it is expected that (5.12) will still capture the general dynamical effects which are implied by the experimental data. In order to account for the relationship between energy loss and the incident and exit angles, a ballistic two-body model would need to be employed in place of (5.12), which would take us back to the difficulties of working with a structurally detailed model of the liquid surface.

Figure 5.3 shows the local mode picture of a gas-liquid collision, which is now complete. The addition to the picture is the equations of motion (5.13) for the motion of the particle in the gas-liquid potential. Chapter 6 will test this picture against experimental data, but...
Figure 5.3: The complete local mode picture of a gas-liquid collision, as constructed with the random local mode model, the random walk on parabolas, the impulsive energy loss constraint, and the equations of motion for the incoming atom (shown in the top right).

before doing that we need a means to obtain reliable solutions to (5.12).

5.2 Numerical Solutions to the Equations of Motion

The equations of motion in (5.12) are a set of four coupled nonlinear stochastic differential equations (the other two are for $X_t$ and $Y_t$) which is closed by the random walk on parabolas process, which itself is a function of $X_t$. Due to this complexity, numerical integration is required in order to obtain solutions.

5.2.1 Implementation of the Runge-Kutta algorithm

The corollary in section 3.2 shows that the integrals in (5.12) are Reimann-Stieltjes integrals, provided that they are computed path-by-path. This means that we can employ classical Taylor’s series algorithms to obtain accurate numerical solutions. The obvious choice is the 4th order Runge-Kutta (RK) algorithm. However, directly applying the usual ‘textbook’ recipe for the RK algorithm is inappropriate for (5.12), because the random walk on parabolas needs to be simulated at each step in the calculation. Moreover, the algorithm needs to be conditioned to remove energy from the atom when it hits the hard-sphere wall of the potential function. It is actually easier to work with (5.13), and to write the equation for $U_t$ as $dU_t/dt = (d\Omega/dR_t)\partial Q_t/\partial X_t$. Otherwise, impractically small time steps are required to ensure that the derivative $dQ_t/dt$ behaves smoothly near a kink in the path of $Q_t$. A reliable integrator code for (5.12) was written in R 2.9.2 [118]. It is not shown here in the interests of space but is available upon request. In summary, the integrator runs as follows.

1. Input calculation parameters (Boltzmann’s constant, liquid temperature ($T$, not to be confused with the set $T$ defined earlier), surface tension ($\gamma$), mass of incoming...
atom \((m)\), incident angle of incoming atom \((\theta_i)\), initial kinetic energy of the incoming atom \((E_i)\), \(\rho\), \(h\) (half-width of the local modes), parameters for the gas-liquid interaction potential function, length of time step \((\tau)\), not to be confused with a collision time defined earlier), number of time steps to perform integration over \((M)\), and number of times to repeat the integration \((N))\).

2. Generate a large vector \(N_0 (~10^6\) elements\) of normal random variables with mean zero and standard deviation \(\sqrt{k_B T/\pi \gamma}\). Sort the values by size.

3. Define a function \(B(q)\), which selects an element from \(N_0\) at random which is at least as large as \(q\).

4. Define a function \(f_U(X,Y,Q)\), which corresponds to right hand side of the \(U_t\) equation in (5.13) (written as described above), and a function \(f_V(X,Y,Q)\), corresponding to the right hand side of \(V_t\).

5. Set the initial conditions \((U_0,V_0,X_0,Y_0,Q_0)\) of the stochastic differential equations.

6. At the first time step \((t = 1\tau)\), perform the RK algorithm to obtain \(U_{1\tau},V_{1\tau},X_{1\tau}\) and \(Y_{1\tau}\), using the value of \(Q_0\).

7. Use the value of \(X_{1\tau}\) to calculate \(Q_{1\tau}\).

8. If \(Y_{1\tau} \leq Q_{1\tau} + \sigma\) (i.e., the atom is touching the hard-sphere wall at time \(1\tau\)), set \(X_{1\tau}\) and \(Y_{1\tau}\) to their values from the previous time step, and reflect the atom from the surface and deduct an energy \(E\) from the distribution (5.7) (using the value of the kinetic energy at the previous time step \(0\tau)\).

9. Terminate the trajectory if \(\sqrt{X_{1\tau}^2+Y_{1\tau}^2} \geq \sqrt{X_0^2+Y_0^2}\) (i.e., the atom crosses the detector radius).

10. Repeat steps 6 - 9 \(M\) times (using the value of \(Q_t\) at the previous time step in step 6) to simulate an entire trajectory.

11. Repeat steps 6 - 10 \(N\) times to simulate a representative ensemble of trajectories.

Some steps may require further explanation.

Step 7 begins by checking whether the isotropy conditions are satisfied (where \(U_0 \leq 0\) and \(X_0 \leq a\), or \(U_0 \geq 0\) and \(X_0 \geq a\), where \(a\) is the center of the local mode on the \(x\) axis; see section 3.1.2). If they are, then the integrator generates a uniform random number between 0 and 1 and checks whether it is less than \(\rho\) (the probability of which is \(\rho\)). If so, then the random walk component of the random walk on parabolas (\(Z_t\) in (3.5)) makes a transition to a new local mode. The amplitude of this local mode at \(X_{1\delta}\) must be at least as large as the current value of \(Q_0\), or else a discontinuity will appear in the surface profile. It is therefore generated by means of the function \(B(Q_0)\). The center of the new local mode is found by rearranging the parabola in equation (3.1) (setting \(f(X_{1\tau}) = B(Q_0))\),
\[ a = X_{1\tau} \pm h \sqrt{1 - Q_0/B(Q_0)} \]

where we take the plus solution for the case where the particle is travelling left-to-right across the surface \((U_{1\tau} > 0)\) and the minus solution when travelling from right-to-left \((U_{1\tau} < 0)\). Step 7 also uses boundary conditions for when the random walk on parabolas (and hence the surface profile) is about to take on negative values. In this case, the random walk is forced to make a transition, this time to a local mode with amplitude \(B(0)\) at \(X_{1\tau}\) and center \(a = X_{1\tau} \pm h\).

Step 8 is required because it is not possible to directly incorporate the infinite potential step of a hard-sphere potential into a discrete numerical scheme. It supposes that the action of the hard-sphere wall on the incoming particle is to reflect it across a tangent to the surface at the point of contact, much as was discussed in testing the random local mode model in section 2.3. Thus, if at time step \(n\), \(Y_{n\tau} \leq Q_{n\tau} + \sigma\) (which corresponds to the particle either touching the wall or being a short distance beyond the hard-sphere wall), the velocity vector \(\hat{V}\) of the atom becomes (cf. equations (2.36) to (2.39))

\[ \hat{V} = HRH^{-1}V \]

where

\[
H = \begin{pmatrix}
\cos \alpha & -\sin \alpha \\
\sin \alpha & \cos \alpha
\end{pmatrix},
\]

\[
R = \begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix},
\]

\[ \alpha = \tan^{-1}(-G_{1\tau}) \text{ and } G_t = dQ_{1\tau}/dX_{1\delta} = -bh^2(X_{1\tau} - a)/2, \text{ the slope of the surface at point } X_{1\tau}. \]

Following this, the magnitude of the velocity vector \(\hat{V}\) has to be reduced on account of collisional energy loss to the surface. Assuming a small enough time step, the potential energy of the particle at this point will essentially be zero, and the total energy of the particle at this time will be very close to its kinetic energy. Thus, collisional energy loss is incorporated by deducting an energy \(E\) (from the distribution \(g(e) (5.7)\)) from the kinetic energy of the particle. The method of simulating \(g(e)\) distributed random variables runs as follows. Consider a plot of \(g(e)\) against \(e\), such as the one in Figure 5.4 (dark line). The maximum energy that the particle could lose is its kinetic energy \(e_k\) at the time of the impact (= \(e_{r+}\) in (5.7)), which corresponds to the point \((3/2)1/e_k\) on the \(y\) axis. Since the distribution \(g(e)\) is an increasing function of \(e\), the point \((e_k,(3/2)1/e_k)\) is the maximum of the curve in this plot. The routine simulates a uniform random variable \(z_1\) between 0 and \((3/2)1/e_k\) and another uniform random variable \(z_2\) between 0 and \(e_k\). If the \(g(z_2) \geq z_1\), then the energy lost is \(z_2\), otherwise the routine is repeated. This procedure was constructed intuitively, and the fact that it works is demonstrated in Figure 5.4, which
Figure 5.4: A histogram of $1 \times 10^6$ energy losses simulated by the method described in the text compared to a plot of the density function $g(e)$, for the case $e_k = 1$ (arbitrary units).

shows a histogram of $10^6$ energy losses simulated by this method and compares it to a plot of $g(e)$, for the case $e_k = 1$, in arbitrary units. Having found an energy loss for the atom, the magnitude of the reflected velocity vector $\hat{V}$ is reduced by fraction $\sqrt{(z_2 - e_k)/e_k}$. This affects both components equally, as required by (5.8) and (5.12). If the final kinetic energy of the atom is less than $\epsilon$, the depth of the gas-liquid potential well, then the trajectory is terminated and the atom is assumed to be trapped at the surface.

The RK algorithm in Step 6 is standard and can be found in most texts on numerical integration (such as reference [11]).

Figure 5.5 plots a representative solution to (5.12) using this integration method for a 29 kJ mol$^{-1}$ neon atom incident upon a 290 K squalane surface at 45$^\circ$ to the surface normal using $\rho = 0.005$ and the time step, initial conditions and potential discussed in the next two sections. The convention that is adopted throughout the following is that the atom approaches the surface from the right hand side of the $y$-axis. The corresponding $Q_t$ process is plotted underneath, explicitly showing the local mode surface profile observed by the incoming atom.

### 5.2.2 Interaction potential and the local mode half width

All calculations reported here used a hard-sphere 3-9 potential of the form

$$\Omega(R_t) = \begin{cases} 
4\epsilon \left( (\sigma/R_t)^9 - (\sigma/R_t)^3 \right) & R_t > \sigma \\
\infty & R_t \leq \sigma
\end{cases} \quad (5.15)$$

where $\epsilon$ is the depth of the gas-liquid potential well and $\sigma$ is the radius of the incoming atom. This potential is appropriate for studying atom-flat surface interactions, and comes about from considering pairwise additivity of the van der Waals (6-12) interactions between
Figure 5.5: A representative trajectory of a 29 kJ mol$^{-1}$ neon atom incident upon a 290 K squalane surface at 45° to the surface normal using $\rho = 0.005$, as calculated by solving the equations of motion 5.12.

the surface atoms and the gas-phase atom [107]. Since the local modes are assumed to be relatively flat, the flat surface requirement of (5.15) should be satisfied. The values $\sigma$ and $\epsilon$ will be given as appropriate in the next chapter.

The random local mode model considers only local modes with comparable physical dimensions to the incoming atom. This means that $h$ should be set close to the molecular radius of a liquid molecule (see section 2.2.1). In the following, the wave vector half width $h$ is set equal to be 1.5 times this value (0.75 times the molecular diameter). This takes crude account of the fact that a liquid molecule won’t necessarily assume a tight spherical conformation at the surface, but rather one between a sphere and its fully unfolded conformation. Since the distribution of $h$’s is heavily weighted towards the smallest values (because the distribution of wave vectors is heavily weighted towards the largest values; see section 2.2.1), this approximation will not have a large effect for molecular scale local modes, and will be discussed in detail in the next chapter.

5.2.3 Time step and initial conditions

It is important to put the initial position of the atom a large distance from the surface, so that by the time the atom goes to collide with the local modes of the surface, the random walk on parabolas process $Q_t$ has had enough time to become ergodic (independent of its initial condition $Q_0$). Since $Q_t$ relates to the profile of the liquid surface, it does not make physical sense for $Q_t$ to be dependent upon its initial conditions at a collision time. The initial conditions $X_0$ and $Y_0$ were set relative to the mean-square height $\langle b \rangle = \sqrt{k_B T/\pi \gamma}$ of the surface local modes. For the systems studied here, it was found that $Q_t$ began to
\( \theta_i = 45^\circ \ \tau / \text{fs} \)

<table>
<thead>
<tr>
<th></th>
<th>10</th>
<th>1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E ) / kJ mol(^{-1} )</td>
<td>-2.79</td>
<td>-0.03</td>
<td>-3.12 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>( \theta_f ) / degrees</td>
<td>48.05</td>
<td>45</td>
<td>45</td>
</tr>
</tbody>
</table>

\( \theta_i = 65^\circ \ \tau / \text{fs} \)

<table>
<thead>
<tr>
<th></th>
<th>10</th>
<th>1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E ) / kJ mol(^{-1} )</td>
<td>-1.28</td>
<td>-0.02</td>
<td>-1.50 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>( \theta_f ) / degrees</td>
<td>67.99</td>
<td>65.03</td>
<td>63.88</td>
</tr>
</tbody>
</table>

Table 5.1: Energy changes and final scattering angles for a 29 kJ mol\(^{-1}\) Ne atom incident upon a flat surface at 45\(^\circ\) and 65\(^\circ\) to the surface normal, as calculated for various time steps using the RK method, but excluding energy loss at step 8.

show ergodic behaviour at \( Y_0 \sim 50 \langle b \rangle \) and \( X_0 \sim Y_0 \tan \theta_i \), where \( \theta_i \) is the incidence angle of the incoming atom relative to the surface normal. All calculations therefore used initial conditions \( Y_0 = 100 \sqrt{k_B T \pi \gamma} \) and \( X_0 = Y_0 \tan \theta_i \). By convention, \( Q_0 \) was set to \( 2 \langle b \rangle \), although under ergodic conditions the choice is inconsequential. An accurate formula for the scattering angle is \( \theta_f = \tan^{-1}(X_\infty/Y_\infty) \). To estimate this, note that after travelling a sufficient distance from the liquid surface, the velocity of the atom will essentially be constant. Hence, if \( t_f \) is the time at which the atom exceeds the detector radius \( \sqrt{X_0^2 + Y_0^2} \), then we may take the estimate \( \theta_f \approx \tan^{-1}(U_t/V_{t_f}) \).

The accuracy of the RK algorithm discussed above is essentially determined by how small a time step \( \tau \) is used in the calculations. However, the smaller the time steps become, the more computer time required to perform the calculation. In the present study, the equations of motion (5.12) must be integrated a large number of times to get a good sample of the dynamics of a gas-liquid interaction, so using extremely short time steps is not practical. Moreover, the need to repeat the calculations with different values of \( \rho \) until the predicted angular distribution most closely matches the experimental distribution makes the situation even more cumbersome. To choose an appropriate time step, we can consider a single trajectory of a neon atom striking an artificially flat surface. The flatness can be achieved by setting \( \delta \), the local mode half width, to a very large value (10\(^9\) m in this case). Under these conditions, the identity of the surface (encapsulated by the local mode amplitude term \( \sqrt{k_B T / \pi \gamma} \) and the half width parameter \( h \)) does not play a role. If we remove the energy loss routine from the integrator, then the accuracy of the time step can be checked by looking at how well energy is conserved over the entire trajectory, as well as looking at how close the scattering angle \( \theta_f \) is to the incident angle \( \theta_i \) of the atom. Table 5.1 shows scattering angles and final energy differences (= final energy - initial energy) for a 29 kJ mol\(^{-1}\) neon atom incident upon a flat squalane surface, for incident angles of 45\(^\circ\) and 65\(^\circ\). It can be seen that as the time step decreases, the algorithm does a better job of conserving the particle’s energy. The exit angle also approaches the incident angle for smaller time steps, although in the 65\(^\circ\) case the exit angle for the smallest time step is about a degree smaller than the incident angle. This is probably because the approximation \( \Omega(X_t, Y_t) \approx \Omega(R_t) \) tends to exaggerate the vertical component of force acting on the particle, causing it to approach the flat surface more parallel to the y-axis.
than what would occur in reality. This effect is only noticeable for larger incident angles, where the vertical component of velocity should be small. Because of this, the analysis in the next chapter will put more emphasis on the 45° exit angle case. Since the 0.1 fs time step involves too long a computational time, this work uses the 1 fs time step. According to Table 1, the above algorithm is sufficiently accurate with this time step. 5000 independent integrations of the equations of motion are used to estimate the angular distributions in the next chapter, which takes around 3 full days for an iMac desktop computer with a 2.16 GHz processor and 1 GB of RAM to compute using a 1 fs time step.
Chapter 6

Analysis of Neon Scattering Dynamics

The last four chapters built up a new dynamical theory of a light rare gas atom approaching, colliding with and scattering from a liquid surface, and culminated in the equations of motion in (5.12). In pictorial terms, the theory is shown in the local mode picture of a gas-liquid collision, Figure 5.3. This picture contrasts greatly with that provided by the two-body collision models shown in Figure 1.1, and therefore it is of interest to test it against experimental data and to see what kind of conclusions it can draw on the nature of a gas-liquid collision. The extent to which this can be done is somewhat limited, because the theory is still in its early stages and so far is only suitable for the case of a light rare gas atom, such as neon. Nonetheless, this still leaves plenty of data to study and gives the theory plenty of opportunity to deliver insights into the dynamical nature of a gas-liquid collision event.

6.1 Neon Scattering from Squalane

This analysis will largely focus on neon scattering from squalane, because of the availability of a large amount of experimental data in the literature [46, 109]. Particular focus will be on comparing predicted and experimental angular distributions. Less attention will be given to average energy losses and trapping probabilities, because it was shown in Chapter 4 than the collisional energy loss constraint in the equations of motion does a good job of predicting these for the neon-squalane system. The parameters used in these calculations are given in Table 6.1.

6.1.1 Key dynamical results

Figure 6.1 compares the angular distribution estimated from 5000 solutions to (5.12) for a 29 kJ mol$^{-1}$ Ne atom incident upon a 290 K squalane surface at 45° to the surface nor-
Table 6.1: Parameters and initial conditions used to calculate trajectories for neon passing over a squalane surface.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Default</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau)</td>
<td>Time step</td>
<td>1 fs</td>
<td></td>
</tr>
<tr>
<td>(E_i)</td>
<td>Initial energy</td>
<td>29 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(\theta_i)</td>
<td>Incident angle</td>
<td>45°</td>
<td></td>
</tr>
<tr>
<td>(m)</td>
<td>Projectile mass</td>
<td>3.37 (\times) 10(^{-26}) kg</td>
<td>[58]</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Collision radius</td>
<td>0.92 Å</td>
<td>[21]</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>Potential well depth</td>
<td>3.86 kJ mol(^{-1})</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>(T)</td>
<td>Liquid temperature</td>
<td>290 K</td>
<td></td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Surface tension</td>
<td>29 mN m(^{-1})</td>
<td>[52]</td>
</tr>
<tr>
<td>(b)</td>
<td>Local mode half width</td>
<td>7.65 Å</td>
<td>[61]</td>
</tr>
<tr>
<td>(Q_0)</td>
<td>Initial condition of (Q_t)</td>
<td>2(\sqrt{k_B T / \pi \gamma})</td>
<td></td>
</tr>
</tbody>
</table>

The value of \(\rho\) was adjusted until the fitted histogram best matched the experimental data. As mentioned in Chapter 2, the distributions estimated here will not be completely comparable to experimental distributions, because the latter also include a cosine-shaped component corresponding to the trapping-desorption fraction. However, the TD fraction emerges from the liquid with only thermal translational energies, limiting its contribution to the total detected flux and not significantly changing the shape of the angular distributions of the inelastically scattered fractions [61, 46]. The agreement is Figure 6.1 is quite good, with the predicted distribution taking the left-skewed shape that the data suggests. The small dip in intensity between -10° and 0° is an artefact of the hard-sphere potential and is absent when a full 3-9 potential (with energy loss at the point of closest contact with the surface) is used in a hard-sphere potential. The agreement in Figure 6.1 implies that the random local mode model of the liquid surface provides sufficient ‘surface roughness’ to account for the wide range of inelastic scattering geometries of the incident particle that are observed in an experimental angular distribution, bolstering the tentative claims made in Chapter 2 with the test model.

Figure 6.2a plots 50 trajectories for a 29 kJ mol\(^{-1}\) neon atom incident upon a 290 K squalane surface at 45° to the surface normal. This shows a representative range of in-plane neon scattering dynamics from a squalane surface, giving an insight into the interaction between an incoming gas-phase atom and a liquid surface profile as modelled with the random local mode model. The dynamical interaction is pleasingly uncomplicated, with almost every trajectory undergoing only a single collision with the liquid surface. To illustrate this more quantitatively, the Figure 6.2b and c present bar graphs of the number of collisions with the surface (number of \(t\)’s in a trajectory such that \(Y_t \leq \sigma + Q_t\)) and number of turning points in a trajectory (number of \(t\)’s in a trajectory such that \(U_t \neq U_{t-\tau}\) or \(V_t \neq V_{t-\tau}\), where \(\tau\) is the time step of the integrator) for this system. These are both measures of the number of interactions with the liquid surface, and it can be seen
that there is an overwhelmingly large probability of a trajectory only undergoing one such interaction. Specifically, we find that \( \sim 92\% \) of the trajectories only collide once with the surface, and that \( \sim 67\% \) only experience one turning point. The percentage of trajectories colliding with the surface only once will be larger than the number undergoing only one turning point, because the latter category does not include particles which become trapped at the surface through large collisional energy losses. Furthermore, some trajectories change their horizontal component of velocity just prior to striking the surface, which occasionally leads to two turning points in a single collision trajectory. These quantities actually slightly underestimate the number of multiple interactions, as some trajectories which 'bounce' across the surface scatter from the repulsive part of the 3-9 potential (in (5.15)), but without ever touching the hard-sphere wall. However, such cases account for less than 10 \% of all trajectories, so their contribution does not significantly change the conclusions drawn here. Recalling the discussion in Chapter 1, the lack of multiple collisions observed contrasts greatly with the findings of several molecular dynamics simulations. For example, a recent simulation on the Ne-squalane system found that \( \sim 56\% \) of the in-plane trajectories underwent more than one turning point [128]. A possible reason for the discrepancy is that, in order to create the parabolic depressions assumed in the collisional energy loss constraint (Chapter 5), successive collisions across several nearby surface atoms are required [128], such that several interactions with the surface are implied by the turning point of a single collision trajectory. Thus, while MD simulations in general do not adequately describe collective motions of the surface molecules, the present coarse grained model undoubtedly over emphasizes the collective motions. In a two-body
Figure 6.2: A. Thirty trajectories for a 29 kJ mol$^{-1}$ neon atom scattering from a 290 K squalane surface, as computed with $\rho = 0.012$. B. Number of trajectories undergoing one, two or three collisions with the surface. C. Number of trajectories experiencing one, two, ..., ten turning points, as seen from 5000 integrations of the equations of motion.
collision context, if the incoming atom strikes a surface fragment with a sufficiently small effective mass, then it will forward scatter into the fragment and a second collision will be required to send the atom back into the gas-phase [35]. In the present model, individual elements of the surface are assumed to be sufficiently massive that multiple collisions is not required to return the incoming atom to the gas phase, an assumption that is valid for the limiting case of a light projectile with high kinetic energy. Multiple collisions are expected to occur once an atom is trapped in the gas-liquid potential well, and multiple collisions would be an inevitable part of the trapping-desorption process. Atoms trapped in the potential well would eventually acquire energies in the order of $k_B T$, and therefore their motion would depend intimately on the molecular structure of the gas-liquid interface, rather than on the local modes themselves. This motion is clearly beyond the capabilities of the equations of motion. The results in Figure 6.1 show that it is not necessary to invoke multiple collisions in order to describe the in-plane dynamical interaction of a fast neon atom approaching a squalane surface and scattering in the IS channel, at least as far as can be inferred from an experimental angular distribution. The last statement can be extended to include experimental average fractional energy losses and trapping probabilities, in view of the fact that direct application of the collisional energy loss constraint to neon colliding with squalane can also account for these measurements (Chapter 4).

Figure 6.3 plots a histogram of fractional energy losses for neon striking a squalane surface, using the same conditions as used for Figure 6.1. This result is of interest given that the broadness of experimental energy loss distributions are often attributed to multiple collisions with the liquid surface [109]. The distribution in Figure 6.3 is indeed broad, essentially resembling the experimental curve measured by Sæcker and Nathanson [109].
and reaffirming our conclusions that multiple collisions are not necessary to account for experimental data. While the experimental curve (and, in particular, the experimental curve for neon striking glycerol [109]) does show deviation from the square root dependence of (5.7), the collisional energy loss constraint is nonetheless able to calculate average energy losses and trapping probabilities for this system and for glycerol with good accuracy (Chapter 4), suggesting that the high energy loss end of the experimental distributions are quite sensitive to the dependence between energy loss and scattering angle (see Chapter 1), which our energy loss theory neglects. The bins of the histogram in Figure 6.3 have been made reasonably large, each spanning a range of 10 % fractional energy loss. The reason for this is that the distribution in (5.7), on its own, abruptly cuts off to zero when \( e = \epsilon \) (the minimum energy loss for trapping), whereas in reality this cut off would probably not be so well-defined (and subject to error in partitioning experimental data into IS and TD fractions [46, 109]), such that for all atoms losing energy close to \( \epsilon \), there is also a chance of becoming trapped at the surface and hence leading to a lower resolution at far-right of the energy loss distribution. This explanation is supported by the observation that the trapping curve in the previous chapter (4.5) is quite sensitive to the value of \( \epsilon \). Physically, this might correspond to a situation where the thermal motion of the surface molecules causes small fluctuations in the well depth parameter \( \epsilon \). In doing this, we are able to tentatively reproduce the weak low energy shoulder of the distribution beyond energy losses of about 80 % [109]. As could be deduced from Figure 6.3, multiple collisions make essentially no contribution to this region (or any others), which also supports the claim that current experimental data for fast neon inelastically scattering from squalane can be interpreted almost exclusively in terms of single interactions with the liquid surface. Note that the shoulder region is not apparent if narrower bins are used to plot the histogram, so it must be assumed that the trapping cut off is poorly defined in order for the shoulder in Figure 6.3 to be meaningful. Indeed, in Chapter 4 we saw that the prominent low energy shoulders seen in neon-liquid metal scattering is not necessarily due to multiple collisions either. The major dynamical insight here is that multiple collisions are not necessary to explain experimental neon-liquid surface scattering data.

To check whether the optimal value of \( \rho \) used to obtain Figure 6.1 was consistent with other experimental data, the analysis was repeated for the case of a neon atom incident upon a squalane surface at 65° to the surface normal, with the other parameters fixed at their values given in Table 6.1. If the value of \( \rho = 0.012 \) for the 45° case is meaningful, then the optimal value for the 65° should be approximately 0.012 \( \cos(90° - 65°) \)/ \( \cos(90° - 45°) \) = 0.0155, assuming that \( \rho \) roughly scales as the amount of horizontal length covered per unit time by the incoming atom. We find that, while this value produces essentially the same shape as the experimental data, the predicted distribution peaks \( \sim 20° \) too far to the left (Figure 6.4). Calculated intensities near 0° are expected to be overestimated because this is where the TD contribution to the experimental data is at its greatest. The result that the distribution peaks too early is anticipated as a result of the approximation in
Figure 6.4: Predicted angular distribution of inelastically scattered 29 kJ mol\(^{-1}\) neon atoms from a 290 K squalane surface (histogram) incident at 65° to the surface normal compared to an experimental total angular distribution (points), as estimated with \(\rho = 0.0155\) and 5000 solutions to the equations of motion. Experimental data from reference [46]. The predicted distribution has the correct shape and follows experimental trends (see text), but peaks too early on account of the approximation \(\Omega(X_t, Y_t) \approx \Omega(R_t)\).

Equation (5.1) in the previous chapter. As discussed there, the effect of this approximation is to exaggerate the vertical component of force on the incoming atom, which would cause the trajectory of a atom coming in at a larger incidence angle to deviate more into the steeper regions of a local mode than would be the case for a atom at a smaller incidence angle. Consequently, specular scattering would be reduced, causing the distribution to peak ahead of the specular angle. With this in mind, the value \(\rho = 0.012\) for the 45° case appears consistent. The dynamics of the 45° and 65° cases are summarised in Table 6.2a by the quantities \(N_1, M_1\) and \(f_{\text{trap}}\), which respectively give the percentage of trajectories in the calculation that only underwent a single collision with the surface, the percentage that only experience one turning point and the percentage that become trapped at the surface. These quantities are referred to as ‘dynamical statistics’. It can be seen that the dynamical statistics for the 45° and 65° cases are virtually identical. Furthermore, decreasing the incidence angle to 25° also yields comparable dynamical statistics. These results show that the dynamics of a rare gas atom as it passes over a surface of randomly superimposed local mode displacements are largely independent of the incident angle. This is due to the fact that the individual local modes are very wide and shallow, which reduces the apparent roughness of the local mode surface from the point-of-view of an incoming atom.

The cases of a 10 kJ mol\(^{-1}\) and a 50 kJ mol\(^{-1}\) atom incident upon a 290 K squalane surface at 45° to the surface normal were also investigated as a means to study the dependence of neon-squalane collision dynamics on the incident energy of the neon atom.
Table 6.2: Dynamical statistics for various values of the calculation parameters, as calculated from samples of 500 trajectories. $N_1$ is the fraction of trajectories undergoing only one collision with the surface, $M_1$ is the fraction which undergo only one turning point, and $f_{\text{trap}}$ is the fraction that become trapped at the surface. $^a h$ is in units of the squalane molecular diameter (10.2 Å; reference [61]), $^\ast \ast \gamma$ in units of the squalane surface tension (26 mN m$^{-1}$; reference [52]), and $^\ast \ast \ast \epsilon$ in units of the squalane well depth (3.86 kJ mol$^{-1}$; see Chapter 4). $^\ast \rho$ calculated by scaling 45$^\circ$ value; $\rho = 0.012(\sin \theta_i/\sin 45^\circ)$. $^b \rho$ calculated by scaling 29 kJ mol$^{-1}$ value; $\rho = 0.012\sqrt{E_i/29}$ kJ mol$^{-1}$

<table>
<thead>
<tr>
<th>Table a</th>
<th>$\theta_i$ / degrees</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>93 %</td>
<td>71 %</td>
<td>22 %</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>88 %</td>
<td>66 %</td>
<td>17 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table b</th>
<th>$E_i$ / kJ mol$^{-1}$</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>94 %</td>
<td>35 %</td>
<td>56 %</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>89 %</td>
<td>71 %</td>
<td>18 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table c</th>
<th>$T$ / K</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>91 %</td>
<td>67 %</td>
<td>20 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table d</th>
<th>$\rho$</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>93 %</td>
<td>65 %</td>
<td>25 %</td>
<td></td>
</tr>
<tr>
<td>0.009</td>
<td>93 %</td>
<td>67 %</td>
<td>23 %</td>
<td></td>
</tr>
<tr>
<td>0.012</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>94 %</td>
<td>68 %</td>
<td>23 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table e</th>
<th>$h^*$</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>92 %</td>
<td>68 %</td>
<td>23 %</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>91 %</td>
<td>66 %</td>
<td>25 %</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>91 %</td>
<td>63 %</td>
<td>25 %</td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>93 %</td>
<td>68 %</td>
<td>24 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table f</th>
<th>$\gamma^\ast\ast$</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>94 %</td>
<td>71 %</td>
<td>21 %</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>92 %</td>
<td>66 %</td>
<td>25 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table g</th>
<th>$\epsilon^\ast\ast\ast$</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>93 %</td>
<td>34 %</td>
<td>58 %</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>95 %</td>
<td>14 %</td>
<td>80 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table h</th>
<th>Energy loss</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic</td>
<td>88 %</td>
<td>86 %</td>
<td>0 %</td>
<td></td>
</tr>
<tr>
<td>Inelastic</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table i</th>
<th>Surface</th>
<th>$N_1$</th>
<th>$M_1$</th>
<th>$f_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Squalane</td>
<td>91 %</td>
<td>67 %</td>
<td>24 %</td>
<td></td>
</tr>
<tr>
<td>PFPE</td>
<td>89 %</td>
<td>62 %</td>
<td>27 %</td>
<td></td>
</tr>
</tbody>
</table>
The dynamical statistics for these cases are shown in Table 6.2b. It is seen that, while the trapping fraction of the incident atoms increases as the incident energy decreases (in accord with (4.5)), the statistics $N_1$ and $M_1$ are essentially the same as in the 29 kJ mol$^{-1}$ case discussed above. Thus, the major dynamical features of the neon-squalane interaction are independent of incident energy. This shows that the increase in trapping fraction at lower incidence energy is not necessarily due to an increased likelihood of multiple gas-liquid collisions. Also of interest is the dependence of the collisional dynamics on the temperature of the liquid surface. Experimentally, the lack of dependence of energy loss of rare gas atoms colliding with a perfluorinated polyether surface has been taken as evidence for the dominance of single collision events for trajectories scattered in-plane [47]. Over the range from 290 K to 350 K, there is no surface temperature dependence of the dynamics of a 29 kJ mol$^{-1}$ Ne atom striking a squalane surface at 45° to the surface normal, and the same dynamical statistics are seen as before (Table 6.2c). As the temperature of the surface increases, the average amplitude of the local modes across the surface increases (since the average amplitude is $\sqrt{k_B T / \pi \gamma}$), but the resulting slight enhancement of surface roughness is insufficient to produce a significant increase in the likelihood of multiple interactions with the surface. Thus, the random local mode model of the liquid surface predicts the lack of an increase in the occurrence of multiple collisions with increasing temperature. It is also found that the fraction of incoming atoms which are trapped at the liquid surface is essentially invariant with temperature ($\sim 20 - 25\%$ for each case), whereas experimentally the trapping fraction increases weakly with increasing surface temperature [47]. This latter effect is possibly due a dependence of $\epsilon$ on surface temperature, as a hotter surface should have enhanced molecular (as opposed to local mode) surface roughness, which would serve to create larger fluctuations in the value of $\epsilon$ across the surface [7]. Thus, hotter surface molecules could more readily accommodate an incoming gas-phase atom. The dynamics of this interaction is beyond the scope of the model presented here, which is limited to dynamics governed by the local mode structure of the liquid surface, rather than by its detailed molecular structure. Thus, the results presented here suggest that the major features of the dynamics of a small, fast rare gas atom colliding with and recoiling from a liquid surface can be adequately accounted for in terms of the local mode structure of the liquid surface.

### 6.1.2 Squalane surface profile

Figure 6.5 plots a representative trajectory of a 29 kJ mol$^{-1}$ neon atom incident upon a 290 K squalane surface at 45° to the surface normal with $\rho = 0.012$, as in Figure 6.1. Also plotted is the corresponding random walk on parabolas process $Q_t$, which shows a representative local mode surface profile as seen from the viewpoint of the incoming neon atom. It can be seen that the local modes on the squalane surface are closely clustered together. Interpreting the local modes as a coarse grained representation of the surface molecules, this suggests that the squalane surface molecules are in close contact
and tightly associated. This is consistent with the fact that squalane is a highly viscous, low vapour pressure fluid. The profile in Figure 6.5 is weakly corrugated, which contrasts with the picture of the liquid surface generated by some MD simulations. For instance, in modelling the squalane surface as a system of Lennard-Jones spheres, Lipkin et al. observed corrugation on a scale of 10 to 50 Å [61]. Highly corrugated surfaces have also been noted in a recent simulation by Peng et al., whereas in Figure 6.5, where we see no local modes with heights more than 2 Å above their neighbours. Furthermore, inclusion of negative-going local modes would make very little difference, because they lead to essentially the same topography as positive-going modes on this scale. Our lack of surface corrugation is not responsible for the absence of multiple gas-surface interactions (Figure 6.2) because we do not see a significant increase in the number of multiple interactions with decreasing $\rho$ (see the next section), which would serve to widen the spaces between the local modes. If the random local mode model of the liquid surface is a good representation of an actual equilibrium liquid surface — and the results here suggests that it is — then it may be that the MD simulations are ran over too short a time scale or with too few molecules to properly model many-body effects such as capillary phenomena, thereby leading to a picture of enhanced surface corrugations and multiple gas-liquid interactions.

6.1.3 Sensitivity of the dynamics to model parameters

A useful way to gain insight into the origin of the dynamics presented in Figure 6.2 is to study the sensitivity of the predictions of the equations of motion (5.12) to small variations in the model parameters. This procedure is particular important when adjustable
Figure 6.6: Angular distributions for a 29 kJ mol$^{-1}$ neon atom striking a 290 K squalane surface computed with A. $\rho = 0.006$, B. $\rho = 0.009$, C. $\rho = 0.012$, and D. $\rho = 0.016$, with all other parameters held at the values given in Table 6.1. The histograms A, B, and D were plotted from 2000 solutions to the equations of motion. Figure C is the same as Figure 6.1.
parameters are involved, because if a model's output is overly sensitive to small changes in an adjustable parameter, then it may be that that parameter carries an excessive amount of the model's information. In turn, this would suggest that our conclusions are based on poorly defined physics. Table 6.2d summaries the neon-squalane scattering dynamics predicted with various values of \( \rho \) from 0.006 to 0.015, with the other calculation parameters kept at the values given in Table 6.1. It can be seen that the dynamical statistics \( N_1 \) and \( M_1 \) remain constant at \( \sim 93 \% \) and \( \sim 67 \% \) respectively, matching the case \( \rho = 0.012 \). This shows that the dynamical features discussed above are largely independent of \( \rho \). Figure 6.6 plots angular distributions for each value of \( \rho \) in Table 6.2d. It can be seen that, as \( \rho \) is increased towards its optimal value 0.012, the distribution becomes less strongly peaked around the specular angle, and becomes more skewed (as opposed to peaked) toward the specular angle as \( \rho \) increases beyond its optimal value. It is important to observe that the distribution at \( \rho = 0.009 \) is of very similar shape to the distribution at the optimal value at \( \rho = 0.012 \), showing that the angular distribution is not overly sensitive to changes in \( \rho \), and therefore suggesting that \( \rho \) does not carry an excessive amount of the model’s information. The sharply peaked angular distribution at small \( \rho \) implies that gas-liquid collision events at small \( \rho \) mostly involve very similar regions of a local mode surface. At small \( \rho \), the local modes across the surface are more widely spaced, and the incoming atoms may sample the steeper parts near the base of a local mode. As \( \rho \) increases towards the optimal value 0.012, the spaces between the local modes decrease and the incoming atoms tend to sample more from the top regions of the local modes. The slopes of the local modes change more quickly at these regions than in the basal regions, leading to a wider variety of exit angles for the colliding atom.

The half width parameter \( h \) in this model presents some difficulties. In this work, the value of \( h \) is fixed, however in reality the widths of the local modes across the surface would vary, due to the distribution of possible molecular conformations and numbers of molecules contributing to a single mode. In section 2.2.1, we this choice was justified by noting that the distribution of \( h \)'s peaks very strongly at the smallest (molecular-sized) values. In other words, our results should be insensitive to small variances in our choice of \( h \). To test this reasoning, the cases of \( h = 0.6d, 0.7d, 0.8d \) and \( 0.9d \), where \( d \) is the molecular diameter of squalane (10.2 Å [61]) have been studied, in addition to the 0.75d case considered so far. These calculations fixed the other parameters at their values in Table 6.1 and \( \rho \) at 0.012. The dynamical statistics presented in Table 6.2e are essentially unchanged, suggesting that treating \( h \) as a constant near the molecular diameter does not change the dynamical picture from what would be obtained by treating \( h \) as a random variable. Figure 6.7 presents the angular distributions predicted from each value of \( h \). As \( h \) decreases from the value 0.75d, the distribution slowly becomes more peaked. The reason for this is that, as the width of the local modes decreases with the average distance between them remaining constant (i.e., \( \rho \) is kept constant), more of the individual local modes are exposed and the incoming atom tends to sample more from the steeper basal
Figure 6.7: Angular distributions for a 29 kJ mol$^{-1}$ neon atom striking a 290 K squalane surface computed with A. $h = 0.6d$, B. $h = 0.7d$, C. $h = 0.75d$, D. $h = 0.8d$ and E. $h = 0.85d$, with all other parameters held at the values given in Table 1. The histograms A, B, and D were plotted from 2000 solutions to the equations of motion. Figure C is the same as Figure 6.1.
regions of the local modes, rather than from the wave tops where there is a wider variety
of slopes available. Similarly, as $h$ is increased, the local modes flatten and become more
smooth, leading to a sharper peak near the specular angle. Despite these trends, the
sensitivity of the angular distribution to $h$ is not dramatic. In particular, the angular
distributions at $0.7d$ and $0.8d$ are quite similar, which largely alleviates issues associated
with our choice of $h$ and the fitted value of $\rho$.

The heights of the local modes depend on the surface force parameter $\gamma$ through the
relation $\langle b \rangle = \sqrt{k_B T / \pi \gamma}$, where $\langle b \rangle$ is the standard deviation of local mode amplitudes
across the surface. So far, this parameter has been assumed equal to the macroscopic
surface tension of squalane. This also presents some issues to the theory, because the
behaviour of the surface tension on the molecular-scale is not well understood and has
not been quantified. For example, it has been suggested on the basis of x-ray scattering
data that the surface tension of water decreases by up to 75% as the scale of resolution
approaches nanometer dimensions [29] Hence, it is important to understand how variations
in $\gamma$ change the dynamical picture described so far. Table 6.2f presents dynamical statistics
obtained from calculations with various values of $\gamma$, with the values of the other calculation
parameters held at the values given in Table 6.1, and $\rho = 0.012$. Fortunately, the dynamical
statistics do not show any significant variation, suggesting that the error in estimating the
surface force with the macroscopic surface tension does not account for the dynamical
features of the gas-liquid interaction described so far. Conversely, we do find a modest
sensitivity in the angular distribution to the value of $\gamma$ (Figure 6.8), in that doubling and
halving $\gamma$ both cause the angular distribution to become more peaked. As $\gamma$ is increased,
the local mode heights decrease, which renders them more flat and hence causes more
specular scattering. As $\gamma$ decreases, the local mode heights increase, leading to fewer
collisions with the upper regions of the local modes, where the variation in slopes is greater.
These results highlight the importance of establishing good values of the microscopic
surface tension $\gamma$ if this theory is to be used to extract local mode surface profiles from
experimental data in future studies.

The parameters $\rho$, $h$ and $\gamma$ have been examined because their values relate to the
shape of the local modes and the structure of the surface profile, and are therefore central
to the concepts of this work. In contrast, the value of the well depth parameter $\epsilon$ is
more fundamental, relating to concepts such as atom-surface molecule van der Waals
interactions, which suggests that variations in $\epsilon$ may affect the gas-liquid interaction in
a different way. Table 6.2g presents the dynamical statistics from calculations using well
depths of $3\epsilon$ and $5\epsilon$, with other parameters kept at the values in Table 6.1. While $f_{\text{trap}}$
increases as the well depth increases (in accord with (4.5)), $N_1$ remains essentially constant.
Note that the decreases in $M_1$ reflects the increase in $f_{\text{trap}}$, rather than any significant
change in the gas-liquid interaction dynamics. These results show that the dynamical
picture discussed so far is essentially independent of the depth of the potential well at the
liquid surface. That is, variations in $\epsilon$ do not notably alter the dynamics of the gas-liquid

---

110
Figure 6.8: Angular distributions for a 29 kJ mol$^{-1}$ neon atom striking a 290 K squalane surface computed with A. $\gamma = \text{half the squalane surface tension}$, B. $\gamma = \text{the squalane surface tension}$, and C. $\gamma = \text{twice the squalane surface tension}$, with $\rho = 0.012$ and all other parameters held at the values given in Table 1. The histograms A, and C were plotted from 2000 solutions to the equations of motion. Figure B is the same as Figure 6.1.
interaction and, in particular, multiple gas-liquid interactions cannot be assumed to be a consequence of small variations in the well depth parameter across the liquid surface.

As well as studying the sensitivity of the theory to variations in the parameter values, it is also useful to consider the role of collisional energy loss in the dynamics discussed above. 'Elastic' equations of motion can be obtained from (5.12) by setting the sum to zero (note that the result can be written as (5.13)). Table 6.2h compares dynamical statistics from the elastic equations of motion to the inelastic equations (5.12), as calculated using the same parameters as in Table 6.1 and $\rho = 0.012$. The number of single collision trajectories remains essentially unchanged, showing that the essential dynamical features of the gas-liquid interaction for a small, fast incoming rare gas are not notably affected by collisional energy loss. Note that the large increase in the number of trajectories only undergoing a single turning point is due to the fact that atoms cannot be trapped in the absence of collisional energy loss. The corresponding angular distribution is more strongly peaked at the specular angle (result not shown), which shows that the broadness of the experimental angular distribution is partly due to energy loss at the surface. Thus, while the single collision dynamics remain for the elastic case, proper account of collisional energy loss is necessary to describe the trajectory of the outgoing atom following collision with the liquid surface.

6.2 Extrapolation to Neon Scattering from Perfluorinated Polyether

It is of interest to try an extend this analysis to the case of neon scattering from perfluorinated polyether, due to the availability of experimental data for this system at the 45° incidence angle [46]. There are reservations about doing this, because the collisional energy loss constraint is not so successful for this system (Chapter 4). However, the energy losses observed for this system are smaller than those that are predicted by our model, suggesting that the PFPE surface is relatively 'hard' and does not deform so readily under the force of an impacting neon atom. A convenient consequence of restricting this theory to light, fast atoms is that the dynamics of the surface retraction may be assumed slow enough not to affect the trajectory of the outgoing atom, and therefore it should be the case that this theory should still give some insight into the nature of neon scattering dynamics from a PFPE surface. To obtain a crude estimate of a value of $h$ for PFPE, we imagine a flat surface profile divided into segments of length $2h$, with each segment representing the smallest fragment of surface that may be displaced from zero. If the density of the liquid is $D$, then $(2h)^2D$ is roughly the amount of matter contained per segment. This quantity should be a constant for all liquids ($\sim 1$ molecule in this case), which allows us to write $h_{PFPE}^2D_{PFPE} = h_{squalane}^2D_{squalane}$, or $h_{PFPE} = 5.00$ Å (densities from references [109, 8]). We take $\epsilon$ to be the well depth for neon interacting with squalane,
which is reasonable given the insensitivity of the neon-squalane scattering dynamics to small perturbations in the well depth parameter, and $\epsilon = 19 \text{ mN m}^{-1}$ [25].

Figure 6.9a compares an experimental angular distribution for 29 kJ mol$^{-1}$ Ne atom incident upon a 290 K PFPE surface to the predicted distribution computed with the optimal $p$ of 0.0066. The comparison is reasonably good, although it needs to be noted that there is no clear maximum in the experimental data, meaning that the predicted shape may still deviate from the one which occurs in reality. Nonetheless, these results show that the theory presented in this work can be used for systems beyond the prototypic neon-squalane case. Figure 6.9b plots a representative trajectory for the neon atom from this calculation, as well as the corresponding random walk on parabolas process. Here, the local modes in the surface profile are not as closely clustered as in the squalane case, suggesting that the molecular features of the PFPE surface are rather more prominent. This observation is consistent with the findings of several MD simulations of carbon dioxide - perfluorinated alkanethiol self assembled monolayer (F-SAM) scattering, in which the simulated results are comparable to experimental carbon dioxide scattering from a perfluorinated polyether surface [91, 79]. The picture of the PFPE surface produced by the F-SAM MD simulation studies is one in which various molecular features of the PFPE surface, such as the $-\text{CF}_3$ groups, cleanly protrude at the interface, which is similar to what could be inferred from the local mode surface profile shown in Figure 6.9b. The dynamical statistics of the neon-PFPE case are essentially the same as with the neon-squalane case (Table 6.2i). Therefore, the tentative implication is that the predominantly single collision dynamics between a small, fast atom and a liquid surface composed of local modes is a general observation.

### 6.3 Final Remarks

The results in the previous two sections have shown that our equations of motion for a rare gas atom passing over a liquid surface do an adequate job of accounting for experimental angular distributions. They are also capable of handling energy losses and trapping probabilities, although this point has not been emphasised here because it was discussed at length in Chapter 4. Thus, the local mode picture of a gas-liquid collision on which the theory is based (Figure 5.3) seems to be reasonably accurate. While we now have sufficient reason to reject the tenet of gas-liquid collisions discussed in Chapter 1 for the case of neon colliding with squalane and PFPE surfaces, the theory still needs a lot of development before it can say anything about more exotic systems.

A notable feature of the theory is that it predicts considerably fewer multiple neon-surface collisions than reported by the MD simulation community. While we have given reasons why multiple collisions may be underestimated by the theory and why MD simulations may overestimate their occurrence, we have also shown that they are not necessary to account for experimental data. Indeed, all data which has been considered as signatures of multiple collisions — large energy losses, broad energy loss distributions, broad angular
Figure 6.9: A. Predicted angular distribution of inelastically scattered 29 kJ mol$^{-1}$ neon atoms from a 290 K perfluorinated polyether ether surface (histogram) compared to an experimental total angular distribution (points), as estimated with $\rho = 0.0066$ and 5000 solutions to the equations of motion. Experimental data from reference [109]. B. A representative trajectory from the top angular distribution with the corresponding random walk on parabolas process (surface profile) plotted underneath.
distributions and low energy shoulders — have here been accurately modelled with only single collisions. We return to this point in the next chapter.

General conclusions of this work are reserved for the next chapter, as well as suggestions for future developments for the theory.
Chapter 7

Conclusions and Future Work

The previous six chapters have developed a set of closed equations of motion for a gas-phase atom over a liquid surface have been developed. These equations constitute a novel dynamical theory of a gas-liquid collision event. At the moment, the theory only applies to light rare gases such as neon. Due to this limited applicability, the theory is probably best considered an early version of a possibly more versatile future theory. What we have developed has nonetheless led to some new concepts and delivered some new insights. The theory also has significance beyond gas-liquid collisions, as it is the first dynamical theory of a gas-phase atom interacting with a liquid surface. There is therefore plenty of motivation to develop the theory further. Some ideas for doing this are given in this chapter, although first we review our work and draw some conclusions.

7.1 The Local Mode Picture of a Gas-Liquid Collision

The theory is best summarised by the so-called local mode picture of a gas-liquid collision in Figure 5.3. The essential content of the picture is that the atom flies over a surface of randomly superimposed local mode displacements. Each local mode is interpreted as a coarse grained surface molecule. Due to the inherent disorder in the surface profile, we cannot make precise statements as to what local mode topography lies ahead of the atom. When the atom strikes the surface, it is assumed to be travelling fast enough for its collision period to be much less than the time required for the surface degrees of freedom to collectively respond to the collision. The actual trajectory that the atom follows is understood as one of an ensemble of possible trajectories, each corresponding to a possible realisation of the underlying local mode topography. Therefore, the local mode picture of a gas-liquid collision is inherently statistical.

This summarises the essential concepts of the theory. Thus, while going from this picture to useful equations involved some technical mathematics, the key ideas are relatively simple. The theory also involves an unknown parameter $\rho$. $\rho$ is the probability that, upon
an infinitesimal shift in the atom’s position along the horizontal axis, a new local mode will be seen looking straight down at the surface from the viewpoint of the incoming atom. By adjusting this parameter, the theory allows us to extract dynamical insights into the atom’s motion during the collision event from experimental data, as well as insights into the surface topography itself. The theory is a means to an end rather than an end in itself, and is therefore useful. Of the three exemplary hallmarks of Baule’s two-body collision model that were described at the start of section 1.1, we have identified two in our own theory. Whether or not the theory is intuitive depends on how strongly the reader believes in ‘the tenet of gas-liquid collisions’ which was introduced in section 1.3.

7.1.1 Contrasts with the ‘current’ picture

Gas-liquid collisions are currently interpreted with the two-body collision picture shown in Figure 1.1. This picture is based on the qualitative success of two-body collision theories in accounting for experimental energy loss data, and considers the liquid surface to be composed of discrete molecular fragments, each of which can absorb energy from the colliding atom independently of the others over the collision period. The picture is rich in molecular detail, which contrasts with the local mode picture in Figure 5.3. However, the picture is also less complete, because it does not say anything about the dynamics of the atom as it passes over the surface.

There are some similarities between the two-body and local mode pictures. For instance, both assume that collisional energy transfer occurs over a period much shorter than dissipation into the bulk, and both attribute the topography of the surface to individual entities (local modes versus discrete molecular fragments). In some sense, the local mode picture might be regarded as a coarse grained version of the two-body picture. To understand this relationship, it is important to appreciate why we did not need to say anything about molecules in creating the theory. The random local mode model of the liquid surface is based on the assumption that hydrodynamic disturbances to a surface profile persist down to the molecular scale, becoming an accurate coarse grained description of a surface molecule in this limit. At the end of Chapter 2, this idea was rationalised on the grounds that, if it were not true, there would be a critical resolution beyond which the nature of the liquid surface would appear dramatically different than before. It was then mentioned that hydrodynamic velocity fields are quantitatively accurate down to motions over only a few intermolecular distances, and that local modes would result from motions spanning several intermolecular distances [2]. If an incoming atom was travelling sufficiently fast, the atomic details of the liquid surface would appear to be ‘blurred out’, meaning that the coarse grained description in terms of local modes would be an accurate description of what the incoming particle observes upon looking straight down at the liquid surface. Thus, the actual appearance of the liquid surface to a fast incoming particle passing over a surface of molecules (such as in the current picture) should essentially be what would be seen if the particle were passing over a field of randomly superimposed local mode
displacements. It is the ‘fast atom’ assumption that keeps the two pictures consistent.

The two pictures contradict one another in how they describe the nature of energy transfer into the surface. In the two-body picture, energy transfer depends on how close the mass of the atom and mass of the surface fragment match. In our picture, none of this matters; the collective response of the surface degrees of freedom renders the atomistic nature of the collision event irrelevant. In molecular terms, this means that there are so many channels for energy dispersal in a liquid that energy transfer does not depend on how or where the collision takes place; all collision possibilities lead to essentially the same result. This is a significant discrepancy between the two-body and local mode pictures, and it is difficult to see where the consistencies lie. However, it is not recommended that the two-body models be abandoned just yet. Not only is the local mode picture restricted to light neon collisions, but it does not properly capture the (albeit weak) dependence of energy loss on incident angle. Until it can be shown that such dependence can be accounted for by generalising the parabolic surface response assumption, such effects are best interpreted in terms of the two-body models.

In place of a theory describing the dynamics of a gas-liquid collision, the current picture has been bolstered by molecular dynamics simulations of a gas-liquid collision event. MD simulations provide us with a microscopic insight into the dynamics of a large molecular system, which appeals strongly to our chemical sensibilities. But no matter how fascinating they may be, microscopic descriptions are never the most simple descriptions of a large dynamical system. Thus, while MD simulations have described elaborate dynamics involving multiple collisions across various functional groups of various molecules [87], the observation is irrelevant. Our theory shows that multiple collisions are not necessary to account for neon-liquid surface collision dynamics. Indeed, without multiple collisions, we can account for angular distributions, trapping probabilities, average energy losses, and even the broad shape of energy loss distributions, including their low energy shoulders. A striking feature of our results is that the dominance of single collisions does not change with perturbations in the model’s parameters, showing that these conclusions are stable with respect to small inaccuracies in these values. The key result of this work is that multiple collisions and molecular surface details are not necessary to describe available neon-liquid surface collision data. ‘Not necessary’ is used in the same sense as how quarks are ‘not necessary’ to explain a typical chemical reaction; multiple collisions may occur, but they might as well be absent.

7.1.2 What is a typical neon-liquid surface collision?

During a typical neon-liquid surface collision, the neon atom strikes the surface, loses around 60% of its energy to the surface, and bounces back into the vacuum. In response to the collision, the surface degrees of freedom slowly retract, forming a paraboloid-shaped indentation before recovering to their equilibrium positions. That is all that happens!
7.2 Future Work

7.2.1 Looking beyond neon-squalane collisions

As developed here, the theory gives a reasonably complete account of the dynamics of a small, fast gas-phase atom passing over and colliding with a liquid surface. For the most part, the assumptions used in devising the impulsive energy loss constraint are responsible for the limitation of the theory to the case of small, fast atoms. Therefore, in order to develop the theory to handle more exotic situations, the following problems need to be addressed.

1. As mentioned at in Chapter 4, heavy atoms such as xenon and argon lose between 75% and 90% of their energy upon collision with a squalane surface [46], which is larger than the 60% maximum of our collisional energy loss constraint. This is probably due to a break down in short collision period assumption (assumption 1 in Chapter 4), caused by the heavy atom actually entering the the cavity created by the impact, rather than bouncing off while the surface is still beginning to retract, which makes the collision duration at least comparable to the retraction time of the surface. If these problems were solved, then additional work would be needed to ensure consistency with the random walk on parabolas process. For instance, if an impulsive constraint appropriate for a heavy atom was deduced, then the random walk on parabolas process would need to accommodate the longer collision period and resulting deformation of the surface profile.

2. The energy loss constraint does not work well for a fast neon atom colliding with a perfluorinated polyether (PFPE) surface, in which a 60 kJ mol$^{-1}$ beam loses only 43% of its incident energy [110]. As described in Chapter 6, the fact that gas scattering from a PFPE surface is well-modelled by scattering from a perfluorinated alkanethiol self assembled monolayer [91] suggests that the molecular features of the PFPE surface are rather prominent and cleanly separated from collective modes, which results in comparatively poor transfer of energy into the collective modes of the surface molecules. Therefore, the parabolic local mode retraction assumption of the collisional energy loss model needs to be adjusted to accommodate these cases.

3. Since sinusoidal capillary waves are never damped to local mode displacements on a liquid metal surface, the random walk on parabolas is inappropriate for closing the equations of motion for these cases. Rather, we would need a sort of ‘random capillary wave model’, in which the Fourier series representation of a capillary wave surface profile would be approximated by a field of randomly superimposed sinusoidal capillary waves. This would lead us to develop a sine function analogue of the random walk on parabolas stochastic process. Mathematically, the construction of such a process would be much different than that presented in Chapter 4, because
a long memory stochastic process would be needed to account for the indefinite extension of the component capillary waves in space. These developments would allow us to investigate the dynamics of atom motion over a liquid metal surface.

### 7.2.2 Possible projects for a more developed theory

With the above problems solved, a wider range of atom-liquid surface collision dynamics could be investigated. Some other interesting projects are listed below.

1. An obvious problem would be to try and drop the static surface assumption (assumption 3 in Chapter 5) and make the theory more appropriate for slower atoms. In this case, $Q_t = Q(t, X_t)$, and the (differential) equation of motion for the horizontal component of velocity turns out to be

$$U_t \frac{dU_t}{dt} = \frac{1}{m} \frac{d\Omega}{dR_t} \left( \frac{dQ_t}{dt} - \frac{\partial Q_t}{\partial t} \bigg|_{X_t} \right)$$

$$= \frac{1}{m} \frac{d\Omega}{dR_t} \left( \frac{dQ_t}{dt} - \frac{Q_t}{C_t} \frac{dC_t}{dt} \right),$$

where $C_t$ is a process describing the time evolution function of the local mode (equation (2.25)), similar to the $C_t$ component of the process $(A_t, C_t)$ used in the test of the random local mode model in Chapter 2. The equation for the vertical component remains the same as in (5.16). Thus, now we need to specify a local mode rise and fall process $C_t$, as well as a random walk on parabolas process which explicitly includes the time evolution of the local modes. Nonetheless, this task would probably not be so useful because the probability of the atom becoming trapped at the surface rapidly increases as the energy of the atom decreases to lower incidence energies (see Figure 4.2 in Chapter 4). We also have to introduce two new parameters into the theory, namely the viscosity of the fluid and its density (see equation (2.25)). Neither of these parameters are well-defined on the microscopic scale.

2. A limitation of our formulation of the theory was seen when estimating angular distributions in Chapter 6, which required repeatedly integrating the equations of motion and plotting a histogram of scattering angles. A more elegant approach to this task would have been to derive an analytic expression for the exit angle distribution from the equations of motion and the random walk on parabolas process. Alternatively, we could seek a differential equation describing the evolution of the probability distribution of the trajectory as a function of time. This equation would do for our equations of motion what the Fokker-Planck (FP) equation does for Langevin’s equations of motion for a particle undergoing Brownian motion.
Since a probability density function is more useful in certain problems than individual trajectories of the particle, this task could widen the scope of problems that the theory could tackle. There is still some work to do before this task could be approached, because we fell short of properly defining the distribution of the random walk process $R_t$ in the formulation (see section 2, Chapter 3).

3. It would be interesting to consider the case of a liquid surface in contact with a bulk gas phase at room temperature, rather than in the path of a superthermal atomic beam. Then, we could investigate how the behaviour of the bulk gas, as described by the Boltzmann equation [81], evolves into the behaviour described by our equations of motion. For this task, it would be useful to have a FP-type representation of the equations of motion available, as described above. A particularly important investigation along these lines would consider the Knudsen layer. This is a region which extends from the local modes into the gas-phase by a distance of about two mean free paths [95], and is arguably the most poorly understood aspect of the gas-liquid interface. The characteristic feature of the Knudsen layer is that the distribution of velocities of particles travelling away from the surface is different from the distribution travelling towards the surface, although what these distributions are is unknown [95]. This problem could be directly investigated by solving the FP-type equations for the two fluxes. For the outward flux, initial conditions appropriate for a particle which has just evaporated from the local mode surface would be necessary. A starting point for finding these initial conditions is provided by Knox and Phillips [50]. Since collisions between two gas-phase species play an important role in bulk gas-phase dynamics, the underlying theory would need to be adjusted to include these effects if we were to tackle such problems.

4. As will be seen in Chapters 8 and 9, some interesting and important chemical reactions can take place in the gas-liquid interfacial region. These reactions all require a gas-liquid collision as their initiating step, and it could therefore be interesting to see how the dynamics described by our theory are involved. In particular, what sort of collisions have the highest probability of leading to a reaction? Does the incoming particle need to be trapped at the surface before a reaction can occur? How does the local mode surface topography aid in a chemical reaction? A natural reaction to this task is to perform quantum chemical calculations to find which collision configurations would result in the highest reaction probabilities. However, with a well-defined adjustable parameter and some good experimental data, such calculations may not be required.

5. The dynamics of molecule collisions with liquid surfaces presents a rather interesting challenge due to the presence of internal degrees of freedom. A project suggested by the Nesbitt group at the University of Colorado, Boulder, studies carbon dioxide collisions with squalane and PFPE surfaces. Some ideas for approaching the problem
7.3 Extension to Rotor Scattering

The molecular beam approach of studying gas-liquid collisions was recently extended to study the internal state of scattered molecules by Perkins and Nesbitt [88]. Instead of studying TOF spectra, these experiments probe the scattered product by measuring their infrared absorption spectra with an infrared diode laser. Translational energy distributions are obtained by studying the Doppler profiles of the scattered product. A nice advantage of this approach is that the IR beam can be rotated about the target, allowing for easier study of in-plane scattering over a variety of exit angles, as well as out-of-plane scattering of the product. So far, these studies have restricted themselves to carbon dioxide collisions, and have investigated the roles of liquid identity, incident collision energy of the carbon dioxide [89], surface temperature [90], and the orientation and alignment of the scattered rotor [92]. Trends relating to final translational energies and contributions to the TD channel are qualitatively similar to what is seen in rare gas collisions with liquid surfaces. The key findings regarding internal energy excitation are rather interesting. The scattered molecules are invariably rotationally excited, but remain vibrationally cold.

In order to understand these trends, Perkins and Nesbitt fit their data to a two-temperature Boltzmann model [88]. This is a curve fitting procedure, in which a fraction $\alpha$ of the curve is attributed to a Boltzmann curve at the temperature of the liquid (corresponding to the TD channel), and a fraction $(1 - \alpha)$ is attributed to a Boltzmann curve at a much higher temperature ($\sim 720$ K for carbon dioxide scattering from room temperature PFPE [90], for instance). The key point is that the rotationally excited fraction can be fit to a high temperature Boltzmann distribution, which appeals to the idea that molecules scattering in the IS channel undergo equilibrium, ‘TD-like’ dynamics, which possibly means multiple collisions [88]. However, Boltzmann does not necessarily mean equilibrium; a Boltzmann function is an exponential decay, which is a fairly ubiquitous probability density function. Therefore, there are probably other ways to interpret this result as well. The lack of vibrational excitation is expected on the grounds of the lack of vibrational energy transfer seen in gas-gas collisions, in which the vibrational energy spacings are too large for efficient collisional excitation [56].

7.3.1 Rotational excitation and the local mode model

Given the success of the local mode model in the previous chapters, it is natural to investigate whether rotational excitation of scattered CO$_2$ could be anticipated on the basis of random local mode topography at the liquid surface. In principle, this problem could also be tackled by setting up equations of motion, this time for a gas-phase rotor approaching, colliding with and scattering from a liquid surface. A classical approach
should be sufficient, because classical molecular dynamics simulations of carbon dioxide scattering from a perfluorinated alkanethiol self assembled monolayer are able to model the rotational excitation in near quantitative agreement [91]. On account of the extra degree of freedom, constraints between the degrees of freedom, the need for a theory of energy exchange appropriate for the relatively heavy CO$_2$ molecule, and the need for a potential more appropriate than (5.15) (namely, a polarisable potential), the equations would be rather elaborate and would almost be verging on a computational simulation rather than a theoretical investigation. However, since the essential question is whether the random local mode profile of the liquid surface can account for the rotational excitation, it would be more efficient to pursue a simpler study like the one in Chapter 2, in which rotational excitation due to local mode surface topography is investigated directly. We finish this chapter with some ideas into how this might be done and discuss some expected results.

It should first be noted that the theory developed in Chapters 2 through 5 does not capture a key piece of physics of the rotor problem, namely that higher rotational excitations are correlated with lower translational energy losses [89]. To see the inadequacy of the framework, recall our assumption that collisional energy exchange is impulsive. Under these conditions, the energy gained by the surface after being struck by a rotor, $E_s$, is equal but opposite in sign to the change in kinetic energy of the rotor immediately after the collision,

$$-E_s = \left( \frac{P_f^2 - P_i^2}{2m} \right) + \left( \frac{M_f^2 - M_i^2}{2I} \right),$$

(7.1)

where $P_i$ and $P_f$ are respectively the initial and final linear momenta of the rotor, $m$ the rotor’s total mass, $M_i$ and $M_f$ the initial and final magnitudes of angular momentum, and $I$ the moment of inertia of the rotor. ‘Initial’ and ‘final’ are taken to mean immediately before and after the collision, respectively. Under the impulsive assumption, it is these final states that are detected experimentally. Since the rotor is detected in a rotationally excited state, the second term in (7.1) is positive. However, the total energy of the rotor is reduced upon collision [90], and so $-E_s < 0$. The first term in (7.1) must therefore be less than zero and larger in magnitude than the second term. This gives the inequality

$$\frac{1}{2I} (M_f^2 - M_i^2) \leq \frac{1}{2m} |P_f^2 - P_i^2|,$$

(7.2)

which shows that large values of ($M_f^2 - M_i^2$) are associated with large values of $|P_f^2 - P_i^2|$. Hence, under the impulsive collision assumption, higher rotational excitations are associated with higher translational energy losses, which is opposite to what is observed experimentally. It is the impulsive gas-surface collision assumption of our theory which limits our ability to explore the rotor scattering problem.

Nonetheless, let us make the impulsive collision assumption and see what comes about. Consider a rotor approaching the surface parallel to the vertical axis and aligned with the origin of the horizontal axis, as in Figure 7.1. This configuration can be probed
Figure 7.1: A rotor approaching a liquid surface parallel to the vertical axis and aligned with the origin of the horizontal axis. The rotor rotates in the plane of the diagram (the $xy$ plane), and eventually one of its outer atoms (circles) will collide with the local mode centered at point $a$. The angle $\phi$ is defined between the horizontal axis of the center of mass frame shown in the diagram and the bond connecting the center of mass and the atom closest to the surface.

experimentally [90]. The only purpose of the following is to illustrate how local mode topography might be able to account for collisional rotational excitation, and so we ignore the gas-liquid interaction potential and translational energy loss at the surface, and also assume that, initially, the rotor is not rotating. In this situation, the only role of the surface is to apply an impulsive torque to the rotor at the instant of the collision (i.e., $\Delta E = Mf^2 / 2I$, where $\Delta E = -E_s$, the change in energy of the rotor following collision). We further assume that the rotor lies in the $(xy)$ plane, with its angular momentum vector projected perpendicular to this plane. Hence, the change in angular momentum upon striking the surface is [23]

$$\Delta M = r_1 \times J_1 + r_2 \times J_2 = 2r_1 \times J_1,$$  \hspace{1cm} (7.3)

where $r_i$ is radius vector from the center of mass of the rotor to particle $i$ in the rotor and $J_i$ is the impulse of the force acting on particle $i$ when it strikes the surface. The second equality follows because, for a rotor with a two-fold axis of symmetry such as CO$_2$, $r_1 = -r_2$ and $J_1 = -J_2$. In this model, only one of the two outer particles of the rotor will strike the surface in a single collision. It seems reasonable to suppose that the impulse is directed along a unit vector perpendicular to the normal to the surface at the point struck by this particle. If $f(x)$ represents a local mode displacement, then this vector is

$$I = \nabla (f(x) - y) = if' / dx - j$$ \hspace{1cm} (7.4)

In this illustrative demonstration, we only consider the direction of the impulse, and not its magnitude. Let $g = df / dx$, the slope of the point on the surface struck by the
incoming rotor. Since $\Delta M$ only has a component along the $z$ axis (perpendicular to the $(xy)$ plane), we have

$$
\Delta M_z = 2(r_x J_x - r_y J_y) = 2r(g \cos \phi - \sin \phi) \quad (7.5)
$$

by (7.3), (7.4) and Figure 7.1, and hence the rotational energy of the rotor following collision is

$$
\Delta E = \frac{2r^2}{I} (g \cos \phi + \sin \phi)^2. \quad (7.6)
$$

Since

$$
g = -\frac{2h(r \cos \phi - a)}{k^2}, \quad (7.7)
$$

where $b$ is the amplitude of the local mode that the incoming rotor collides with and $a$ its center along the horizontal axis, the problem is one of finding the distribution of $b$ and $a$, from which we might be able to obtain the distribution of rotational excitations, $\Delta E$. For simplicity of presentation, only $a$ is treated as a random variable in what follows. Treating the amplitude $b$ as a random variable would not require any great effort, and would begin by recalling that the amplitudes in the random local mode model are from a collection of normal random deviates with mean zero and standard deviation $\sqrt{k_B T/\pi \gamma}$.

To find the distribution of $a$, consider Figure 7.1. The rotor is travelling towards the surface parallel to the vertical axis, and at the origin of the horizontal axis. The horizontal axis extends by a distance $h$, the local mode half width, in either direction about the origin. The figure shows a local mode centered at point $-h$ along the horizontal axis, as well as another local mode located a distance $a$. By sliding the latter local mode along the interval $[-h, h]$ on the horizontal axis, we can acquire the full range of possible local mode topographies that the incoming rotor could collide with. The quantity $z_0$ gives the distance from the center of the local mode at $-h$ to the point along the horizontal axis where it is intersected by the local mode centered at $a$. To find the distribution of $a$, we follow the style of the random walk on parabolas and suppose the following. Consider sitting at the top of the local mode centered at $-h$. If we were to move a short distance $\delta x$ to the right of that point, there is a probability (equal to a constant) that we would end up sitting on the local mode centered at point $a$. And similarly for if we were to shift another short distance $\delta x$ from that point, and so on. The distance between where we started, $-h$, and where we first found ourselves on the local mode at point $a$ is equal to $z_0$. Following the same reasoning as presented in section 3.2, the distribution of $z_0$ is therefore an exponential distribution (see section 3.2).
Figure 7.2: Same as Figure 7.1, but viewed from the opposite side of the $xy$ plane. While the angle $\phi$ and the positive direction of the horizontal axis have been redefined, the problem is identical to the one in Figure 7.1.

\[ f_1(z_0) = N\lambda e^{-\lambda z_0}, \]

where $\lambda$ is the parameter of the distribution and $N$ its normaliser. Since $z_0 \leq h$, $1 = \int_0^h f_1(z_0)dz_0$, which gives $N = (1 - \exp(-\lambda h))^{-1}$. By the diagram, $a = 2z_0 - h$, and therefore $z_0(a) = (a + h)/2$. The probability integral transform $f_2(a) = f_1(z_0(a))|dz_0/da|$ yields the distribution for $a$,

\[ f_2(a) = \lambda e^{-\lambda(a+h)/2} \frac{2(1 - e^{-\lambda h})}{2(1 - e^{-\lambda h})} = A_2 e^{-\lambda a/2}, \]

where $A_2 = \lambda e^{-\lambda h/2}/(1 - e^{-\lambda h})$. The distribution of rotational excitations, $\Delta E$, can be found by successive application of the integral transform technique. We first apply it to (7.7) to find the distribution of slopes $f_3(g)$, and then to (7.6) to obtain the distribution of rotational energies. This is a straightforward but messy procedure, so is not shown here. The result is

\[ f(\Delta E) = A \frac{e^{-\beta \sqrt{\Delta E}}}{\sqrt{\Delta E}}. \]

where $A$ and $\beta$ are constants\footnote{Explicitly, $A = \lambda h^2 \exp \left( \lambda (h^2 \tan \phi/(2b) - h - r \cos \phi)/2 \right) / (4b | \cos \phi | (1 - \exp(-\lambda h)))$ and $\beta = \lambda h^2 \sqrt{1/2r^2}/(4b \cos \phi)$.}. At this simplistic level of enquiry, we ignore the exact expressions for the constants and look only at the form of the distribution. The sign of the constant $\beta$ is the same as the sign of $\cos \phi$. $\phi$ can take on any value between $0^0$ and $180^0$, however, as Figure 7.2 shows, the case $0^0 \leq \phi \leq 90^0$ is equivalent to the case $90^0 \leq \phi \leq 180^0$ when viewed from the opposite side of the scattering plane (that is, the two cases are related by a two-fold rotation of Figure 7.1 about the vertical axis), so we can take $0^0 \leq \phi \leq 90^0$, without loss. Note that the same arguments can be used
Figure 7.3: Plot of $f(x) = \exp(-\sqrt{x})/\sqrt{x}$ (dark line). If translational energy loss was properly incorporated into the model, then collisions which lead to rotational excitation below a certain threshold (indicated by the vertical dotted line) would have a higher chance of leading to trapping at the surface. This would diminish the intensity of the rotational distribution below this threshold, possibly producing the shape indicated by the dotted curve.

to take $90^\circ \leq \phi \leq 180^\circ$, but they can be ignored because they lead to a probability density function with unbounded growth in $\Delta E$. Thus, $\beta$ is always positive, and equation (7.8) has the same functional form as $ae^{-c\sqrt{x}}/\sqrt{x}$, where $a$ and $c$ are constants. Figure 7.3 plots this curve for the case $a = c = 1$. The key observation that it looks like an exponential decay. This shape is due to the propagation of the exponential factor in the distribution of $a$ through the analysis, which itself is due to the distribution of local mode positions across the surface. A more realistic treatment would account for the fact that low rotational excitations are experimentally correlated with high translational energy losses. This would imply that the region between 0 and some small $\Delta E$ would have a diminished intensity due to the high likelihood of the rotor becoming trapped at the surface. Such a possibility is illustrated by the dotted line in Figure 7.3, and it seems reasonable to expect that the final curve would take on the shape of a Boltzmann distribution for a quantum rotor ($f(J) = a(2J + 1)\exp(-cJ(J + 1))$, where $a$ and $c$ are constants and $J = 0, 1, \ldots$), which has a similar right-skewed shape.

While the arguments used above are obviously very weak, they do suggest that local mode topography may be able to account for the apparently Boltzmann distribution of rotational states seen for CO$_2$ molecules scattering in the IS channel. Once again, the key obstacle in proceeding with this study is the lack of a good approach to collisional energy exchange which can handle long collision periods, as well as heavy molecules such as CO$_2$. Furthermore, we need this model to describe how translational energy loss relates
to rotational energy excitation at the local mode surface. An understanding of these is
necessary to obtain the correct form of the rotational energy excitation distribution at low
rotational excitations, as well as to compare with experimental data in a quantitative way.
Nonetheless, the results presented here are an encouraging first step in this direction.
Chapter 8

Irreversible Thermodynamics of a Gas-Liquid Interface

The final two chapters describe two smaller investigations that have been carried out in addition to the theoretical work on gas-liquid collisions. One of these is an experimental study of the irreversible thermodynamics of a gas-liquid interface, which is discussed in this chapter, and the other describes a computational study of the kinetics of aerosol chemistry, which is described in the next chapter. Both chapters continue with the gas-liquid interface theme of this work.

We now move from individual atom collisions with liquid surfaces to a macroscopic flux of a gas-phase matter through the entire gas-liquid interface. In this chapter, ‘gas-liquid interface’ is taken to mean the entire gas-phase region from the edge of the capillary waves on the liquid surface to a short distance (∼ 2 - 4 mean free paths) into the bulk gas-phase. The transport of gas-phase matter through the gas-liquid interface is of crucial importance for many planetary processes. For example, the geochemical cycling of climate and health related gases involves exchange between the atmosphere and the ocean via the air-sea interface. In particular, absorption of carbon dioxide by the ocean slows the rate of anthropogenic global warming and is contributing to the decreasing pH of the oceans [125].

Due to the macroscopic scale of the system, a flux of matter through the gas-liquid interface raises fundamentally different questions than an individual gas collision with a liquid surface. Of particular interest in this chapter is the question ‘What is the relative contribution of a temperature gradient and a pressure gradient in the gas-liquid interface in driving a flux of gas through the interface?’ The intuitive answer is that the pressure gradient would make the overwhelming contribution, however for a large body of water such as a lake or an ocean, the temperature difference across the interface could be substantial and long lived. Nonetheless, field studies of air-sea exchange often assume that the gas flux $J$ through the interface is proportional to the pressure difference between a layer of gas immediately above the surface ($p_s$) and in the bulk liquid ($p_b$), namely
\[ J = k (p_b - p_s), \quad (8.1) \]

where \( k \) is a constant known as the transfer velocity [125]. In practice, values of \( k \) obtained from (8.1) from experimental data are widely scattered when plotted against wind speed (see, for example, reference [62]), so it is likely that some important variables, such as a temperature difference across the air-sea interface, are neglected. It could therefore be the case that (8.1) provides too simplistic a view of air-sea exchange.

This chapter describes work which directly measures the relative contributions of a temperature gradient and a pressure gradient in driving a flux of nitrous oxide through a water surface. The problem is approached thermodynamically, by treating the gas-liquid interface as a non-equilibrium system and applying a gas-flux equation which, unlike (8.1), contains both a pressure gradient and a temperature gradient term. A key feature of this equation is that it contains a coefficient which gives the relative importance of the two gradients. The problem is then one of setting up the system in the laboratory in a way that this coefficient can be measured. Section 1 reviews irreversible thermodynamics as it applies here, and section 2 discusses the essential experimental apparatus and some earlier measurements for other systems. Section 3 describes efforts to extend these measurements to the cases of nitrous oxide and carbon dioxide fluxes through an aqueous surface. While we fall short of completing these measurements, we find unexpected evidence for an interesting surface reaction.

8.1 Irreversible Thermodynamics and the Gas-Flux Problem

Figure 8.1 illustrates the problem at hand. It consists of a box containing a gas phase sitting over a liquid surface. The small region between the liquid surface and the bulk gas is the gas-liquid interface. The bulk liquid and bulk gas are thermostated at different temperatures \( T \) and \( T + \Delta T \), respectively, which generates a temperature gradient across the gas-liquid interface. Furthermore, the pressure of the gas right at the surface of the liquid is \( P \), and differs from the bulk gas-phase pressure, \( P + \Delta P \), which generates a pressure gradient across the interface. These gradients establish heat and matter fluxes through the gas-liquid interface. The interface constitutes the system of the problem and, due to the presence of heat and matter fluxes, exchanges heat and matter with its surroundings (the bulk gas and underlying liquid). We wish to determine the contribution that the temperature gradient makes to the magnitude of the matter flux.
Figure 8.1: A diagram illustrating the gas flux problem, showing a gas-phase (white region) sitting over a liquid phase (grey region). These phases are isolated from the surroundings by the dark grey walls. The region of the gas-phase between the liquid surface and the dotted line is the gas-liquid interface. The size of the interface has been exaggerated in this diagram for clarity. The temperature of the bulk liquid is $T$, and the temperature and pressure of the gas-phase at the very edge of the liquid surface is $T$ and $P$, respectively. Meanwhile, the temperature and pressure of the region above the interface is kept at $T + \Delta T$ and $P + \Delta P$, respectively, which generates a temperature and a pressure gradient across the gas-liquid interface, and hence a vertical heat flux $J_1$ and a matter flux $J_2$ across the interface.

8.1.1 The linear formulation

We clearly cannot approach the gas flux problem in Figure 8.1 by means of equilibrium thermodynamics. Equilibrium thermodynamics applies to equilibrium states, which are defined as the time independent states of a system which result when all constraints on the system are removed. In the case of the gas flux problem, removal of the pressure and temperature difference constraints will cause the system to transit to another state, and therefore the present state is not an equilibrium state. Nonetheless, in order to appreciate the following framework for irreversible thermodynamics, it is worth recalling the essential methods of equilibrium thermodynamics. Equilibrium thermodynamics supposes that equilibrium states can be characterised by the internal energy of the system, as well as by a set of state variables, such as temperature and pressure. By application of the first, second and third laws, we obtain relationships between the state variables and hence a means to measure the state variables in the laboratory.

Everyday experience suggests that state variables such as pressure and temperature should be understood as time- and space dependent fields in a non-equilibrium system such as in Figure 8.1. However, on their own, the familiar laws of equilibrium thermodynamics are inadequate for dealing with field variables and generating relationships between them. Therefore, frameworks for irreversible thermodynamics must introduce additional postulates to supplement the laws of equilibrium thermodynamics. While modern physics lacks a complete, unified framework of irreversible thermodynamics [81], the simple linear
framework developed by Onsager and others between early and mid last century will be adequate for tackling the gas flux problem. Here, it is proposed that the flux of heat \( J_1 \) (units of \( \text{J s}^{-1} \text{m}^{-2} \)) and flux of matter (units of \( \text{mol s}^{-1} \text{m}^{-2} \)) are linear functions of thermodynamic forces,

\[
\begin{align*}
J_1 &= L_{11}X_1 + L_{12}X_2 \\
J_2 &= L_{21}X_1 + L_{22}X_2
\end{align*}
\]  

(8.2)

where \( X_1 \) is the thermodynamic force for the heat flux, and \( X_2 \) is the thermodynamic force for the matter flux, and the \( L_{ij} \) are constant coefficients set by the system. While the nature of the thermodynamic forces are not clear from (8.2) alone, it can be seen that the key feature of these equations is that both fluxes depend on both driving forces. The meaning of the thermodynamic forces is clarified by the second postulate, which introduces entropy into the framework in a similar way that second law introduces entropy into equilibrium thermodynamics:

\[
T \frac{dS}{dt} = J_1X_1 + J_2X_2,
\]

(8.3)

where \( T \) is the temperature at the reference end of the temperature gradient and \( \delta \) the width of the region of interest. For the gas flux problem, \( T \) is taken as the temperature right at the liquid surface and \( \delta \) as the width of the gas-liquid interface. The quantity \((dS/dt)/\delta\) is the rate of entropy production per unit length by the fluxes \( J_1 \) and \( J_2 \). The postulate in (8.3) is a thermodynamic analogue of the mechanical definition of work \((\text{work} = \text{distance} \times \text{force})\), and shows that the effect of the fluxes is to turn useful energy into heat, and thus generate entropy. In other words, the fluxes are the ‘irreversible’ feature of the system. In particular, when the fluxes or forces are absent from the system, entropy production is minimised and the system is in an equilibrium state. The third postulate, which Onsager famously proved from considerations of microscopic reversibility, expresses a symmetry in the coupling of the heat force to the matter flux and of the matter force to the heat flux,

\[
L_{12} = L_{21}.
\]

(8.4)

Equations (8.2), (8.3) and (8.4) complete the formulation of linear irreversible thermodynamics. The linear framework holds for systems ‘close to equilibrium’. How close a system needs to be to equilibrium in order for the linear framework to be sufficient is not clear, however it is well known that many transport processes can be adequately described by linear laws [81]. The gas flux problem in Figure 8.1 is certainly expected to fall within this category [19, 20].
8.1.2 The heat of transport and the gas flux equation

We now introduce the quantity $Q^*$, the heat of transport, which will play the key role in determining the relative contributions of a temperature gradient and a pressure gradient in generating a flux of matter through the gas-liquid interface. The heat of transport is the heat carried per mole of material transported through a region of width $\delta$ in the absence of a temperature gradient. There are a variety of ways to derive an expression for the heat of transport (see references [18] and [20], for instance), however the most simple is to add a fourth postulate to the linear formulation,

$$L_{12}X_2 = Q^* J_2. \quad (8.5)$$

To see that this expression fits our definition of $Q^*$, we need expressions for the heat and matter forces. Plausible expressions are derived in the Appendix of this chapter. There, it is shown that for the case of gradients in the vertical direction only,

$$X_1 = -\frac{1}{T} \frac{\Delta T}{\delta}, \quad (8.6)$$

and

$$X_2 = -\frac{RT}{P} \frac{\Delta P}{\delta} \quad (8.7)$$

where $R$ is the gas constant. Thus, as might have been expected, the heat and matter forces are related to temperature and pressure gradients $\Delta T/\delta$ and $\Delta P/\delta$, respectively. Now, substituting (8.5) and (8.6) into (8.2) and taking the limit $\Delta T \to 0$ gives

$$Q^* = J_1 / J_2, \quad (8.8)$$

which matches the definition for $Q^*$ given above. Note that taking the limit $\Delta T \to 0$ is allowed in the linear formulation because it is assumed that the temperature gradient contributes to the matter flux even when it is very small.

In order to derive a useful gas flux equation in terms of $Q^*$, we again consider the limit $\Delta T \to 0$. Substituting (8.5) and (8.6) into (8.2) and taking the limit gives

$$Q^* = L_{12} / L_{22}, \quad (8.9)$$

which shows that $Q^*$ can be also interpreted as the relative contribution of the heat force to the matter force in producing a flux of gas through the gas-liquid interface in the limit of zero temperature gradient. Substituting (8.6), (8.7) and (8.9) into the equation for $J_2$ in (8.2) gives the gas flux equation,

$$J_2 = -\frac{L_{22}RT}{\delta} \left( \frac{Q^*}{RT} \frac{\Delta T}{T} + \frac{\Delta P}{P} \right). \quad (8.10)$$

The key feature of the gas flux equation (8.10) which is missing from (8.1) is that the
gas flux explicitly depends upon both the temperature gradient and the pressure gradient. Moreover, the contribution made by the temperature gradient over the pressure gradient in producing the gas flux is given by the weighting factor $Q^*/RT$. This is the coefficient that was alluded to earlier, and is the quantity that we wish to determine experimentally.

In order to measure $Q^*/RT$, we consider the special case of a stationary state, in which $J_2 = 0$. The gas flux equation then yields the expression

$$\frac{Q^*}{RT} = -\frac{T \Delta P}{P \Delta T}.$$  \hspace{1cm} (8.11)

How to obtain a stationary state will be discussed in the next section. Equations equivalent to (8.10) and (8.11) were obtained by Denbigh and Raumann in 1952, who used them to determine $Q^*$ for a variety of gases passing through natural rubber membranes at room temperature [19, 20]. For these systems, $Q^*$ turned to be rather small, in the order of 1 - 2 kJ mol$^{-1}$, making the fraction $Q^*/RT$ smaller than unity. We will find that the situation is quite different for the case of a flux through the gas-liquid interface.

8.2 Measuring the Heat of Transport

8.2.1 Apparatus and procedures

A scale cross section of the cylindrical, 15 cm diameter stainless steel apparatus for measuring heats of transport is shown in Figure 8.2. It is a new version of several older models, each of which have been discussed in detail elsewhere [69, 68, 41, 42, 99, 86]. As with all previous models, the current apparatus was built by Danny Leonard at the Department of Chemistry. It consists of a gap for gas-phase material sitting over a reservoir containing the liquid of interest. The temperatures of the upper plate and lower plate are controlled by a computer program (written by Leon Phillips) which balances the cooling effect of a flow of antifreeze through the upper and lower regions of the apparatus (not shown in the diagram) against the output of two sets of cartridge heaters. The temperatures of the two plates are monitored with PT100 platinum resistance thermometers. When the temperatures of upper and lower plate are set, the temperature gradient across gas-liquid interface is fixed by the temperature of the upper plate and the liquid acquires the temperature of the lower plate. In previous versions of the apparatus, the depth of the liquid reservoir was only 3 mm. However, due to the relatively low solubility of N$_2$O and CO$_2$ in water, the depth has been increased to 30 mm in this apparatus to ensure that the aqueous concentration of these species remains essentially constant during the experiment. A magnetically driven stirrer ensures that the composition of the liquid is uniform during the experiment. By vigorously stirring the solution, we can also assume that the whole liquid volume acquires the temperature of the lower plate. The entire assembly is surrounded by a vacuum jacket, which isolates the gas and liquid phases from the surroundings. The liquid enters the cell via a bellows valve leading to a liquid reservoir. In all cases, the liquid
Figure 8.2: Diagrammatic cross section of the stainless steel apparatus for measuring heats of transport. The diameter of apparatus is 15 cm. 1. Reservoir containing a liquid. 2. Gap for the gas. 3. Tube to baratron and vacuum line *via* a bellows valve. 4. Stirrer. 5. Magnetic rotary. 6. Tube to external reservoir *via* a bellows valve. 7. Vacuum jacket. 8. Tube to vacuum line. 9. Tilted IR transmitting windows. 10. Hole for cartridge heater. 11. Upper plate. 12. Lower plate. 13. Hole for platinum resistance thermometer. Not shown in the diagram are the cavities situated above the upper plate and below the lower plate, through which coolant flows. Diagram drawn by Leon Phillips.
was thoroughly degassed before being introduced into the cell by repeatedly freezing it under vacuum, pumping off expelled gases via a vacuum pump, and boiling the liquid. Gases were introduced into the cell via a valve leading to an external bulb. Before entry into the cell, the gases were purified by freezing them in a cold finger and pumping off impurities.

Having set the liquid and bulk gas phases to different temperatures, a temperature gradient develops across the gas-liquid interface. This causes a net flux of gas towards (or away from) the liquid surface, however the flux is not sustained because eventually the molecules in the gas phase redistribute and adjust to the temperature gradient. The system then reaches a stationary state and equation (8.11) applies. Thus, to measure $Q^*/RT$ from (8.11), the lower plate is set to a temperature $T$, the upper plate to a temperature $T + \Delta T$, and the pressure of the bulk gas is measured once it reaches a stable value, which corresponds to the onset of the stationary state. This procedure is repeated for several $\Delta T$, and a plot of cell pressure against $\Delta T$ is drawn. Assuming $\Delta T$ to be small enough for the linear regime to hold, this plot will produce a straight line with slope $\Delta P/\Delta T$ and intercept $P$, which allows $Q^*$ and $Q^*/RT$ to be explicitly calculated via (8.11) [69, 68, 41, 42, 99, 86].

In the case of N$_2$O and CO$_2$ fluxes and a water surface, the pressures of interest are much smaller than the pressure of water vapour, and therefore straight baratron measurements are inappropriate for determining partial pressures for use in equation (8.11). For these cases, pressure measurements are replaced by integration of a rotational line obtained by directing a beam from a high resolution infrared diode laser (single mode, 0.0007 cm$^{-1}$ nominal bandwidth, Laser Components GmbH) through the windows of the cell. A diagram of the laser spectroscopy system is shown in Figure 8.3. The windows are made of
barium fluoride (Laser Components), and are tilted to avoid etalon fringes that would be produced by parallel windows. The interior of these windows are coated with SiO$_2$ (coating by NDC Infrared Engineering) to prevent the build-up of water condensation during the experiment. The procedure for measuring areas of rotational lines is illustrated in Figure 8.4 for the case of the R17 line of the $(0,1,0) \leftarrow (0,0,0)$ band of nitrous oxide. Graph A in this figure shows the spectrum, as viewed on an analog oscilloscope (Fluke Combiscope in analog mode) with the chopper interrupting the beam asynchronously. This scan was used to measure the baseline-to-peak amplitude of the signal. Graph B plots the spectrum without the chopper running after averaging over 4096 scans and downloading 32768 data points from the scope, and shows four markers which are placed at desired points on the spectrum. The middle two markers are chosen so that the peak lies between them. Graph C shows a 5$^{th}$ order polynomial fit to the four markers, which is used to estimate the shape of the spectrum in the absence of the peak. Graph D plots the region between the inner two markers (the peak) as absorbance ($\ln(I_0/I)$, where $I_0$ is the measured current across the peak and $I$ the baseline current) as a function of $I_0$, which is integrated by summing the absorbance of every point across the spectrum. For this integration, the same number of points (6400) was used from each scan. Note that the plots themselves contain 512 points which are averaged over 64 points from the raw data; the actual calculation of the peak areas used all of the raw data. The analysis program was written by Leon Phillips and runs in a Chipmunk Basic interpreter.
8.2.2 Summary of results from previous studies

Figure 8.5 shows a typical plot of $P$ against $\Delta T$ for water vapour over a 0°C liquid water surface, obtained working downward from large $\Delta T$ to small $\Delta T$ [99]. An important feature of this plot which is seen in many other systems is the presence of two linear regions. The first linear region (marked 1) corresponds to cool-to-warm distillation, which results in condensation of liquid on the upper plate. Cool-to-warm distillation occurs because a film of water that is adsorbed to the upper plate experiences a negative temperature gradient, which lowers its effective vapour pressure relative to the vapour pressure of the water in the reservoir. During the second linear region (marked 2), the upper plate is too warm for condensation to occur, and there is a temperature jump between the gas-phase and the upper plate. Values of $Q^*$ derived from this region will be erroneous, because the gas has a lower temperature than the upper plate. Measurements are therefore obtained from the first region, although they are subject to some error because slow condensation onto the upper plate means that the system is not quite in a stationary state. Measurements are usually taken in order of decreasing $\Delta T$ so that the transition from the second linear region to the first is clear. For this system, $Q^*$ turns out to be 24.3 kJ mol$^{-1}$, which corresponds to $|Q^*/RT| \sim 10.6$. In other words, a temperature gradient is over ten times more important than a pressure gradient in producing a flux of water vapour through the vapour-water interface! These large values of $Q^*/RT$ are not uncommon, as can be seen from Table 8.1, which lists all published measurements so far.

An equivalent definition of the heat of transport is as the energy released at the edge of the bulk gas and absorbed at the edge of the bulk liquid as material is transported through the interfacial region. We might therefore expect that the heat of transport
would have a similar magnitude to the latent heat of vaporisation of the liquid. In fact, heats of transport for single component systems are often comparable to the latent heat of vaporisation, with the comparison becoming stronger as the number of mean free paths in the gas-phase gap (and hence in the interfacial region) decreases. This is demonstrated in Figure 8.6 for the case of \( n \)-heptanol vapour over an \( n \)-heptanol surface [68]. The number of mean free paths in the gap can be calculated from the pressure of the \( n \)-heptanol vapour and its collision diameter. The result is sensible because only material that is within a few mean free paths of the surface should be influenced by processes which occur at the surface. Similarly, if a sufficiently endo- or exothermic chemical reaction occurs between the molecules of the gas flux and surfactants on the liquid surface, then we might expect the heat of transport to have a comparable magnitude to the heat of the reaction.

A particularly important result was found when studying ammonia over a water surface, namely that exposure of the cell to high pressure ammonia (\( \sim 1 \) atmosphere) conditioned the upper plate so that region 2 in the plots of \( P \) against \( \Delta T \) did not occur [15]. The conditioning remained after pumping on the cell to remove the ammonia gas, and could only be completely eliminated by setting the upper and lower plate to very high temperatures (\( > 40^\circ C \)) and pumping on the cell over several days. In the following work with nitrous oxide and carbon dioxide, we take advantage of this observation and condition the cell walls before starting the experiment. This was achieved by filling the cell with \( \sim 1 \) atmosphere of ammonia, leaving the apparatus overnight for the ammonia to condition

| System          | \( Q^\star \) (kJ mol\(^{-1}\)) | \( T \) (\(^\circ C\)) | \( |Q^\star/RT| \) | Reference |
|-----------------|-------------------------------|------------------------|-----------------|-----------|
| Aniline         | -15 to -40                    | -5                     | 7 to 18         | [69]      |
| \( n \)-Heptanol| -36 to -57                    | -7                     | 16 to 26        | [68]      |
| \( H_2O / H_2SO_4 \) | -10                           | -29                    | 5               | [41]      |
| \( H_2O \)     | -28                           | 2                      | 10.6            | [99]      |
| \( n \)-octane | -32                           | 3                      | 14              | [96]      |
| \( NH_3 / H_2O \) | -7.7                          | 10                     | 3.3             | [15]      |

Table 8.1: Summary of heats of transport measured for various one- and two component systems. The two component systems have been written in the left hand column as gas / liquid.
the cell, and then pumping the cell out to about 0.05 Torr with a liquid nitrogen trapped Welch 1397 rotary pump.

Before moving on, it should be noted that there is no satisfactory molecular or statistical theory that provides a general account of these observations. It is very difficult to give even a qualitative molecular interpretation of the heat of transport without embarking on a long-winded and confusing discussion. For this reason, we avoid rationalising our values of $Q^*$ with molecular pictures. However, when we go to measure $Q^*$ for a CO$_2$ flux, it will be easy to explain its value in terms of a surface reaction.

### 8.3 Heat of Transport Measurements for N$_2$O and CO$_2$

Due to the importance of air-sea exchange of carbon dioxide, measurements of $Q^*$ for a carbon dioxide flux through the surface of water would be useful to test the suitability of equation (8.1). However, there are certain experimental difficulties with such measurements. For example, background IR absorption by atmospheric CO$_2$ needs to be accounted for, and the strong dependence of CO$_2$ solubility on pH could require impractically long waiting times between measurements. Moreover, the solution chemistry of CO$_2$ might interfere with our measurements of $Q^*$ in a way which is very sensitive to the temperature of the bulk liquid.

For these reasons, we first consider the case of a nitrous oxide flux through an aqueous surface. As well as being free of the above issues, nitrous oxide is expected to be a good model system for carbon dioxide. For instance, CO$_2$ and N$_2$O have identical masses and molecular geometries, similar Henry’s law constants ($7.00 \times 10^{-5}$ M Torr$^{-1}$ and $9.73 \times 10^{-5}$ M Torr$^{-1}$, respectively) and enthalpies of solution (-25.5 and -26.6 kJ mol$^{-1}$, respectively) [86]. Hence, by starting with N$_2$O we can focus on problems of IR absorption measurements, rather than distracting side issues.

#### 8.3.1 N$_2$O measurements

Figure 8.7 plots measurements of peak area against $\Delta T$ for the R27 line in the $\sim 2200$ cm$^{-1}$ (0,0,1)$\rightarrow$(0,0,0) band of N$_2$O (as shown in Figure 8.4). The measurements presented here were acquired jointly with Leon Phillips. During this experiment, the liquid temperature was held at $2.00 \pm 0.01^\circ$C, and the Julabo cooling bath set at $-10^\circ$C. The stirrer ran near 100 rpm and around 12 hours were allowed for the system to reach a stationary state after the temperature of the upper plate had been set. The points were measured in a random order so that any systematic drift due to a gradual pressure rise would be converted into random deviations. The interior of the cell was conditioned with ammonia prior to the experiment to eliminate the onset of the knee, as described at the end of the previous section.
Figure 8.7: Plot of $R_27$ line area for $N_2O$ over a 2 °C aqueous surface as a function of temperature difference $\Delta T$ across gas-phase gap. Figure by Leon Phillips.

A least squares fit to the data in Figure 8.7 gives an intercept of $11.47 \pm 0.13$, a slope of $0.12 \pm 0.02$, where the errors are 95% confidence limits. This gives $Q^* = -6.42 \pm 0.83$ kJ mol$^{-1}$, and hence $|Q^*/RT| = 2.81 \pm 0.36$. While this value of $|Q^*/RT|$ is smaller than measurements from other systems, it is still almost three times larger than unity. It is therefore the temperature gradient, and not the partial pressure gradient, which makes the dominant contribution to a flux of nitrous oxide through the water-water vapour interface. If a similar measurement is obtained for a carbon dioxide flux at a pH of 8.3 (the typical pH of the ocean [57]), then it will suggest that the air-sea temperature difference can have a significant effect on the local rate of absorption of $CO_2$ by the ocean, and in turn that equation (8.1) is an inadequate for such measurements.

### 8.3.2 CO$_2$ measurements

An attempt for extend these measurements to the case of a carbon dioxide flux yielded very large values of $Q^*$, which in turn suggested that we were measuring the heat of a reaction between carbon dioxide and surfactant ammonia. Ammonia forms a monolayer on a water surface [66] and is highly soluble. Moreover, during the experiment the pressure of the cell would gradually rise ($\sim 0.2 - 0.5$ Torr per day), suggesting that ammonia was slowly desorbing into the gas gap and adsorbing to the water surface. It is therefore reasonable to suppose that the carbon dioxide flux reacts with the ammonia monolayer as it passes through the liquid surface.

The method was identical to the one described above for nitrous oxide. To minimise interference by atmospheric carbon dioxide, 99 atom % $^{13}CO_2$ (Icon Isotope Services) was
Figure 8.8: Figure A shows a scan across R40 line of $^{13}$CO$_2$ for a 5.1 $^\circ$C solution and a 5 $^\circ$C temperature difference across gas-phase gap. The markers and polynomial fit from the peak area analysis are shown. Figure B shows the same peaks measured with various temperature differences across the gas-phase gap. From top to bottom, $\Delta T = 5, 4, 3, 2, 1$ and 0 $^\circ$C. Figures created by Leon Phillips.
used and the R40 line at 2310.348 cm$^{-1}$ in the (0,0,1) ← (0,0,0) band (which is sufficiently far from any $^{12}$CO$_2$ lines) was scanned. Absorption due to atmospheric $^{13}$CO$_2$ was very weak and pressure broadened, and did not notably change the shape of the absorption line. Only $\sim$ 2 hours were needed for the system to reach a stationary state. This was expected, because the liquid is likely to have contained a large amount of ammonium bicarbonate, which allows the liquid phase to quickly adjust to new temperatures due to its relatively fast decomposition kinetics. Figure 8.8a shows a typical scan across the absorption line with the lower plate temperature ($T$) at 5.1 $^\circ$C and the upper plate temperature ($T + \Delta T$) at 5 $^\circ$C, and Figure 8.8b plots ln($I_o/T$) for the same line with the lower plate at 5.1 $^\circ$C at various $\Delta T$. As Figure 8.8b shows, the variation in CO$_2$ partial pressure with $\Delta T$ is very large, and consequently a plot of peak area against $\Delta T$ was not linear, but had a gentle upwards curve. As will be seen in the appendix of this chapter, the expression for $X_2$ in (8.7) assumes that the ratio $\Delta P/P$ is very small, and that this ratio is better represented by $\Delta \ln P$ when the variation in pressure is larger. The corresponding stationary state equation is (cf. (8.11))

$$\frac{Q^*}{RT} = -T \frac{\Delta \ln P}{\Delta T}.$$  

The calculation of $Q^*$ now involves plotting $\Delta \ln P$ against $\Delta T$, which should give a straight line with slope $\Delta \ln P/\Delta T$. Figure 8.9 presents such a plot for the peaks in Figure 8.8b. The data in Figure 8.8b are representative of typical results. Figure 8.10 plots $Q^*$ measurements for surface temperatures 0.1, 5.1 and 10.1 $^\circ$C as a function of time elapsed since the first measurement. The error bars are 95% confidence limits for the slope of the line of the $\Delta \ln P - \Delta T$ plots. We see no significant trend with lower plate temperature, but do see that the measured values of $Q^*$ tend to decrease with time. This is probably due to a decrease in ammonia monolayer coverage on the water surface, due to ammonia desorbed from the stainless steel walls eventually dissolving into the aqueous phase. This explanation agrees with the high pH of the liquid that was measured at the end of these experiments (9.04). We therefore consider the earlier results to be the most accurate, which give $Q^* = -180$ kJ mol$^{-1}$, with an error in the order of $\pm 10$ kJ mol$^{-1}$.

This measurement is an order of magnitude larger than the one measured for nitrous oxide, and it is clear that a carbon dioxide flux partakes in a different set of processes as it dissipates heat and accommodates into the water bulk. Our explanation is that CO$_2$ undergoes a reaction with the NH$_3$ of the surface monolayer to form ammonium carbamate,

$$2\text{NH}_3(\text{adsorbed}) + \text{CO}_2(\text{g}) \rightarrow \text{NH}_4\text{CO}_2\text{NH}_2(\text{adsorbed}) \quad (8.12)$$

and the heat of this reaction is incorporated into $Q^*$, just as the enthalpy of vaporisation is incorporated into $Q^*$ in single component systems. We assume that the heat of the reaction in (8.12) accounts for almost all of the heat dissipation encapsulated by $Q^*$.  

143
Figure 8.9: Natural logarithm of $^{13}$CO$_2$ peak area as a function of temperature difference across gas-phase gap, with a solution temperature of 5.1 °C. Figure created by Leon Phillips.

Figure 8.10: Measured values of $-Q^*$ as a function of time elapsed since the first measurement. Filled circles are for $T = 0.1$ °C, filled squares are for $T = 5.1$ °C and unfilled circles are for $T = 10.1$ °C. Figure created by Leon Phillips.
Indeed, Figure 8.11 presents a thermodynamic cycle that relates the value of $Q^*$ to the heat of reaction of $\text{NH}_3(g)$ and $\text{CO}_2(g)$ ($\Delta H_0$), the heat of adsorption of $\text{NH}_3(g)$ on water ($q_1$) and the heat of transferring ammonium carbamate from the solid (crystalline) state to the adsorbed state on a water surface ($q_2$). Now, the heat of transport for ammonia at the surface of water should mainly be a measure of $q_1$, so we take $q_1 = -7.7 \pm 2.8 \text{ kJ mol}^{-1}$ (Table 8.1). According to reference [1], $\Delta H_0 = -159.4 \text{ kJ mol}^{-1}$. Combining these values with our measured value of $Q^*$ gives $q_2 = -36 \pm 16 \text{ kJ mol}^{-1}$, which is within error of a reasonable heat of adsorption ($\sim 5$ to $20 \text{ kJ mol}^{-1}$).

8.3.3 Final remarks

While we did not manage to measure $Q^*$ for a carbon dioxide flux through an aqueous surface, we did show that measurements of the heat of transport can be potentially useful for studying the energetics of surface reactions. As will be discussed in the next chapter, reactions which occur at the surfaces of liquids are only beginning to be studied experimentally, so the results presented in this chapter could be very useful. However, these results should only be taken as an exploratory step in this direction. For instance, if we were to study the reaction in (8.12) in detail, then we would need to use a known ammonia monolayer coverage at the liquid surface, and would have to introduce a known amount of carbon dioxide into the apparatus.

Measurements of $Q^*$ for transfer of carbon dioxide through an aqueous surface remain the desired result of this research. Work in this direction has just began, and this time will be performed without prior conditioning of the cell walls with ammonia gas. This will require peak area measurements at small $\Delta T$. This will be difficult because the increased tendency for water to condense onto the windows of the cell under these conditions diminishes the intensity of the beam. It is expected that $Q^*$ for carbon dioxide at the surface of water will be close to the value reported above for nitrous oxide, $\sim 6.5 \text{ kJ mol}^{-1}$. If this is the case then there will be good reason to doubt the applicability of the gas flux equation in (8.1) to the problem of air-sea exchange of carbon dioxide.
8.4 Appendix

The purpose of this section is to show how the forces $X_1$ and $X_2$ in equations (8.6) and (8.7) are obtained from the entropy generation equation (8.3). The framework for irreversible thermodynamics that is developed in section 8.1.1 assumes that we have an expression for $dS/dt$ available a priori. This situation is familiar from equilibrium thermodynamics. For instance, deriving the expression $w = -nRT\ln(V_f/V_i)$ for the isothermal reversible expansion of an ideal gas requires knowing the equation of state for an ideal gas. In our case, we need to find an expression for entropy generation which is appropriate for the gas flux problem in Figure 8.1. The expression used in this work was developed by Denbigh, and is clearly inspired by problems from fluid dynamics [18]. Consider a small region of fixed volume and mass in a fluid mixture (such as a volume of the gas-liquid interface), across which heat and matter flows occur. The differential of the internal energy $U = U(S, V, n_1, \ldots, n_k)$ of this region is

$$dU = TdS + \sum_{i=1}^{k} \mu_i dn_i,$$

where $\mu_i$ is the chemical potential of species $i$ in the region and $n_i$ is the amount of species $i$ in the region. The term $-pdV$ does not appear because the region is of fixed volume. This equation can be rewritten as

$$du = Tds + \frac{1}{\rho} \sum_{i=1}^{k} \mu_i dc_i$$

(8.13)

where $c_i$ is the concentration of species $i$ in the region, $\rho$ is the density of the region, and $u$ and $s$ are, respectively, the internal energy and entropy in the region per unit mass of material. The derivation proceeds by developing balance equations for the energy and mass in the region, and then uses them in combination with (8.13) to obtain an expression for $dS/dt$.

8.4.1 Energy balance equation

The internal energy of a small element of volume $dV$ in the region is $\rho udV$, and therefore the total internal energy of the region is

$$u = \int_{\mathcal{F}} \rho u dV,$$

where $\int_{\mathcal{F}} \cdots dV$ denotes a volume integral. The rate of change of internal energy of the region is the rate at which energy enters or leaves the region by crossing the containing surface $\mathcal{F}$. Let $E$ denote an energy flow vector, which is the rate of total energy flow across an arbitrary unit area of the surface, which is taken as positive for outward flow of energy from the region. Let the vector $dA$ be an element of the surface. The magnitude of this
vector is the area of the surface element, and its direction corresponds to the orientation of the element. The energy passing through the element \( d\mathbf{A} \) is \( \mathbf{E} \cdot d\mathbf{A} \), and the total energy leaving the region per unit time is

\[
\int_{\mathcal{S}} \mathbf{E} \cdot d\mathbf{A},
\]

where \( \int_{\mathcal{S}} (\cdots) \cdot d\mathbf{A} \) denotes a surface integral. By the law of conservation of energy, the rate of change of energy in this region must be equal and opposite to the rate at which energy enters or leaves the region, namely

\[
\frac{d}{dt} \int_{\mathcal{V}} \rho u \, dV + \int_{\mathcal{S}} \mathbf{E} \cdot d\mathbf{A} = 0.
\]

By Gauss’s theorem, the surface integral \( \int_{\mathcal{S}} \mathbf{E} \cdot d\mathbf{A} \) is equal to the volume integral \( \int_{\mathcal{V}} \text{div} \mathbf{W} \, dV \). The above equation can then be rewritten as

\[
\int_{\mathcal{V}} \left( \rho \frac{du}{dt} + \text{div} \mathbf{W} \right) \, dV = 0.
\]

Since the volume of the region is arbitrary, the integrand must be zero everywhere. This gives a balance equation for energy,

\[
\rho \frac{du}{dt} + \text{div} \mathbf{W} = 0.
\]  

(8.14)

### 8.4.2 Mass balance equation

The mass balance equation expresses conservation of mass for each species in the volume, much like the continuity equation (2.1) from Chapter 2. The amount of species \( i \) contained in the region is

\[
\int_{\mathcal{V}} c_i \, dV
\]

Let \( \mathbf{F}_i \) the the rate at which species \( i \) flows across an arbitrary element of the surface \( \mathcal{S} \) of the region. This vector is taken as positive for outward flow of material from the region. Assuming no chemical transformation (i.e., no creation of material in the region),

\[
\frac{d}{dt} \int_{\mathcal{V}} c_i \, dV + \int_{\mathcal{S}} \mathbf{F}_i \cdot d\mathbf{A} = 0.
\]

By employing Gauss’s theorem as before, we obtain a balance equation species \( i \) in the region,

\[
\frac{dc_i}{dt} + \text{div} \mathbf{F}_i = 0.
\]  

(8.15)
8.4.3 Entropy generation equation

Equation (8.13) can be rewritten as

$$\frac{ds}{dt} = \frac{\rho}{T} \frac{du}{dt} - \sum_{i=1}^{k} \mu_i dc_i.$$  

With (8.14) and (8.15) we obtain

$$\frac{ds}{dt} = \frac{-1}{T} \text{div } E + \sum_{i=1}^{k} \frac{\mu_i}{T} \text{div } F_i. \quad (8.16)$$

Recall that, if $x$ is a vector and $a$ a scalar,

$$a \text{ div } x = \text{div } ax - x \cdot \text{grad } a.$$  

(8.16) can be then rewritten as

$$\frac{ds}{dt} = -\text{div } \frac{E}{T} + \frac{E}{T} \cdot \text{grad } \frac{1}{T} + \sum_{i=1}^{k} \frac{\mu_i F_i}{T} - \sum_{i=1}^{k} F_i \cdot \text{grad } \frac{\mu_i}{T}.$$  

This equation can be rewritten as

$$\rho \frac{ds}{dt} + \text{div } z = \theta \quad (8.17)$$

where

$$z = \frac{1}{T} \left( E - \sum_{i=1}^{k} \mu_i F_i \right)$$

and

$$\theta = E \cdot \text{grad } \frac{1}{T} - \sum_{i=1}^{k} F_i \cdot \text{grad } \frac{\mu_i}{T}. \quad (8.18)$$

Equation (8.17) is an equation for the rate of creation of entropy due to the irreversible heat and matter fluxes. To clarify its interpretation, we employ Gauss’s theorem once again,

$$\frac{d}{dt} \int_{V} \rho s \, dV + \int_{\partial V} z \cdot dA = \int_{\gamma} \theta \, dV$$

This expression must hold in the case of an isolated system. For an isolated system, $E$ and $F_i$, and hence $z$, are zero (more precisely, null vectors), and hence

$$\frac{d}{dt} \int_{V} \rho s \, dV = \int_{\gamma} \theta \, dV.$$  

This equation shows that the rate of entropy production in the region is equal to the
volume integral over the quantity $\theta$. We can finally identify $\theta$ as the rate of entropy production per unit volume of the region due to the irreversible fluxes in the system. The same interpretation must hold even when the system is open to its surroundings. Hence $\theta$ in equation (8.18) is equal to $(dS/dt)/V$, entropy production per unit volume, in postulate (8.3). Note that (8.3) is written as entropy production per unit length, and holds for the case of fluxes with components along the vertical axis only.

To obtain expressions for the forces $X_1$ and $X_2$, multiply (8.18) by $T$ and set the result equal to $\sum_i J_i \cdot X_i$, as in (8.3). This gives

$$\sum_{i=1}^{k+1} J_i \cdot X_i = E \cdot T \, \text{grad} \left( \frac{1}{T} \right) - \sum_{i=1}^{k} F_i \cdot T \, \text{grad} \left( \frac{\mu_i}{T} \right).$$

For the case of only two fluxes (heat flow and matter flow of a single component), $k = 1$, and we can identify the thermodynamic forces as

$$X_1 = T \, \text{grad} \left( \frac{1}{T} \right) \quad \text{and} \quad X_2 = -T \, \text{grad} \left( \frac{\mu}{T} \right).$$

$X_1$ can be rewritten as $-(1/T) \, \text{grad} \, T$. We now consider the case of the forces and fluxes having components only along the vertical $y$ axis, as in the gas flux problem of Figure 8.1. If the height of this region, $\delta$, is sufficiently small, then $\text{grad} \, T \approx \Delta T/\delta$ and

$$X_1 = -\frac{1}{T} \frac{\Delta T}{\delta}, \quad (8.19)$$

which is the same as (8.6). Since $\mu = \mu_0 + RT \ln P$, where $\mu_0$ is a constant, then

$$-T \, \text{grad} \left( \frac{\mu}{T} \right) = -T \frac{d}{dy} R \ln P = -RT \frac{1}{P} \frac{dP}{dy} \approx -\frac{RT \, \Delta P}{P}. \quad (8.19)$$

This equation assumes that the pressure difference across the region is small compared to $P$. When the variation is large, a better approximation is $-T \, \text{grad} \left( \mu/T \right) \sim -RTd\ln P/dy$. Assuming that $\Delta P$ is sufficiently small, we obtain

$$X_2 = -\frac{RT \, \Delta P}{P}, \quad (8.20)$$

which is the same as (8.7). That completes the derivation of the thermodynamic forces for the gas flux problem.
Chapter 9

Bromine Production from the Oxidation of Sea Salt Aerosol

The last chapter finished by proposing a reaction at the surface of water between adsorbed ammonia and carbon dioxide. This final chapter considers reactions that occur at the gas-liquid interface of an aerosol droplet. For many years, it was widely believed that aerosol chemistry could be understood in terms of familiar gas-phase and aqueous-phase reactions and mass transfer between the phases [27]. Over the last decade, however, evidence has emerged which suggests that interfacial reactions play a substantial role in some atmospherically relevant systems. A good example was found in a joint experimental and computational effort by Knipping et al., in which the reactions of deliquesced sodium chloride aerosol in the presence of ozone were investigated under photolytic conditions [49]. Sodium chloride aerosol serves as a model for sea salt aerosol, which exists in the troposphere and is produced from the action of waves on the ocean surface [57]. The experiments involved a teflon aerosol chamber, into which sodium chloride aerosol and other gases are introduced and from which gas samples are taken at regular intervals. The relative humidity of the chamber is maintained above the deliquescence point of sodium chloride aerosol, and the chamber is thermostatted at room temperature. In this study, chlorine concentrations measured in the chamber could only be reproduced by the aerosol kinetics computer model MAGIC (= Model of Aqueous, Gaseous and Interfacial Chemistry) if the reaction

$$\text{OH}_\text{(g)} + \text{Cl}^-\text{interface} \rightarrow \frac{1}{2}\text{Cl}_2\text{(g)} + \text{OH}^-\text{aq}$$  \hspace{1cm} (9.1)

was included in its mechanism.\textsuperscript{1} This reaction is between a gas-phase hydroxyl radical (produced from the photolysis of ozone in the presence of water vapour) and a chloride ion bound to the surface of an aerosol particle. There are two key results which support

\textsuperscript{1}In this chapter, the word ‘mechanism’ refers to the database of chemical reactions which are included in an aerosol kinetics model, rather than the workings of an individual chemical reaction. This terminology is standard amongst atmospheric modellers.
the role of reaction (9.1). Molecular dynamics simulations of water slabs by Jungwirth and Tobias [43] show that, despite conventional wisdom that ions are stabilised by solvating interactions of the bulk, halide ions prefer to reside at the water interface, with the preference increasing with the polarisability of the ion. In particular, a simulation of a concentrated sodium chloride solution found that chloride ions cover a significant fraction (∼12%) of the surface, with the sodium ions preferring to reside in the bulk [49]. The concept of a surface-bound chloride ion is therefore supported by simulation studies. The second is that reaction (9.1) could be assumed to proceed through a bound \((\text{OH} \cdots \text{Cl})^-\) intermediate, which has been observed in the gas-phase from studies of HCl and N\(_2\)O mixtures [16], meaning that the products could result from plausible self-reaction,

\[
2(\text{OH} \cdots \text{Cl})^- \rightarrow \text{Cl}_2 + 2\text{OH}^-.
\]

Thus, the interfacial reaction (9.1) appears quite reasonable. However, it should be noted that the details of this reaction have not been determined, so (9.1) is best regarded as an heuristic depiction of a presumably multi-step process.

There have been several laboratory studies which have observed gas-phase Br\(_2\) produced from deliquesced sea salt aerosol in the presence of ozone [38, 17]. This is an important observation, because bromine plays a key role in ozone destruction in the upper- and lower atmosphere [27]. Specifically, photolysis of Br\(_2\) produces Br radicals, which react directly with ozone. Although the concentration of bromide ion in a sea salt aerosol droplet is relatively small (∼0.001 M compared to a chloride concentration of ∼0.57 M [57]), the bromine production appears quite efficient. Since simulations predict that the relatively polarisable bromide ion should have a greater preference to reside at the interface than a chloride ion, it is natural to ask whether interfacial reactions such as (9.1) are involved in the production of gas-phase Br\(_2\). To this end, Hunt et al. performed a joint aerosol chamber experiment and computer kinetics modelling investigation to understand the production of bromine from deliquesced NaBr aerosol in the presence of ozone [39]. As in the NaCl study by Knipping et al. described above, the MAGIC model significantly underestimated the Br\(_2\) production seen in the chamber experiments when its mechanism was restricted to known aqueous- and gas-phase chemical reactions. Since Br\(^-\) ions may be oxidised by ozone, Hunt et al. considered an interfacial reaction similar to (9.1),

\[
\text{O}_3(g) + \text{Br}^-_{(\text{interface})} \rightarrow \frac{1}{2} \text{Br}_2(g) + \text{O}_3^-_{(aq)}.
\]  

(9.2)

This interfacial reaction was also proposed by considering formation of an \((\text{O}_3 \cdots \text{Br})^-\) complex at the interface and the possible pathways which could result in gas-phase Br\(_2\) and aqueous O\(_3\). When (9.2) was included in its mechanism, MAGIC was able to reproduce experimental bromine production, providing good evidence that an interfacial reaction such as (9.2) is key to understanding bromine production from the oxidation of deliquesced sea salt aerosol. As with (9.1), the chemical details of (9.2) are currently unknown, and
the overall reaction equation should be taken as the net outcome of a larger process.

Under photolytic conditions, it might be expected that the OH radical could react with surface-bound Br\(^{-}\) ions in a similar way to (9.1),

\[
\text{OH}(g) + \text{Br}^{-}_{(\text{interface})} \rightarrow \frac{1}{2} \text{Br}_2(g) + \text{OH}^{-}_{(aq)}.
\]

(9.3)

However, Thomas \textit{et al.} showed that when included in MAGIC’s mechanism, reaction (9.3) is only a significant contributor to bromine production at very short reaction times [119]. This result contrasts with the case of chlorine production at the surface of an NaCl aerosol, and is consistent with the fact that bulk aqueous-phase oxidation reactions for Br\(^{-}\) are more rapid than for Cl\(^{-}\) [27].

While the MAGIC model of aerosol kinetics has shown that the interfacial reaction (9.2) can account for experimental bromine production from oxidation of deliquesced NaBr, there have been no studies so far into the relative importance of this reaction compared to aqueous- or gas-phase routes of bromine production. Similarly, we have no indication of how important bulk aqueous-phase reactions are compared to (9.3) in the generation of bromine under photolytic conditions, or which particular reactions play the dominant roles. This task is not a simple case of looking at every parameter in the MAGIC model individually and examining its contribution to its bromine output. For one, the number of parameters in MAGIC is too large for this to be practical. MAGIC includes 38 gas-phase rate constants, 122 aqueous-phase rate constants, nine Henry’s law coefficients, nine accommodation coefficients, ten equilibrium constants, a kinetic salt effect parameter and two reaction probabilities for the interfacial reactions (9.2) and (9.3) above. Moreover, each of these parameters interacts with each other in a complicated, nonlinear way, meaning that the contribution of an individual parameter to the net generation of bromine cannot be examined without simultaneously investigating the other parameters.

This chapter describes a sensitivity and uncertainty analysis of the input parameters used by MAGIC in the work of Hunt \textit{et al} and Thomas \textit{et al}. This analysis considers two key questions. How sensitive is MAGIC’s bromine output to each of its input parameters? Which of these parameters contribute the most to the variance in the bromine output? An answer to the first question provides an understanding of which physical and chemical processes make the largest contribution to the production of bromine from an NaBr aerosol, whereas an answer to the second will suggest processes which require further experimental attention, with a view towards improving the accuracy and precision of computational kinetics studies involving the MAGIC model and others. The first section describes the MAGIC model in some detail, and the second introduces the Latin hypercube sampling method, which provides a statistical means to answer the questions posed above. In particular, Latin hypercube sampling allows the bromine output to be examined by simultaneous perturbations in the parameter values, and is fast enough for the large number of parameters to not be a problem. The method employed here is essentially the same as used by Nissenson \textit{et al}. in a similar study of chlorine production from an NaCl
aerosol [78]. The third section presents the key findings for the cases of NaBr aerosol under dark and light (photolytic) conditions. This study was conducted at the University of California, Irvine, in close collaboration with (now Dr.) Paul Nissenson and Professors Barbara Finlayson-Pitts (Department of Chemistry) and Donald Dabdub (Department of Mechanical and Aerospace Engineering).

9.1 The MAGIC Model of Aerosol Kinetics

MAGIC’s job is to calculate the concentrations of various aqueous- and gas-phase chemical species as functions of time, using a set of initial aqueous- and gas-phase concentrations and a library of relevant physiochemical parameters. The MAGIC model also accounts for mass transfer between the two phases, as well as interfacial reactions. The overview presented here is a summarised version of a description given by Knipping and Dabdub elsewhere [48]. MAGIC calculates concentrations by integrating the following rate equations, here written for species $i$.

\[
\begin{align*}
\frac{dC_{g,i}}{dt} &= -k_{m,i} w_L C_{g,i} + \frac{k_{m,i}}{H_i RT} C_{aq,i} + R_{g,i} + R_{int,i} \\
\frac{dC_{aq,i}}{dt} &= k_{m,i} C_{g,i} - \frac{k_{m,i}}{H_i RT} C_{aq,i} + \langle R_{aq,i} \rangle + \frac{R_{int,i}}{w_L}
\end{align*}
\] (9.4) (9.5)

Equations (9.4) and (9.5) describe the production of species $i$ in the gas-phase and just beneath the surface of the aqueous aerosol droplet, respectively. The following sections describe the terms in these equations in detail.

9.1.1 Gas-phase chemistry

The term $R_{g,i}$ in (9.4) is the rate of production of $i$ via gas-phase reactions. The reactions are listed in Table 2 of reference [39] and Table 3 of reference [48]. This list includes all species that the JPL / NASA evaluation panel recommends for models of aerosol kinetics [111]. Photolysis reactions are also included. In the chamber experiments, ozone is photolysed selectively by means of 254 nm mercury lamps. The photolysis rates of gas-phase species at 254 nm are estimated from the experimentally determined rate for ozone in the chamber, and then scaling this value by the ratio of the absorption cross section for the species of interest to the absorption cross section of ozone at 254 nm. This value is then scaled again by the ratio of the quantum yield for photolysis of the species to the quantum yield for photolysis of ozone at 254 nm.

9.1.2 Mass transfer

The first and second terms in (9.4) and (9.5) are the rate of mass transfer of species $i$ from the gas-phase to the aqueous phase, and from the aqueous phase to the gas-phase,
respectively. These involve Schwartz’s mass transfer coefficient $k_{m,i}$ [112], namely

$$\frac{1}{k_{m,i}} = \frac{r_a^2}{3D_{g,i}} + \frac{4r_a}{3v_i\alpha_i}, \quad (9.6)$$

where $r_a$ is the mean radius of the aerosol particles in the chamber, $D_{g,i}$ the gas-phase diffusion coefficient for species $i$, $v_i$ the average velocity of species $i$ in the gas-phase and $\alpha_i$ the accommodation coefficient of species $i$ on the aerosol surface. The accommodation coefficient is the probability that a collision of the gas-phase species with the droplet surface will result in species being transferred to the bulk aqueous phase (this is different from $P_{\text{trap}}$ derived in Chapter 4, which gives the probability of the colliding species being trapped at the interface, irrespective of whether it dissolves into the bulk aqueous phase or scatters back into the interface). The mass transfer coefficient is derived by analogy with electrical circuits, and involves summing ‘resistances’ to mass transfer due to gas-phase diffusion (first term in (9.6)) and transport across the gas-liquid interface (second term in (9.6)).

In (9.4) and (9.5), $H_i$ and $R$ are the Henry’s law coefficient for species $i$ and the ideal gas constant, respectively. The definition of the Henry’s law constant used by MAGIC is $H_i = (\text{aqueous concentration at equilibrium at 298 K})/(\text{gas-phase pressure at equilibrium at 298 K})$. (9.4) and (9.5) show that the deviation from Henry’s law is what drives the transfer of species $i$ from the gas-phase to the aqueous phase. For instance, when the aqueous concentration of species $i$, $C_{aq,i}$, is large compared with $H_iRT$, there is an excess of aqueous $i$ over equilibrium concentrations and a large amount of mass transfer of $i$ from the aqueous phase to the gas-phase.

The factor $w_L$ in (9.4) and (9.5) is the dimensionless volumetric liquid water mixing ratio, defined as the mass ratio of water to dry air in a given volume of the aerosol chamber. $w_L$ can be thought of as the fraction of mass in the aerosol chamber which is aqueous aerosol. Its appearance in the mass transfer terms in (9.4) and (9.5) is to scale $k_m$ according to the mass of aerosol available in the chamber.

### 9.1.3 Aqueous-phase chemistry

The term $\langle R_{aq,i} \rangle$ is the spatially averaged rate of production of species $i$ due to aqueous-phase reactions. Table 3 of reference [39] and Table 5 of reference [48] lists the aqueous-phase reactions that are included in MAGIC, and has mostly been compiled from the NIST database of aqueous-phase chemistry [105]. The rate constants are provided near 298 K, which is the temperature at which the chamber experiments are performed. The treatment of aqueous-phase chemistry is rather thorough, and considers the following.

If species $i$ is transported between the gas- and aqueous-phases, then concentration gradients will appear in the droplet. This concentration gradient needs to be accounted for in the rate equations in the term $\langle R_{aq,i} \rangle$. MAGIC approximates matters by instead using spatially averaged concentrations for the rate equations in this term. To obtain an
expression for a spatially averaged concentration, Knipping and Dabdub considered the full diffusion equations for species \( i \) inside a spherically symmetric droplet [48]. On the basis of work by Schwartz and Freiberg [113], they argued that the steady-state solution \((dC_i/dt = 0)\) to the full diffusion equation does not greatly exceed the rate calculated from the time dependent solution. Solving the steady state diffusion equation gives the spatially averaged solution

\[
\langle C_{aq,i} \rangle = Q_i C_{aq,i} + (1 - Q_i) P_i / k_{L,i} \tag{9.7}
\]

Where \( C_{aq,i} \) is the concentration of species \( i \) near the surface, \( P_i \) is the effective global first order rate constant for production of \( i \) by aqueous reactions (= sum of rate laws for all production reactions) and \( k_{L,i} \) is the effective global first order for loss of \( i \) by aqueous reactions (= sum of rate laws for all loss reactions with \( C_{aq,i} \) factored out of the expressions). The quantities \( Q \) are

\[
Q_i = 3 \left( (\coth q_i) / q_i - 1 / q_i^2 \right)
\]

where \( q_i = r_a \sqrt{k_{L,i} / D_i} \), with \( r_a \) the aerosol radius (as defined above) and \( D_i \) the aqueous phase diffusion coefficient for species \( i \). At the end of each time step in the numerical integration of (9.4) and (9.5), the surface concentration \( C_{aq,i} \) is used to calculate a spatially averaged concentration via (9.7), which in turn is used as the concentrations in the rate laws appearing in the term \( \langle R_{aq,i} \rangle \).

Since the ionic strength in an aerosol droplet is typically high (5 - 6 M), concentrations appearing in rate expressions between ions need to be scaled by activity coefficients and rate constants for reactions between ions need to account for kinetic salt effects. The MAGIC model uses the Pitzer ion interaction model to calculate activity coefficients of ionic species [97], which has been validated in multicomponent systems with ionic strengths up to 6 mol kg\(^{-1}\). This is no limitation to the present study, because it is above the ionic strength for saturation of NaBr in water. Since Pitzer ion data is available for only a few species in the MAGIC model, some activity coefficients were calculated with the Debye-Hückel limiting law. For neutral species, activity coefficients are calculated with an approximation by Moldanova and Ljungstrom [63]. Kinetic salt effects are incorporated into MAGIC by the so-called Debye-Hückel-Brönsted equation, which results from an application of transition state theory and the extended Debye-Hückel limiting law to the ionic reaction \( A^+ + B^- \rightarrow C \),

\[
\ln k = \ln k_0 - \frac{A \sqrt{T}}{1 + \sqrt{T}}, \tag{9.8}
\]

where \( k_0 \) is the rate constant for the reaction at infinite dilution. While (9.8) is not valid for high ionic strengths (beyond around 0.5 M) and limits MAGIC’s ability to produce quantitative comparisons to experimental data, it still allows for insight into the relative importance of the various processes which occur in the MAGIC model. More general models
for handling kinetic salt effects which are appropriate for aerosol modelling are not yet available.

9.1.4 Interfacial reactions

The rate of generation of species \( i \) via interfacial reactions such as (9.1) - (9.3) is included in the term \( R_{\text{int},i} \). For the case of interfacial reactions involving bromide ions, MAGIC supposes that the rate of the interfacial reaction

\[
\text{Br}^-_{(\text{interface})} + A_{(g)} \rightarrow \frac{1}{2} \text{Br}_2(g) + A_{(aq)}^-
\]  

is given by the expression

\[
R_{\text{int}} = \left( \frac{r_a^2}{3D_{g,A}} + \frac{4r_A}{3
\nu_A} \right)^{-1} [A_{(g)}],
\]

where \( r_a \) is the mean aerosol radius in the chamber, \( D_{g,A} \) is the gas-phase diffusion coefficient for reactant \( A \), \( \nu_A \) is the mean velocity of \( A \) in the gas-phase, and \( p \) is the probability of a surface reaction when \( A \) collides with an aerosol surface. The rate constant in (9.10) can be recognised as Schwartz’s mass transfer coefficient \( k_{m,i} \) in equation (9.6), but with the accommodation coefficient replaced with a surface reaction probability. The surface reaction probability is supposed to be

\[
p = \varphi p' f
\]

where \( f \) is the fraction of the aerosol droplet surface covered by bromide ions, \( \varphi \) the average number of contacts between gaseous \( A \) and surface-bound \( \text{Br}^- \) per gas-liquid collision event, and \( p' \) is the probability that surface-bound \( \text{Br}^- \) ions and gaseous \( A \) will undergo chemical reaction upon contact. The values of \( \varphi \) and \( f \) are chosen by the results of MD simulations, which suggest 2 and 0.07, respectively [119], despite our earlier comments on multiple gas-liquid collisions. There are no experimental or theoretical values for \( p' \), and in a MAGIC calculation, it is treated as a fitting parameter.

9.2 Analysis Methodology

The starting point for a sensitivity and uncertainty analysis of MAGIC’s input parameters is an extensive literature search for parameter values and their uncertainty ranges. The result of this long, but straightforward task is tabulated as supporting information for reference [77]. Typically, the literature reported parameter values as a mean of several measurements, and gave its uncertainty range as its standard error. Several issues were encountered in compiling the rate constant data. i. Often, two or more sources reported different measurements for the same quantity. In these cases, the parameter value was taken as the mean of these values, and the standard deviation of the measurements taken
as its uncertainty range. ii. Rate constants were often cited without an estimate of error. In the case of gas-phase rate constants, this issue was dealt with by simulating an uncertainty range from a distribution of collected gas-phase uncertainty ranges. This amounted to plotting a histogram of $\sigma/k$, where $\sigma$ is the uncertainty range of the rate constant $k$, noting that it was roughly lognormal, and generating random numbers from a lognormal distribution with mean and variance computed with maximum likelihood estimators [60]. A similar procedure was used for aqueous-phase rate constants, although in this case the distribution of uncertainty ranges was bimodal. Values of $\sigma/k < 0.3$, which lay in the region of the first mode, were not used in the histogram of $\sigma/k$. The remaining distribution was roughly normal if allowance was made from the truncated tail. Uncertainty ranges were then estimated by simulating values from a normal distribution with mean and standard deviation computed from the standard estimators. iii. The final issue was when only an upper- or lower-bound was cited for a rate constant. In these cases, the bound was taken as the input parameter value, and an uncertainty range given as above. This method assumes that the bound is quite close to the parameter’s mean value, which is undesirable, but nonetheless generates reasonable order-of-magnitude estimates of the parameter and its uncertainty range.

No experimental data for the interfacial reaction probability $p'$ in (9.11) is available for reactions (9.2) and (9.3). In the case of (9.2), $p'$ is taken as $2.3 \times 10^{-6}$, which was estimated by Hunt et al. through model fitting to experimental data [39]. A large, but arbitrary uncertainty range of 50 % ($1.15 \times 10^{-6}$) was assigned to this value. This choice merely reflects the lack of good experimental data on reaction (9.2). The rate of (9.3) is expected to be at least as fast as the analogous reaction involving the chloride ion, for which $p'$ is estimated as 0.6 with an uncertainty range of 0.4 [78, 54]. This study therefore sets the reaction probability for (9.2) as 0.6 with an uncertainty range of 0.4, although, based upon the results of Thomas et al., MAGIC’s bromine output is expected to be relatively insensitive to $p'$ for this reaction.

To include kinetic salt effects in this analysis, set $\delta = -2A\sqrt{I}/(1 + \sqrt{I})$ and write (9.8) as $k = k_0 \times 10^\delta$. The extent to which the parameter $\delta$ influences MAGIC’s bromine output can be gauged by multiplying $\delta$ by a factor $\psi$, which varies between zero and one;

$$k = k_0 \times 10^{\psi \delta}.$$

(9.12)

$\psi = 0$ corresponds to no kinetic salt effect ($k = k_0$), and $\psi = 1$ corresponds to the full kinetic salt effect ($k = k_0 \times 10^{\delta}$).

### 9.2.1 Latin hypercube sampling

Latin hypercube sampling is a variant of a Monte Carlo technique for performing a sensitivity analysis. In the Monte Carlo techniques, each input parameter is treated as a random variable. For each parameter, a value of each parameter is drawn from its dis-
tribution, and this sample of values is used as an input for the model of interest. From several such samples, statistical techniques can then be used to measure the sensitivity of the model’s output to each individual parameter. A good example is provided in reference [31]. The standard Monte Carlo technique is a very adequate way to generate input parameter samples for a sensitivity analysis, but is computationally demanding with large sample sizes [103].

The essential idea behind Latin hypercube sampling is shown in Figure 9.1. Here, the probability distribution of each parameter is discretised into \( n \) mutually exclusive intervals of equal probability. For a single parameter, one value is selected from each interval. This value is then randomly paired with one of the \( n \) values for every other parameter, leading to a single sample of parameter values to use as inputs for the MAGIC model [103, 78]. If there are \( N \) parameters, then we can think of this procedure producing an \( n \times N \) matrix, with each row corresponding to a particular sample of input parameters to be run through MAGIC [103]. Each of the samples are independent. In this study, all parameters were assumed to have a lognormal probability density, which follows empirical observations [102]. An exception is the kinetic salt parameter \( \psi \), which was given a uniform probability density. This choice reflects the lack of experimental information on the distributions of kinetic salt effect parameters.

### 9.2.2 Linear regression and uncertainty analysis

Each of the \( n \) Latin hypercube samples generates a different output from MAGIC. From the distribution of outputs, standard statistical techniques can be conducted to perform the sensitivity and uncertainty analysis. Each MAGIC output is a time series of the concentration of gas-phase bromine (denoted by \( [\text{Br}_2(\text{g})] \)), and in order to analyse the \( n \) outputs, we selected several times of interest and looked at the value of each output at these times. A standard linear regression analysis was used to conduct the analysis. This method assumes that, at the times of interest, MAGIC’s gas-phase bromine concentration is linearly related to each of the input parameters, and that the parameters are approximately uncorrelated with one another. The regression coefficients are calculated with the least-squares normal equations,

\[
\beta = (X^T X)^{-1} X^T Y \tag{9.13}
\]

where \( X \) is the \( n \times (N+1) \) matrix

\[
X = \begin{pmatrix}
1 & x_{11}/x_{1}^* & \cdots & x_{1N}/x_{N}^* \\
1 & x_{21}/x_{1}^* & \cdots & x_{2N}/x_{N}^* \\
\vdots & \vdots & \ddots & \vdots \\
1 & x_{n1}/x_{1}^* & \cdots & x_{nN}/x_{N}^*
\end{pmatrix}. \tag{9.14}
\]

In (9.14), \( x_{ij} \) is the value of parameter \( j \) acquired from the \( i^{th} \) Latin hypercube sample,
Figure 9.1: Outline of Latin Hypercube Sampling for $N = 3$ parameters and $n = 5$ Latin hypercube samples. In the first step, the probability distributions of the three parameters are each discretised into five mutually exclusive intervals of equal probability. From each interval, one value of the parameter is randomly sampled. The first sample is formed by taking one of the five values of parameter 1 at random, one of the five values of parameter 2 at random, and one of the five values of parameter 3 at random, and combining them into a single set. The second sample is formed in the same way, but excluding the parameter values that appeared in the first sample, and so on up to the fifth sample. The result is an $n \times N$ matrix of parameters, with each row corresponding to a single Latin hypercube sample and each column corresponding to a particular parameter. In the third step, these five samples are independently run through MAGIC, each producing a unique bromine output. The fourth step (not shown in the diagram) studies the five bromine outputs at several fixed times, and uses them as inputs for a regression analysis.
and $x_j^*$ is the mean value of parameter $j$ across the $n$ samples. $Y$ is an $n$-dimensional vector of bromine concentrations output from the $n$ MAGIC outputs at the time of interest,

$$ Y^T = \frac{1}{[\text{Br}_2(g)]^*} \left( [\text{Br}_2(g)]_1, \ldots, [\text{Br}_2(g)]_n \right) \quad (9.15) $$

where $[\text{Br}_2(g)]^*$ is the gas-phase bromine concentration calculated by MAGIC using the $x_j^*$. The $(j+1)^{th}$ element of the vector $\beta$ is the regression coefficient for parameter $j$, and interpreted as the change in MAGIC’s $[\text{Br}_2(g)]$ output per unit increase in that parameter at the chosen time, with all other input parameters held constant. Hence, the magnitude of an input parameter’s regression coefficient is a measure of the sensitivity of MAGIC’s $[\text{Br}_2(g)]$ output to that parameter.

The contribution that input parameter $i$ makes to the variance of $[\text{Br}_2(g)] / [\text{Br}_2(g)]^*$ is given by the error propagation formula,

$$ u_i = \left( \frac{\sigma_i \beta_i}{x_i^*} \right)^2 \sum_{k=1}^{N} \left( \frac{\sigma_k \beta_k}{x_k^*} \right)^2, \quad (9.16) $$

where $\sigma_i$ is the uncertainty range of input parameter $i$.

To summarise, the sensitivity and uncertainty analysis of MAGIC’s $[\text{Br}_2(g)]$ output involves taking $n$ Latin hypercube samples from the $N$ input parameters, performing a regression analysis of MAGIC’s calculated $[\text{Br}_2(g)]$ on the input parameters at the times of interest, and calculating the uncertainty contributions by (9.16) above. In this study, the number of samples $n = 5000$ was sufficiently large to ensure reliable analysis, but within a permissible computational time. A small pilot investigation did not find any significant differences in the results upon doubling $n$.

### 9.3 Results and Discussion

This work considered seven scenarios, each corresponding to different initial conditions used by MAGIC to solve (9.4) and (9.5). The scenarios are summarised in Table 9.1. Initial conditions for the scenario ‘base case’ are shown in Table 9.2. The initial conditions in the base case are identical to those used by Thomas et al. [119] and are representative of the conditions used in the experimental chamber studies of Hunt et al. [39]. The scenarios include both ‘dark’ and ‘light’ conditions, where the latter means that photolysis reactions (such as (9.3)) are included in MAGIC’s mechanism. Figure 9.2 shows the Br₂ gas-phase concentration predicted the MAGIC for the seven scenarios. Each curve is an average over 5000 Latin hypercube samples of the input parameters. The curves are qualitatively comparable to experimental curves obtained by Hunt et al. [39].
Scenario Description

Base case  
See table 9.2. The system remains in the dark during the entire simulation.

AtmosCO2  
Same as base case, except $[\text{CO}_2(\text{g})]_0 = 380 \text{ ppmv}$.

Acidic  
Same as base case, except aerosol pH held constant at 4.

Large Aerosols  
Same as base case, except mean aerosol diameter increased to 500 nm.

LightT600  
Same as base case. The system is exposed to light from 600 s onwards.

LightT10  
Same as base case. The system is exposed to light from 10 s onwards.

MBL  
Same as base case, except $[\text{CO}_2(\text{g})]_0 = 380 \text{ ppmv}$, $[\text{O}_3(\text{g})]_0 = 100 \text{ ppbv}$, aerosol pH held constant at 4. The system is exposed to light from 600 s onwards.

| Table 9.1: Summary of scenarios examined in this study. The subscript ‘0’ signifies an initial condition. |
|---|---|
| Scenario | Description |
| Base case | See table 9.2. The system remains in the dark during the entire simulation. |
| AtmosCO2 | Same as base case, except $[\text{CO}_2(\text{g})]_0 = 380 \text{ ppmv}$. |
| Acidic | Same as base case, except aerosol pH held constant at 4. |
| Large Aerosols | Same as base case, except mean aerosol diameter increased to 500 nm. |
| LightT600 | Same as base case. The system is exposed to light from 600 s onwards. |
| LightT10 | Same as base case. The system is exposed to light from 10 s onwards. |
| MBL | Same as base case, except $[\text{CO}_2(\text{g})]_0 = 380 \text{ ppmv}$, $[\text{O}_3(\text{g})]_0 = 100 \text{ ppbv}$, aerosol pH held constant at 4. The system is exposed to light from 600 s onwards. |

Table 9.1: Summary of scenarios examined in this study. The subscript ‘0’ signifies an initial condition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median aerosol diameter</td>
<td>243 nm</td>
</tr>
<tr>
<td>Aerosol geometric standard deviation</td>
<td>1.9 nm</td>
</tr>
<tr>
<td>Aerosol concentration</td>
<td>$2.5 \times 10^5 \text{ particles cm}^{-3}$</td>
</tr>
<tr>
<td>Chamber relative humidity</td>
<td>69 %</td>
</tr>
<tr>
<td>Chamber temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>$[\text{NaBr}]_0$</td>
<td>5.8 mol L$^{-1}$</td>
</tr>
<tr>
<td>$[\text{O}_3(\text{g})]_0$</td>
<td>1.5 ppmv</td>
</tr>
<tr>
<td>$[\text{CO}_3(\text{g})]_0$</td>
<td>10 ppmv</td>
</tr>
<tr>
<td>$b$</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 9.2: Initial conditions for the Base Case.

Figure 9.2: Gas-phase bromine predictions for each scenario predicted by MAGIC. Each curve has been averaged over the 5000 Latin hypercube samples. Figure created by Paul Nissenson.
9.3.1 Bromine production in the dark

Table 9.3 summarises the results of the sensitivity and uncertainty analyses for the Base Case by showing the input parameters which are most strongly correlated with predicted \([\text{Br}_2(\text{g})]\) and those which contribute the most to its uncertainty, at the three chosen analysis times (500 s, 1500 s and 2500 s into the simulation). At all three analysis times, the regression coefficient and uncertainty contribution for the interfacial reaction (9.2) are \(\beta \sim 0.55\) and \(u \sim 99.9\%\), respectively, which is considerably larger than all other values in the table. These results demonstrate the importance of the interface reaction (9.2) in dark bromine production from a NaBr aerosol, which reaffirms the conclusions drawn by Hunt et al. and Thomas et al. [39, 119] and provides impetus for further experimental studies on this reaction in order to narrow its uncertainty range. Since its uncertainty contribution overwhelms all others, analysis of other parameters ignored the contribution from reaction (9.2) in calculating the uncertainty contribution \(u_i\) in (9.16) (indicated by the term ‘filtered’ in Table 9.3). This allows for the identification of other parameters that could benefit from experimental attention.

The results in Table 9.3 suggest a significant contribution to gas-phase bromine production by an aqueous pathway. The positive regression coefficients for the Henry’s law coefficient of ozone \((\beta = 0.07, 0.09\) and 0.10 for the three respective times), the positive coefficients \((\beta = 0.04, 0.06\) and 0.08) for the rate constant of the reaction

\[
\text{Br}^{-}_{(\text{aq})} + \text{O}_3(\text{aq}) \rightarrow \text{O}_2(\text{aq}) + \text{BrO}^{-}_{(\text{aq})}, \quad (9.17)
\]

the negative coefficients of the acid-base equilibrium constant for HOBr \((\beta = -0.09, -0.09\) and -0.08), and the positive coefficients \((\beta = 0.07, 0.07\) and 0.06) of the rate constant of the reaction

\[
\text{HOBr}_{(\text{aq})} + \text{Br}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})} \rightarrow \text{Br}_2(\text{aq}) + \text{OH}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})}, \quad (9.18)
\]

suggests the following. Dissolved ozone forms aqueous \(\text{BrO}^-\) via reaction (9.17), which then forms aqueous HOBr via acid-base equilibrium. In turn, HOBr reacts with bromide ions as in reaction (9.18), which generates aqueous \(\text{Br}_2\) which may then diffuse through the aerosol droplet and escape into the gas-phase. The major aqueous loss channels for bromine are the reactions

\[
\text{Br}_2(\text{aq}) + \text{OH}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})} \rightarrow \text{HOBr}_{(\text{aq})} + \text{Br}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})}, \quad (9.19)
\]

\[
\text{Br}_2(\text{aq}) + \text{CO}_3^{2-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})} \rightarrow \text{HOBr}_{(\text{aq})} + \text{Br}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})}. \quad (9.20)
\]

Predicted gas-phase bromine concentrations are 2 to 3 times more sensitive to reaction (9.19) \((\beta = -0.06, -0.06\) and \(-0.05)\) than reaction (9.20) \((\beta = -0.02, -0.03\) and \(-0.03)\). The uncertainty contributions of these two reactions are respectively \(\sim 22\%\) and \(\sim 12\%,\)
Table 9.3: Regression coefficients and uncertainty contributions for the Base Case at the three different simulation times.  

<table>
<thead>
<tr>
<th>Input parameter(^a)</th>
<th>500 s</th>
<th>1500 s</th>
<th>2500 s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\beta)</td>
<td>(u)</td>
<td>(\beta)</td>
</tr>
<tr>
<td><strong>Interface reaction probability ((\phi'))</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O_3(g) + Br^-_{(int)} \rightarrow 0.5Br_2(g) + O_3^{(aq)}) (9.2)</td>
<td>0.55</td>
<td>99.9 % (f)(^c)</td>
<td>0.55</td>
</tr>
<tr>
<td><strong>Gas-phase reaction rate constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Br_2 + \text{wall} \rightarrow \text{loss})</td>
<td>NC (^d)</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td><strong>Aqueous-phase reaction rate constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Br^- + O_3 \rightarrow O_2 + BrO^-) (9.17)</td>
<td>0.04</td>
<td>1.4 %</td>
<td>0.06</td>
</tr>
<tr>
<td>(HOBr + Br^- + H_2O \rightarrow Br_2 + OH^- + H_2O) (9.18)</td>
<td>0.07</td>
<td>21.3 %</td>
<td>0.07</td>
</tr>
<tr>
<td>(Br_2 + OH^- + H_2O \rightarrow HOBr + Br^- + H_2O) (9.19)</td>
<td>-0.06</td>
<td>12.7 %</td>
<td>-0.06</td>
</tr>
<tr>
<td>(Br_2 + CO_3^{2-} + H_2O \rightarrow HOBr + Br^- + HCO_3^-) (9.20)</td>
<td>-0.02</td>
<td>2.1 %</td>
<td>-0.03</td>
</tr>
<tr>
<td><strong>Henry’s law constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O_3)</td>
<td>0.07</td>
<td>1.2 %</td>
<td>0.09</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>0.06</td>
<td>0.7 %</td>
<td>0.07</td>
</tr>
<tr>
<td>(Br_2)</td>
<td>-0.09</td>
<td>1.3 %</td>
<td>-0.09</td>
</tr>
<tr>
<td><strong>Acid / base equilibrium constants</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_2O)</td>
<td>-0.09</td>
<td>1.5 %</td>
<td>-0.08</td>
</tr>
<tr>
<td>(CO_2H_2O)</td>
<td>0.06</td>
<td>2.1 %</td>
<td>0.06</td>
</tr>
<tr>
<td>(HOBr)</td>
<td>-0.09</td>
<td>5.5 %</td>
<td>-0.09</td>
</tr>
<tr>
<td>(HCO_3^-)</td>
<td>NC</td>
<td>NC</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\(^a\) The input parameters in this table have regression coefficients that are significant at the 0.025 level and have either \(\beta \geq 0.03\) or \(u \geq 0.5\%\) for at least one analysis time. Exceptions to the \(\beta\) and \(u\) cutoffs are made for parameters that are of certain interest.  
\(^b\) Input parameters that are given numbers in the main text are listed here with their numbers in parentheses.  
\(^c\) (f) denotes that the parameter was ignored in uncertainty calculations of other parameters \(\text{via equation (9.16)}\).  
\(^d\) NC = not significant correlated with predicted \([Br_2(g)]\) at the 0.025 level at the given analysis time.
which is large enough to warrant further experimental studies.

The regression coefficients are approximately time independent, suggesting that these conclusions are independent of the chosen analysis times. The doubling of the regression coefficient of the rate constant of (9.17) is consistent with the expectation that, as ozone is depleted, (9.17) becomes more of a rate limiting step in the net production of bromine. The two bromine production pathways are illustrated in Figure 9.3. The interfacial reaction is drawn inside of a box to emphasise its dominance over the alternative aqueous route.

Figure 9.4 shows aerosol pH as a function of time, averaged over all samples of input parameters. The pH and gas-phase bromine concentration curves exhibit similar behaviour, increasing rapidly until $\sim 500$ s and then starting to plateau, suggesting that aqueous OH$^-$ production is coupled with either the interfacial reaction (9.2) or the aqueous mechanism described above. Regarding the first possibility, aqueous O$_3^-$ produced from reaction (9.2) generates OH$^-$ through the reactions

$$O_3^{\text{(aq)}} \rightarrow O_2^{\text{(aq)}} + O^{\text{(aq)}}; \quad (9.21)$$

$$O^{\text{(aq)}} + H_2O^{\text{(aq)}} \rightarrow OH^{\text{(aq)}} + OH^{\text{-}} + H_2O^{\text{(aq)}}, \quad (9.22)$$

However, the production rate of OH$^-$ via reaction (9.18) is many orders of magnitude greater than reaction (9.22) (rate constants of $\sim 10^8$ versus $\sim 10^4$ s$^{-1}$ M$^{-1}$ respectively), suggesting that the aqueous mechanism is primarily responsible for the increased alkalinity of the aerosols during a simulation.

The other dark scenarios described in Table 9.3 allow us to check the robustness of the above conclusions under initial conditions more relevant to a real atmosphere.
The ‘AtmosCO2’ scenario is performed at an initial gas-phase CO$_2$ concentration of 380 ppmv, representative of today’s atmosphere, with all other initial conditions kept at the values of the Base Case. For the interest of space, the results of the sensitivity and uncertainty analysis of the AtmosCO2 case are not tabulated here, but are available as supplementary material for reference [77]. The larger initial CO$_2$ gas-phase concentration does not offset the dominance of the interfacial reaction 9.2, which still has the largest regression coefficients ($\beta = 0.69, 0.51$ and $0.47$, for the three respective times). Figure 9.4 shows that the droplets are more acidic for the AtmosCO2 scenario than the Base Case by almost one full pH unit, which is due to the following acid-base equilibria being pushed further to the right.

$$\text{CO}_2\text{(aq)} + \text{H}_2\text{O}_{\text{(aq)}} \rightleftharpoons \text{CO}_2\cdot\text{H}_2\text{O}_{\text{(aq)}}, \quad (9.23)$$

$$\text{CO}_2\cdot\text{H}_2\text{O}_{\text{(aq)}} \rightleftharpoons \text{HCO}^-_3\text{(aq)} + \text{H}^+_{\text{(aq)}} \quad (9.24)$$

$$\text{HCO}^-_3\text{(aq)} \rightleftharpoons \text{CO}_2^-_3\text{(aq)} + \text{H}^+_{\text{(aq)}} \quad (9.25)$$

The higher concentration of aqueous HCO$_3^-$ increases the importance of another channel for aqueous bromine production,

$$\text{HOBr}_{\text{(aq)}} + \text{Br}^-_{\text{(aq)}} + \text{HCO}_3^-_{\text{(aq)}} \rightarrow \text{Br}_2\text{(aq)} + \text{CO}_2^-_3\text{(aq)} + \text{H}_2\text{O}_{\text{(aq)}}, \quad (9.26)$$

In the Base Case scenario, the regression coefficients for the rate constant of reaction (9.26) were not statistically significant. However, under the higher initial gas-phase CO$_2$ concentration, MAGIC’s gas-phase bromine concentrations are sensitive to this reaction.
(β = 0.02, 0.03 and 0.04, for the three respective times), and less sensitive towards the rate constant of the other bromine-producing reaction, (9.18) (β = 0.01, 0.02 and 0.03). Similarly, the reduction in pH due to the larger initial CO₂ concentrations means that the aqueous bromine destruction via reaction (9.19) is no longer significantly correlated with predicted gas-phase bromine concentrations. Due to the increase in carbonate ions, the dominant loss pathway is now through reaction (9.20) (β = −0.02, −0.04 and −0.04).

In natural environments, sea salt aerosol is slightly acidic due to the uptake of nitric acid and SO₂ [44]. The ‘Acidic’ scenario considers this case by buffering the droplets at a pH near 4, with the other initial conditions kept at the values of the Base Case. The results of the sensitivity and uncertainty analysis for the Acidic scenario are available as supplementary material for reference [77]. As before, gas-phase bromine concentrations are correlated most strongly with the interfacial reaction (9.2) (β = 0.88, 0.76 and 0.68 for the respective times). Figure 9.2 shows that the gas-phase bromine concentration is higher in the acidic scenario than in the other two scenarios, suggesting that the aqueous phase production pathways plays a larger role in the production of bromine than in the Base Case and AtmosCO₂ scenarios. The aqueous reaction with the largest regression coefficient is reaction (9.17) (β = 0.04 at all times). Thus, under more acidic conditions, reaction (9.17) becomes more of a rate limiting step in net bromine production than the subsequent protonation reaction of OBr⁻ and production of bromine in reaction (9.18). The generation of aqueous BrO⁻ via (9.17) depends upon O₃ dissolving into the droplets from the gas-phase. Consequently, the Henry’s law coefficient for ozone is significantly correlated with predicted gas-phase bromine in this scenario (β = 0.04 and 0.03 at 500 s and 1500 s, insignificant at 2500 s).

Although the above has focused on the aqueous production pathways, it is important to remember the key result that the interfacial reaction is invariably dominant under dark conditions. The ‘Large Aerosols’ scenario, in which the diameter of the aerosols was increased from 234 nm to 500 nm with the total aqueous volume kept constant, illustrates this point. Under these conditions, the sensitivity of the parameters in the aqueous pathway should increase relative to the interfacial parameters because the surface area-to-volume ratio of the system is decreased. Sensitivity analysis for this case (available as supplementary material in reference [77]) confirms this prediction. While the regression coefficients of the rate constant for reaction (9.17) and the Henry’s law coefficient for ozone increase by ~ 0.05 units and ~ 0.02 units over the Base Case, respectively, they are essentially unchanged for the other important aqueous parameters. Meanwhile, the regression coefficients for the interfacial reaction (9.2) (β = 0.59, 0.55 and 0.54) are almost identical to the Base Case, remaining appreciably larger than any of the coefficients for the aqueous parameters. Note that Figure 9.2 shows that predicted gas-phase bromine concentrations are lower for the Large Aerosols scenario, which is consequence of providing less total surface area for reaction (9.2). In short, even when disadvantaged with a smaller amount of available surface area, interfacial chemistry still dominates the production of
bromine under dark, non-photolytic conditions.

9.3.2 Bromine production in the light

The two main ‘light’ scenarios are listed in Table 9.2 as LightT600 and LightT10, for which the bromine output averaged across all simulations is shown in Figure 9.2. In the LightT600 and LightT10 scenarios, lights are turned out at 600 s and 10 s, respectively, into MAGIC’s calculations. By ‘lights are turned on’, we mean that photochemical parameters are included in MAGIC’s mechanism at these times. The curves faithfully reproduce the dark output until the lights turn on, beyond which there is a rapid increase in bromine production (the ‘bromine explosion’), which reaches a peak and slowly declines thereafter. This behaviour is qualitatively consistent with experimental aerosol chamber observations [39, 77]. In the LightT600 scenario, the dark reactions have had a longer time to affect the chemical composition of the system before photochemical reactions begin. A third scenario, ‘MBL’, uses initial conditions representative of the marine boundary layer (the layer of atmosphere in direct contact with the ocean surface), and tests the robustness of the results of the LightT600 and LightT10 scenarios under atmospherically relevant conditions. However, it should be noted that atmospheric concentrations of various species and their time dependence reflects a complicated interplay between meteorology and chemistry; the present model only studies the chemical part.

Table 9.4 lists the input parameters most strongly correlated with gas-phase bromine concentrations at the time of the peak concentration (\(\sim 1000\) s), as well as at 500 s and 1500 s beyond the peak for the LightT600 scenario. These calculations also used ‘filtered’ uncertainty calculations that ignore the contribution of the interfacial reaction (9.2) to the uncertainty calculated from equation (9.10). The most notable difference between the LightT600 scenario and the dark scenarios is that the gas-phase bromine concentrations are now considerably less sensitive to the interfacial reaction (9.2); with regression coefficients of 0.05 for each of the three analysis times, its contribution to bromine production is now of comparable significance to many other input parameters. Another important observation is that, although OH radicals are now present in the gas-phase, the alternative interfacial reaction (9.3) is not strongly correlated with bromine production (\(\beta = 0.03, 0.02\) and 0.02 for the three respective times). This result is consistent with those obtained by Thomas et al. [119].

Figure 9.5 plots ozone concentrations averaged across all samples as functions of time for each scenario, and strongly suggests that for the photolytic scenarios, the relatively small contribution by the interfacial reaction (9.2) is due to rapid ozone photolysis following the lights turning on. This also implies that the interfacial reaction (9.3) would not be sustained for long as the supply of OH radicals from ozone photolysis would quickly decrease following the lights switching on. As well as \textit{via} photolysis, the rapid loss of ozone is due to a reaction with bromine atoms:
Table 9.4: Regression coefficients and uncertainty contributions for the LightT600 scenario at the three different simulation times. The input parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>% $I'\alpha &gt;$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

(a) The input parameters in parentheses. If $p < 0.05$, the parameter is important in uncertainty calculations of other parameters, and vice versa

(b) The input parameters that are given numbers in the main text are listed here with their numbers in parentheses.

(c) Hologram constant ($\lambda$).

(d) Adsorption constant ($\lambda$).

(e) Aqueous-phase reaction constant ($\lambda$).

(f) Henry's law constant ($\lambda$).

(g) Accommodation coefficient ($\lambda$).

(h) Gas-phase reaction rate constant ($\lambda$).

(i) Interference reaction probability ($\lambda$).
\[ \text{Br}_2(g) + \text{O}_3(g) \rightarrow \text{BrO}(g) + \text{O}_2(g) \] (9.27)

The bromine atoms are formed either by photolysis of bromine or by reaction of bromine with a hydroxyl radical. Reactions (9.21) and ozone photolysis both have rates many times larger than than the interfacial reaction (9.2) (in the order of \(10^9 \text{ mol s}^{-1}\) and \(10^{-3} \text{ molecules s}^{-1}\), respectively [3]). The relatively small role of the interfacial reactions is shown more explicitly in Figure 9.6, which plots the rate of gas-phase bromine production via various pathways in the LightT600 scenario. For the first 600 s, the system is in the dark and most bromine is produced via the interface reaction (9.2). After 600 s, the rapid loss in ozone causes a steady decline in production from (9.2). Bromine production via the interface reaction (9.3) undergoes a rapid, step-like increase at 600 s, but declines too rapidly to be significant. The key point is that, under photolytic conditions, the interfacial reactions (9.2) and (9.3) make a relatively small contribution to net bromine production, and the bromine explosion must be due to either a gas-phase mechanism, an aqueous-phase mechanism, or both.

To understand the bromine explosion, consider the following gas-phase radical reactions.

\[ \text{OH}(g) + \text{Br}_2(g) \rightarrow \text{Br}(g) + \text{HOBr}(g) \] (9.28)

\[ \text{Br}(g) + \text{O}_3(g) \rightarrow \text{BrO}(g) + \text{O}_2(g) \] (9.29)

\[ 2\text{BrO}(g) \rightarrow \text{Br}_2(g) + \text{O}_2(g) \] (9.30)
Reaction (9.30) has a very large regression coefficient ($\beta = 0.56$ for the three analysis times). The regression coefficient for reaction (9.28) is smaller, yet still statistically significant ($\beta = -0.02, -0.03$ and $-0.03$ for the three respective times). However, while the regression coefficient for reaction (9.29) is not statistically significant at any of the three analysis times, if it is removed from MAGIC’s mechanism entirely, the bromine explosion does not occur, and the output continues to follow that of the dark output. Reaction (9.29) clearly plays a crucial role in bromine production, and is probably such that the subsequent reaction (9.30) is rate limiting to the extent that MAGIC’s bromine output is relatively insensitive to the value of the rate constant of (9.29). The aqueous reaction (9.18) also has a rate constant with significant regression coefficients ($\beta = 0.03, 0.03$ and $0.03$), suggesting that HOBr produced by reaction (9.28) may go on to produce bromine by mass transfer to the aqueous-phase. The importance of aqueous-phase chemistry is indicated by Figure 9.4, which shows that aerosol pH increases with the bromine explosion by about three quarters of a pH unit. Moreover, Figure 9.6 shows that much of the produced gas-phase bromine involves mass transfer from the aqueous-phase to the gas-phase. These results suggest that the bromine explosion owes to the gas-phase reactions (9.28 - 9.30) coupled with the aqueous-phase reaction (9.18), which, at the price of one mole of bromine, goes on to produce one and a half moles of bromine. Figure 9.6 shows that both the mass transfer to the gas-phase from the aqueous phase (and hence the aqueous-phase reaction (9.18)), and the gas-phase reaction (9.30) (and hence the overall gas-phase pathway (9.28 - 9.30) make essentially the same contribution to net bromine production. The relatively large regression coefficient for the rate constant of the reaction (9.24) merely indicates its rate limiting nature and hence the sensitivity of bromine production to its value, rather
Figure 9.7: Diagram showing bromine production pathways under photolytic conditions that were uncovered by the sensitivity analysis. The aerosol droplet is drawn as the large grey circle. The dominant pathway involves a combination of gas-phase radical reactions and aqueous-phase reactions, which are drawn inside of a box.

than its dominance over the aqueous production route. These points are summarised by Figure 9.7, which highlights the production routes of bromine from an NaBr aerosol under photolytic conditions, and identifies the gas-phase reactions (9.28 - 2.30) and the aqueous route (9.18) as the most significant contributors. It is important to note that the gas-phase production pathway competes with another efficient reaction,

\[ 2\text{BrO}(g) \rightarrow 2\text{Br}(g) + \text{O}_2(g) \]  \hspace{1cm} (9.31)

The large, negative coefficients for the rate constant of this reaction (\( \beta = -0.57 \) for the three times) reflect the fact that, as the rate of this reaction increases, less bromine is available for the gas-phase production route (9.28 - 9.30). However, observe that this atomic bromine can re-enter the gas-phase pathway above via the relatively slow reaction (9.29). It is also worth noting that reactions (9.30) and (9.31) are important in the catalytic destruction of ozone at polar sunrise, where bromine is photolysed to produce bromine atoms [27]. The result that these two reactions contribute over 90 % to the uncertainty of predicted bromine concentrations should be taken as an indicator for their importance in the net production of bromine under photolytic conditions rather than incentive for further experimental work, as both of these reactions have already been studied extensively (for example, see [3]).

Table 9.4 shows lists some other reactions which are significantly correlated with net bromine production as well. For example, the reaction

\[ \text{HO}_2(g) + \text{BrO}(g) \rightarrow \text{HOBr}(g) + \text{O}_2(g) \]  \hspace{1cm} (9.32)
has a rate constant with significant, positive regression coefficients ($\beta = 0.05, 0.06$ and 0.06). This is expected, because this reaction supplements HOBr generation for the aqueous phase production route (9.18). Curiously, gas-phase bromine concentrations appear to be positively correlated with the photolysis of ozone ($\beta = 0.06, 0.05$ and 0.05). The photolysis of ozone produces $O(^1D)$, which goes on to produce OH radicals through the reaction

$$O(^1D)_{(g)} + H_2O_{(g)} \rightarrow 2OH_{(g)}, \quad (9.33)$$

which is also positively correlated with gas-phase bromine production ($\beta = 0.03, 0.02, 0.02$). However, while OH can destroy bromine by the reaction

$$OH_{(g)} + Br_2(aq) \rightarrow HOBr_{(g)} + Br_{(g)}, \quad (9.34)$$

this reaction also produces atomic bromine for the gas-phase reaction (9.28) and HOBr for the aqueous reaction (9.18), which explains the positive correlation. The bromine wall loss reaction in the table relates to the loss of bromine from the system due to adsorption with the walls of the aerosol chamber, and negative regression coefficients that grow in magnitude with time ($\beta = -0.02, -0.05, -0.12$), which indicates that this process becomes increasingly influential on the concentration of gas-phase bromine as time proceeds from the initial bromine explosion and ozone depletion. The near time independence of the regression coefficients of the reactions discussed above suggests that the bromine production mechanism proposed here applies generally across the ‘lights on’ period of the system.

The results of the sensitivity and uncertainty analysis of the LightT10 scenario is available as supplementary material for reference [77]. As before, sensitivity and uncertainty analysis for the LightT10 scenario was conducted at the time of peak bromine concentration ($\sim 400$ s), 500s beyond the peak, and 1500 s beyond the peak. The essential behaviour of the system is very similar to the LightT600 scenario, in which ozone concentrations rapidly deplete and pH rapidly increases following the lights turning on (Figures 9.5 and 9.4). In this case, gas-phase bromine concentrations are even less sensitive to the interfacial reaction (9.2) ($\beta = 0.01$ for all three times), which is probably due to the smaller length of time during which ozone is available to the system. The regression coefficients for reaction (9.3) ($\beta = 0.03$ for all three times) are essentially the same as before, and the coefficients for the other reactions discussed above are qualitatively similar. In particular, the results indicated no alternate pathways for bromine production, suggesting that the chemistry discussed above and shown in Figure 9.7 are independent of the length of time the dark reactions have been operating before the system is exposed to the light.

In the MBL scenario, initial ozone concentrations are lowered to 100 ppbv, initial CO$_2$ concentrations are increased to 380 ppmv, and droplet pH is buffered at 4, reproducing the conditions found in the marine boundary layer. As in the LightT600 scenario, the sys-
tem is illuminated at 600 s into the simulations. Despite the significant changes in initial conditions, the results of the sensitivity analysis (available as supplementary material for reference [77]) are similar to the LightT600 scenario. The only change to the bromine production mechanism shown in Figure 9.3 is the aqueous bromine is now produced through the reaction

\[ \text{HOBr}_{(aq)} + \text{Br}^-_{(aq)} + \text{H}^+_{(aq)} \rightarrow \text{Br}_2(aq) + \text{H}_2\text{O}_{(aq)}, \]

(9.35)
rather than (9.18). The other significant differences is that the regression coefficient for reaction (9.28) increases from -0.03 in the LightT600 scenario to -0.21 in the MBL scenario, and the regression coefficient for mass accommodation coefficient for OH goes from being insignificant to 0.07, while becoming more insensitive to the other parameters shown in Table 9.4. Thus, the destruction of bromine via (9.28) and removal of OH from the gas-phase play a more important role in net bromine production under conditions representative of the marine boundary layer, although the reactions (9.30) and (9.31) ($\beta \sim 0.44$ and $-0.46$, respectively, for the three times) are still the key limiting steps in the system.

A fortunate consequence of having known aqueous- and gas-phase reactions producing bromine under light conditions is that the uncertainties of the crucial rate constants make a very small contribution to the uncertainty in net bromine production. None of the parameters shown in Table 9.4 have uncertainties large enough to warrant further experimental measurements.

9.4 Final Remarks

Through a sensitivity analysis of the MAGIC model of aerosol kinetics, we have identified pathways which lead to the production of bromine from a deliquesced NaBr aerosol droplet in the presence of ozone under both dark and photolytic conditions. In the dark, it was found that bromine production is dominated by the interfacial reaction (9.2), and is supplemented by the aqueous reaction (9.18). The interfacial reaction (9.2) accounts for almost all of the uncertainty in MAGIC’s dark bromine output, and is therefore recommended as the subject of further experimental attention by researchers wishing to improve the precision of aerosol kinetics models. Reliable measurements of interfacial reaction kinetics are currently unavailable, and experimental investigations along these lines are still in their early stages [78]. Interfacial chemistry was found to play less of a role under photolytic conditions, and instead most of the bromine production was found to be due to a combination of well-understood gas-phase radical chemistry and aqueous-phase HOBr chemistry. Thus, while experimental measurements of the kinetics of the interfacial reaction (9.3) would be fundamentally interesting, they are not expected to greatly improve the precision of aerosol kinetics models.

The results obtained here may have certain atmospheric implications. It is well-
established that dramatic depletion of tropospheric ozone concentrations in the Arctic are correlated with molecular bromine production [4, 28]. Furthermore, so-called ‘sunrise ozone destruction’ has been observed at the mid latitudes, and has been correlated with bromine production from sea salt aerosol [22]. However, while the relationship between bromine concentrations and ozone concentrations is well-established, the chemical reactions involved are not. While the bromine production pathways uncovered in this study provide an insight into the kind of chemistry that is involved in these situations, it needs to be remembered that the MAGIC model applies strictly to the case of bromine production in an aerosol chamber. Meteorological effects, such as air pressure gradients and temperature, play an important role in determining the concentrations of various species in a real atmosphere [77] and are not considered in the MAGIC model. For example, in the polar regions, reactivity of halogen-containing compounds is known to be enhanced by temperatures colder than the 298 K used in the chamber experiments and the MAGIC model [116]. Moreover, bromine may be produced from sources other than sea salt aerosol. For instance, it has been suggested that bromine is produced by the oxidation of bromide ions by gas-phase ozone in the quasi-liquid layer of the Arctic snowpack [115], which is expected to be a much different reaction medium than a gas-liquid interface. Another important point is that naturally occurring sea salt aerosol contains several halogen ions [57], whereas sodium bromide aerosol only contains bromide ions. Bromine-producing chemistry is known to be enhanced in the presence of other halides [100], and it is likely that the current MAGIC model would produce more bromine if inter-halide chemistry was included in its mechanism [77]. Nonetheless, the key conclusions of this work, namely the role of the reaction at the aerosol interface under dark conditions, and the role of aqueous- and gas-phase reactions under light conditions, are likely to be applicable to the chemistry of a real atmosphere.
Chapter 10

Appendix: A Crash Course on Stochastic Processes

While the gas-liquid collision theory can be understood without a specialist knowledge of stochastic processes, the rigorous construction of the random walk on parabolas presented in Chapter 3 requires a more technical background. However, unlike most mathematics that is encountered in the physical sciences, stochastic processes are a direct application of fundamental, set theoretic ideas. Consequently, non-mathematicians must work very hard to penetrate the stochastic process literature. However, that does not mean that the subject is inaccessibly difficult; all that stands in the way of a basic comprehension is a language barrier and some unfamiliar concepts. The following introduces the key ideas needed to work through all of Chapter 3, and is presented as a stand alone appendix as it may be of general interest. The emphasis is on the ideas and the language, rather than on theorems and proofs. While this section is original and has not been lifted from any textbooks, the ideas are standard and can be found in references [30, 80, 98].

The stochastic basis

Consider following the evolution of a physical system from time $t = 0$ onwards. In the case of a system that evolves deterministically, this system would follow a well-defined path from its starting point. In such a case, we have a complete knowledge of the evolution of the system, and can associate the path with a well-defined mathematical formula. However, deterministic evolution is strongly idealised and never occurs in reality; every system undergoes some degree of interaction with its environment, and it is impossible to keep track of every entity in the universe that the system might interact with. It is therefore more realistic to consider an ensemble of paths emerging from the starting point, with each path representing a possible evolution of the system as it interacts with its environment. We call each possible path a sample path, and let $\Omega$ denote the sample space, the collection of all possible sample paths that could be followed by the system.

The goal of stochastic analysis is to assign every sample path a probability of occurring,
with the assignments made on the basis of a priori information that we have available on the system. However, usually such information is not available on the paths themselves, but on the particular events that might occur during the evolution of the system. Indeed, each sample path can be thought of as a combination of particular events. For example, if \( X_s \) is position at time \( s \) of a particle of interest, and a sample path takes the particle beyond point \( M \) at time \( s \), then the event \( \{ X_s > M \} \) would be a part of that sample path. While there might be several sample paths which involve this event, each individual sample path will be unique in the particular combination of events that it contains. As the ‘\{\ldots\}’ notation might suggest, events are subsets of one or more sample paths. Moreover, since sample paths are contained in the sample space, it is correct to say that events are a subset of the sample space. However, since the only explicit elements of a sample space are the sample paths, it is not immediately obvious which events are contained in the sample space. Moreover, if we were to decompose every sample path into its constituent events, many of them would involve very obscure situations that are inappropriate for the assignment of probabilities. It would therefore be convenient to have available a set which contained every useful event of the sample space as its explicit elements. Such a set is called a \( \sigma \) algebra, and is denoted by \( \mathcal{F} \). A \( \sigma \) algebra may be formed in the following way. 1. Take an event which is easily identified, say \( \{ X_s > M \} \), take its complement, \( \{ X_s > M \}^C \) (the set of all events of the sample space which are not contained in \( \{ X_s > M \} \)) and add both \( \{ X_s > M \} \) and \( \{ X_s > M \}^C \) to \( \mathcal{F} \). 2. Take another event from the sample space, take its complement, and also add them to \( \mathcal{F} \). 3. Repeat this for an infinite number of events. \( \mathcal{F} \) now contains an infinite number of events. 4. Now, pick an infinite number of events from \( \mathcal{F} \), say \( A_1, A_2, \ldots \), take their union and add it to \( \mathcal{F} \). Then, add the complement of this union, \( A^C \), to \( \mathcal{F} \). Starting from step 1, repeat this entire procedure until \( \mathcal{F} \) contains all possible events that can be assigned probabilities in a sensible way. Note that \( \Omega \) should be included in \( \mathcal{F} \), as the sample space can be assigned a probability of 1. This means that \( \Omega^C = \emptyset \), the set containing no elements, should also be included in \( \mathcal{F} \), and should be assigned a probability of 0. \( \emptyset \) should not be interpreted as the event where nothing occurs, as this is itself an event which contains elements. This completes the construction of the \( \sigma \) algebra, the collection of all useful events which may occur during the evolution of the system.

**Definition 10.1.** Let \( \Omega \) be a sample space. A \( \sigma \) algebra is a family of subsets \( \mathcal{F} \) of \( \Omega \) with the properties.

1. \( \emptyset \in \mathcal{F} \).

2. If \( F \in \mathcal{F} \), then \( F^C \in \mathcal{F} \).

3. If \( A_1, A_2, \ldots \in \mathcal{F} \), then \( A = \bigcup_{i=1}^{\infty} A_i \in \mathcal{F} \).

Note that \( \Omega \in \mathcal{F} \) is implied by properties 1 and 2.
While the $\sigma$ algebra $\mathcal{F}$ contains every event that might occur, we are usually only interested in events that occur before or at a fixed time $t$. It is therefore convenient to consider a $\sigma$ algebra $\mathcal{F}_t$ which is constructed in the same way as $\mathcal{F}$, but by only considering events that occur before or at time $t$. $\mathcal{F}_t$ is smaller than $\mathcal{F}$ (in the sense that it contains less elements) because the latter also includes events which occur beyond time $t$. Hence, $\mathcal{F}_t \subset \mathcal{F}$. The collection of $\sigma$ algebras $\{\mathcal{F}_s\}_{s \in \mathbb{R}^+}$ is known as a filtration. For convenience, we denote the filtration by $\mathcal{F}$.

With the $\sigma$ algebra in hand, we are ready to assign probabilities to the events that it contains. Our understanding of the phrase ‘the probability that event $A$ occurs’ is based entirely on intuition, and is expressed in terms of a number from the interval $[0, 1]$. This number might be thought of as a length, with lengths closer to 1 corresponding to events which are more likely to occur. The mathematical model for this idea is a measure.

**Definition 10.2.** A measure $M$ is a function of a set $\mathcal{C}$ with two properties.

1. $M \mapsto [0, B]$, that is, $M$ takes on values from the interval $[0, B]$, where $B$ is finite.
2. $M(\emptyset) = 0$
3. If $c_1$ and $c_2$ are mutually exclusive subsets of $\mathcal{C}$ (i.e., they contain no common elements), then $M(c_1 \cup c_2) = M(c_1) + M(c_2)$

While the definition of a measure may appear technical, it merely generalises the concepts of volume, area and length from Euclidean geometry to more abstract situations involving sets such as $\mathcal{C}$. Property 1 of the definition shows that measures, just like volumes, areas and lengths, are non-negative. Property 2 shows that that the measure of the entire set $\mathcal{C}$ is $B$, just as how the volume of an entire Euclidean space is equal to the total volume of the space. Just as the total volume of two separate, mutually exclusive volumes in a Euclidean space is the sum of their volumes, property 3 shows that the total measure to two mutually exclusive sets is the sum of the two measures. Sets on which a measure may be defined are called measurable. A probability measure is defined for the case $\mathcal{C} = \mathcal{F}$, and $B = 1$, and is given the symbol $P$. For an event $F \in \mathcal{F}$, $P(F)$ is interpreted as ‘the probability that event $F$ occurs’. In ‘doing’ stochastic analysis, it is assumed that we have these probabilities available from *a priori* information on the system, from which we can go ahead and analyse the properties of the sample paths in the sample space.

The sample space $\Omega$, $\sigma$ algebra $\mathcal{F}$ and probability measure $P$ are collectively called the stochastic basis for the system of interest. A stochastic basis is denoted by $(\Omega, \mathcal{F}, P)$. In this work, we will be considering a filtered stochastic basis, $(\Omega, \mathcal{F}, \mathcal{F}_t, P)$.

**Random variables and stochastic processes**

An individual sample path describes everything that happens to the system as it evolves from time $t = 0$ onwards. Usually, we are not interested in the sample paths themselves,
but only in particular observable quantities associated with the sample paths, such as the position of the system at a particular point in time or the position of the system as a function of time. The need to consider observable quantities directly leads us to random variables and stochastic processes. For ease of notation, we will restrict attention to observations made in one dimension only. Generalisations to multiple dimensions are straightforward.

Random variables are the mathematical model for observations made on a system at a fixed point in time. Examples of random variables include the position of the system at time \( s \) and the displacement of a liquid surface immediately beneath an incoming atom when it first reaches point \( x \) along the horizontal axis. A random variable is a real valued function of the sample space. That is, the value that it takes on depends upon the sample path that occurs. The fact that random variables take on real values is what lets them correspond to observable, experimentally measurable quantities. Since events can almost always be expressed in terms of random variables (for example, recall \{\( X_s > M \}\), the event that the position of the particle at time \( s \) exceeds \( M \)), and since the events in \( \mathcal{F} \) are associated with the probability measure \( P \), random variables of the sample space \( \Omega \) are also associated with the probability measure \( P \). To highlight that random variables are associated with probability measures on the \( \sigma \) algebra \( \mathcal{F} \), we say that random variables are \( \mathcal{F} \) measurable functions. Indeed, since random variables apply at a fixed time \( s \), they only depend upon events occurring at or before time \( s \) (exceptional cases can be regarded as non-physical), and therefore it is correct to call them \( \mathcal{F}_s \) measurable functions.

Measures of the form \( P(X_s \in A) \), where \( A \) is a subset of \( \mathbb{R} \) are called the distribution of the random variable \( X_s \). When \( A = (-\infty, x) \), the probability \( P(X_s \in x) \) can be expressed as \( P(X_s < x) \), which is called the distribution function of \( X_s \). By differentiating the distribution function with respect to \( x \), we obtain the probability density function of \( X_s \),

\[
f(x) = \frac{dP(X < x)}{dx}.
\]

The density function is interpreted as the probability that \( X_s \) will take on a value between \( x \) and \( x + dx \), and is a special case of a distribution with \( A \) set to \((x, x + dx)\). Observe that if the probability distribution function of a random variable is known, then its density function is known and its distribution can be obtained by integrating the density function over a desired region in \( \mathbb{R} \). In this sense, obtaining a probability distribution function is the key to solving a probabilistic problem.

**Definition 10.3.** Let \((\Omega, \mathcal{F}, P)\) be a given stochastic basis. A random variable is an \( \mathcal{F} \) measurable function of \( \Omega \) which takes values in \( \mathbb{R} \), that is, \( X : \Omega \rightarrow \mathbb{R} \). The measure \( P(X \in A) \) for \( A \in \mathbb{R} \) is the distribution of \( X \), \( P(X < x) \) for \( x \in \mathbb{R} \) is the distribution function of \( X \), and \( f(x) = \frac{dP(X < x)}{dx} \) is the probability density function of \( x \). The expected value and variance of a random variable \( X \) are
\[ E[X] = \int_{\mathbb{R}} x \, dP(X < x) = \int_{\mathbb{R}} x f(x) \, dx, \]

\[ V[X] = \int_{\mathbb{R}} (x - E[X])^2 \, dP(X < x) = \int_{\mathbb{R}} (x - E[X])^2 f(x) \, dx, \]

respectively.

The concepts of expected value and variance will be familiar from elementary statistics. Note that the probability density function does not exist for a random variable which can only take on a discrete range of values (rather than a continuous range) from \( \mathbb{R} \). In such cases, we consider the measure \( P(X = x) \) directly and define the expected value and variance as the sums \( \sum_i x_i P(X = x_i) \) and \( \sum_i (x_i - E[X])^2 P(X = x_i) \), respectively. Note that probabilities of the form \( P(X = x) \) are only well-defined for discrete random variables. For continuous random variables the probability that \( X = x \) is undefined, however there is a non-zero probability that it will be contained in an infinitesimal region about \( x \). Higher moments may also be defined for both continuous and discrete random variables, but are not of interest to this work.

**Example.** Two important types of random variables described in this work are *normal random variables* and *uniform random variables*. Normal random variables have a Gaussian as their probability density function,

\[ f(x) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-(x-\mu)^2/2\sigma^2} \]

where \( \mu \) is the expected value of the random variable and \( \sigma^2 \) is its variance. Normal random variables are denoted with the shorthand notation \( N(\mu, \sigma^2) \). A uniform random variable is one whose density function is constant over the interval \([A, B]\), and is zero everywhere else.

\[ f(x) = \begin{cases} 
 1/(B - A) & x \in [A, B] \\
 0 & \text{otherwise} 
\end{cases} \]

The mean and standard deviation of a uniform random variable are \((B + A)/2\) and \((B - A)^2/12\), respectively.

Just as random variables model observations made at a fixed point in time, stochastic processes model observations recorded as functions of time. A natural mathematical model for a stochastic process is a collection which contains one random variable for every point in time from 0 to \( \infty \), namely

\[ Y = \{ Y_t \}_{t \in \mathbb{R}_+}. \]

Thus, each \( Y_t \in Y \) corresponds to an observation made at a fixed point in time (a random variable), and the entire collection represents the evolution of the observable from
time 0 to time $\infty$.

Stochastic processes put time dependent functions from deterministic mathematics on probabilistic footing. However, this does not mean that stochastic processes have mathematical formulas in the same way that their deterministic analogues do. Instead, their evolution through time is defined by probability measures on their constituent random variables. In turn, these probability measures can be specified by transition probabilities, which give the probability of the event \( \{Y_t \in (q_f, r_f)\} \) given that \( \{Y_s \in (q_i, r_i)\} \) for some time \( s < t \). Mathematically, transition probabilities are expressed as conditional probability measures,

\[ P(Y_t \in (q_f, r_f) | Y_s \in (q_i, r_i)) \]

A transition probability is a probability measure on the \( \sigma \) algebra formed by taking \( F_t \) and removing all events in which \( Y_s \notin (q_i, r_i) \) (i.e., all events which are known not to have occurred). Hence, instead of deriving a formula like we would in analysing a system undergoing deterministic evolution, we are here required to derive appropriate transition probabilities. There are two kinds of distributions that are associated with stochastic processes. For a collection of times \( 0 \leq t_1, \ldots, t_k < \infty \), the joint distribution

\[ P(Y_{t_1} \in A_1, \ldots, Y_{t_k} \in A_k) \]

of random variables is known as the \textit{finite dimensional distribution} of \( Y \), and can be derived from the transition probabilities. The distribution obtained from all times in \( \mathbb{R}_+ \) is \textit{the distribution} of \( Y \). The distribution of \( Y \) gives us the exact probability that the process will follow a particular path. However, it is impossible to ever obtain a distribution of a stochastic process from direct observations on a system. In any real life situation, we can only obtain a finite number of measurements, which in turn correspond to a finite number of times, and hence a finite dimensional distribution.

Two important remarks are necessary. First, for every sample path of the system, there is a corresponding well-defined path for the stochastic process. Since we never know exactly which sample path the system is following as we observe its evolution, the transition probabilities and finite dimensional distributions provide a means to narrow the list of possibilities. The possible paths of a stochastic process are also called sample paths, and should not be confused with the sample paths of the system itself. However, the difference is somewhat immaterial because it is only observables that we are interested in, rather than the entire information content of the system. Second is that the state of the stochastic process \( Y \) at time \( t \) only depends upon the \( \sigma \)-algebra \( F_t \). This is because the constituent random variables \( Y_0 \) to \( Y_t \) only depend upon events occurring at or before the time of their occurrence (that is, they are \( F_s \) measurable). To highlight this fact we say that a stochastic process is \textit{adapted to the filtration} \( \mathcal{F} \) (or just ‘adapted’).
Definition 10.4. Let $(\Omega, \mathcal{F}, \mathcal{F}, P)$ be a given stochastic basis. A stochastic process is a parametrised collection of random variables $Y = \{Y_t\}_{t \in \mathbb{R}^+}$. A stochastic process is adapted to $\mathcal{F}$ if, for every $t \in \mathbb{R}^+$, the random variable $Y_t$ is $\mathcal{F}_t$ measurable. The finite dimensional distributions of a stochastic process are the measures of the form $P(Y_{t_1} \in A_1, \ldots Y_{t_k} \in A_k)$.

Example 1. A stochastic process which appears frequently in applications is the Wiener process. The transition probabilities of a Wiener process are defined as

$$P(W_t \in dw | W_s \in dw) = \frac{1}{\sqrt{2\pi(t-s)}} e^{-(w_t-w_s)^2/2(t-s)}$$

where $dw$ denotes an infinitely small interval centered on $w$. Thus, the increments \{W_t - W_s\} of a Wiener process are normal random variables with expected values of zero and variance $t - s$. The finite dimensional distributions of a Wiener process may be computed by integrating over products of the transition probabilities. For example, let $0 = t_0 < t_1 < \cdots < t_n \leq \infty$. For notational convenience let

$$p_{t, t-1}(w_t, w_{t-1}) = P(W_t \in dw_t | W_{t-1} \in dw_{t-1}).$$

Then, a finite dimensional distribution of the Wiener process is

$$P(W_{t_1} \in F_1, \ldots, W_{t_n} \in F_n) = \int_{F_1 \times \cdots \times F_n} p_{t_n, t_{n-1}}(w_{t_n}, w_{t_{n-1}}) \cdots p_{t_1, t_0}(w_{t_1}, w_{t_0}),$$

where the integration is carried out with respect to the transition measures. A representative sample path of the Wiener process is plotted on the next page, and is reminiscent of the trajectory of a particle undergoing Brownian motion. In fact, the Wiener process was originally developed to study Brownian motion (as might be guessed from the equation $V(W_t) = t$), and is often used to solve Langevin’s equation of motion for a Brownian particle [32].

Note that the statement ‘with probability 1’ appears regularly in stochastic analysis and can be abbreviated to almost surely, or just a.s. The ‘almost’ is slightly superfluous, and emphasises that we are neglecting paths and events with zero probability measure.

Example 2. Arguably the most important class of stochastic processes are the semi-martingales. Loosely speaking, $Y_t$ is a semimartingale if the stochastic integral

$$I_t = \int_0^t f(t, Y_s) dY_s,$$

where $f$ is a bounded function, can be defined as a limit of sums in the same way that the classical Riemann-Stieltjes integral from ordinary calculus can be (see section 3.2.3). Our interest in semimartingales is that the equations of motion for an atom passing over a liquid surface contain a well-defined integral with respect to the random walk on
parabolas process $Q$ (see equation (5.12)). The random walk on parabolas is therefore a semimartingale. Semimartingales are discussed in detail in Protter’s seminal text on the subject [98]. As well as the fact that semimartingales form the basis of *stochastic calculus*, they have the potential for developing dynamical equations without resorting to old fashioned techniques developed for Brownian motion.

Before moving on, recall that a probability measure is defined only for ‘measurable’ subsets. Since the distributions of a random variable (and finite dimensional distributions of a stochastic process) are defined for subsets of $\mathbb{R}$, we need to know what the measurable subsets of $\mathbb{R}$ are. The measurable subsets sets of $\mathbb{R}$ are contained in the *Borel $\sigma$-algebra* of $\mathbb{R}$, $\mathcal{B}$. $\mathcal{B}$ is the $\sigma$-algebra formed from all open intervals (intervals of the form $(x_1, x_2)$) or all closed intervals $[x_1, x_2]$ of $\mathbb{R}$. $\mathcal{B}$ contains all open intervals, all closed intervals, all countable unions of all open intervals, etc, of $\mathbb{R}$. The elements of $\mathcal{B}$ are called *Borel sets*. Thus, a probability measure for a random variable is well defined only if it can be defined for all Borel sets in $\mathcal{B}$. We will need this fact when defining probability measures for the random walk on polynomial process in Chapter 3.

**Convergence of stochastic processes**

It is often the case that, in approaching a certain limit, a particular stochastic process $X$ takes on the behavior of another stochastic process $Y$. In such a situation we say that the $X$ *converges* to $Y$. Convergence is an important contemporary topic in stochastic analysis, particularly for its application of approximating processes with other processes which are easier to study. In section 3.3.2, we gain some insights into the sample paths of the Wiener process by convergence of our random walk on polynomials process.

The basic concepts are best illustrated by considering convergence of random variables.
Let \( X_1^s, X_2^s, \ldots \) be a sequence of random variables and let \( Y_s \) be another random variable.

- Suppose that

\[
P \left( \lim_{n \to \infty} |X_n^s - Y_s| \geq \epsilon \right) = 0
\]

for every \( \epsilon > 0 \). Then we say that \( X_n^s \) \textit{converges in probability} to \( Y_s \). In words, this says that as we go through the sequence \( X_2^s, X_2^s, \ldots \), the probability that the random variables differ from \( Y_s \) by any amount goes to zero. We write \( X_n^s \to Y_s \) to denote convergence of \( X_n^s \) to \( Y_s \) in probability.

- Suppose that, as \( n \to \infty \), the distribution of \( X_n^s \) approaches the distribution of \( Y_s \). Then we say that \( X_n^s \) \textit{weakly converges} to \( Y_s \). We write \( X_n^s \Rightarrow Y_s \) to denote weak convergence of \( X_n^s \) to \( Y_s \).

The difference between convergence in probability and weak convergence is that, in the former case, the event \( \{|X_n^s - Y_s| > 0\} \) has a zero probability measure in the limit, and therefore has no chance of occurring. Weak convergence only shows that the expression for the distribution \( P(X_n^s \in A) \) becomes equivalent to the expression for \( P(Y_s \in A) \) in the limit. The ‘weakness’ of the latter is that the random variables \( X_n^s \) and \( Y_s \) might be defined on different probability spaces, and so the event \( \{|X_n^s - Y_s| > 0\} \) might not be meaningful [40]. In physical terms, the limiting observation \( X_n^s \) might not actually ‘be’ \( Y_s \), but merely look like it. Since convergence in probability implies weak convergence, but weak convergence does not necessarily imply convergence in probability, convergence in probability is considered to be the stronger mode of convergence. In practice, the distinction between ‘being’ and ‘merely looking like’ is not so important and so weak convergence is almost always satisfactory.

A famous example of weak convergence is the \textit{central limit theorem} [30].

**Theorem 10.1.** Let \( X_1^s, X_2^s, \ldots, X_n^s \) be independent and identically distributed random variables with \( E(X_1^s) = 0 \) and \( V(X_1^s) = \sigma^2 \). Then, as \( n \to \infty \),

\[
X_1^s + X_2^s + \ldots + X_n^s \Rightarrow N(0, n\sigma^2)
\]

The random variables \( X_1^s \) and \( X_2^s \) are said to be \textit{independent} when \( P(X_1^s \in A_1 \cap X_2^s \in A_2) = P(X_1^s \in A_1)P(X_2^s \in A_2) \), i.e., the probability that \( X_1^s \) takes on values from \( A_1 \) if not affected by whether \( X_2^s \) takes on values from \( A_2 \). The phrase ‘independent and identically distributed’ is often abbreviated to \textit{iid}. The central limit theorem is used in section 3.3.2 to obtain weak convergence of the random walk on polynomials at time \( s \) to a Wiener process at time \( s \).

Weak convergence of stochastic processes is a more delicate matter. Consider a sequence of stochastic processes \( Y^1, Y^2, \ldots \) and another process \( Z \). We might be tempted to conclude that if the finite dimensional distributions of \( Y^n \) converge to those of \( Z \), i.e.,
\[(Y^n_{t_1}, Y^n_{t_2}, \ldots) \Rightarrow (Z_{t_1}, Z_{t_2}, \ldots)\]

then \(Y^n \Rightarrow Z\). However, it is possible to construct (admittedly pathological) processes whose paths oscillate so rapidly in approaching the limit that the finite dimensional distributions do not smoothly approach those of the target process (see pages 282 - 283 of reference [26], for example). Fortunately, we can obtain weak convergence of a sequence of stochastic processes if the sequence of probability distributions are *tight*. For all stochastic processes described in this work, the following definition of tightness is sufficient.

**Definition 10.5.** Let \(Y^1, Y^2, \ldots\) be a sequence of stochastic processes. The sequence of distributions \(P_1(Y^1_s \in A_1), P_2(Y^2_s \in A_2), \ldots\) is said to be tight if, for every \(\epsilon > 0\) there is are real numbers \(N_\epsilon\) and \(\delta > 0\) such that

\[
P_n\left(\left|Y^n_{t_i} - Y^n_{t_{i-1}}\right| \geq N_\epsilon\right) \leq \epsilon
\]

for every \(t_i - t_{i-1} \leq \delta\) and every \(n\).

Note that the definition allows for each process in the sequence \(Y^1, Y^2, \ldots\) to be on a different probability spaces (as indicated by the subscript on the probability measure), and that the number \(N_\epsilon\) is the same for every value of \(n\). This definition of tightness essentially says that there is a vanishingly small probability (in the order of \(\epsilon\)) that the process will leap to a very large value (in the order of \(N_\epsilon\)) during each vanishingly small time interval (in the order of \(\delta\)). With this definition of tightness and convergence of finite dimensional distributions, we obtain \(Y^n \Rightarrow Z\) [26].

**Theorem 10.2.** Let \(Y^1, Y^2, \ldots Y^n\) be a sequence of stochastic processes. If the finite dimensional distributions of \(Y^n\) converge to those of \(Z\) in the limit of \(n \to \infty\), and the sequence of distributions \(P_1(Y^1_s \in A_1), P_2(Y^2_s \in A_2), \ldots\) is tight, then \(Y^n \Rightarrow Z\) as \(n \to \infty\).
Bibliography


187


[74] G. M. Nathanson. Personal communication.


