Viscosity Of Secondary Organic Material

And Related Atmospheric Implications

by

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Abstract

Aerosols are ubiquitous throughout the Earth’s atmosphere, and secondary organic material (SOM), which is produced from the oxidation of volatile organic compounds, is estimated to constitute a significant fraction of atmospheric aerosol mass. Furthermore, particles containing SOM can cause negative health outcomes, and affect Earth’s climate, both directly by scattering solar radiation, and indirectly by acting as nuclei for cloud droplets.

Despite the importance of particles containing SOM, their physical properties, such as viscosity, are poorly constrained. To address this knowledge deficit, a technique to measure the viscosity of small samples of material, similar to that produced in environmental simulation chambers, was developed and validated. This technique was then used to measure the viscosity of SOM produced via the ozonolysis of α-pinene in an environmental simulation chamber. The viscosity of this material was found to depend strongly on the relative humidity (RH) used when measuring viscosity and the concentration of SOM mass at which the SOM was produced. A difference between the viscosity of the water-soluble component of SOM and the total SOM (water-soluble and water-insoluble components) was also observed.

The viscosity of saccharides and a tetraol were subsequently measured, with these compounds serving as proxies of highly oxidized components of SOM found in the atmosphere. For saccharides, viscosity was determined to increase by at least four orders of magnitude as molar mass doubled. In addition, the tetraol was determined to have a viscosity at least two orders of magnitude lower than that of SOM produced via the oxidation of isoprene, in which the tetraol has been identified.

Finally, literature viscosity data for organic compounds was used to demonstrate that saturation vapour concentration, the mass based equiv-
Abstract

alent of saturation vapour pressure, is a useful parameter for predicting viscosity, and better than elemental oxygen-to-carbon ratio or molar mass, at least for organic compounds containing only one or two functional groups.

The results presented in this dissertation increase our knowledge of the viscosity of SOM, and its dependence on RH, the SOM mass concentration at which the SOM is produced, number of hydroxyl functional groups in the organic molecule, and molar mass.
Preface

Chapters 3-5 are co-authored peer-reviewed journal articles and Chapters 6 and 7 are co-authored work in preparation for submission as peer-reviewed journal articles. The details of my contributions to each research chapter are provided below.


- Assisted with research formulation and design.
- Performed measurements using the poke-and-flow technique.
- Assisted in data analysis.
- Assisted in preparation of the manuscript.
- Additional contributions from co-authors.
  - L Renbaum-Wolff, B. J. Murray, J. E. Shilling, S. T. Martin, and A. K. Bertram also designed research.
  - L. Renbaum-Wolff performed measurements using the bead-mobility technique.
  - A. P. Bateman, M. Kuwata, and J. E. Shilling produced and collected samples.
  - L. Renbaum-Wolff and A. K. Bertram designed models using COMSOL.
Preface

- L. Renbaum-Wolff, M. Sellier, and A. K. Bertram also analyzed data.
- L. Renbaum-Wolff produced all figures in the manuscript.
- L. Renbaum-Wolff, S. T. Martin, and A. K. Bertram also prepared the manuscript.


- Designed and formulated research aims with A. K. Bertram and M. Song.
- Performed measurements on sucrose-water particles using the poke-and-flow technique.
- Took photographs to determine the contact angle of particles comprised of standard solutions.
- Performed data analysis.
- Prepared the manuscript with M. Song and A. K. Bertram.
- Produced all figures in the manuscript.
- Additional contributions from co-authors.
  - M. Song performed experiments on sucrose-water particles and particles comprised of standard solutions using the poke-and-flow technique.
  - M. Song also analyzed data.
  - M. Song supplied some images for Figure [4.1] and all images for Figure [4.3].

- Designed and formulated research aims with A. K. Bertram and L. Renbaum-Wolff.
- Assisted with sample production and collection.
- Performed measurements using the poke-and-flow technique and measured particle-substrate contact angles.
- Analysed data.
- Prepared manuscript, including all of the figures in the manuscript.
- Additional contributions from co-authors.
  - Y. Zhang, A. Mutzel, and O. Böge produced and collected samples.
  - S. Kamal assisted with contact angle measurements.
  - Y. Zhang, A. Mutzel, L. Renbaum-Wolff, S. Kamal, S. T. Martin, and A. K. Bertram also prepared the manuscript.

Chapter 6

- Designed and formulated research aims with A. K. Bertram.
- Performed measurements of the tetraol compound using the bead-mobility technique.
- Took photographs to determine the contact angle of particles comprised of saccharide-water solutions.
- Analysed data.
Preface

• Prepared the writing and all figures in the chapter.

• Additional contributions from co-authors.
  • M. A. Upshur synthesised the tetraol compound studied, and provided a description of the synthesis and the tests of purity and stability.
  • M. Song performed experiments on saccharide-water particles using the poke-and-flow technique.
  • M. Song supplied the images for Figure 6.1
  • M. Song also analyzed data.
  • A. K. Bertram also helped to write the chapter.

Chapter 7

• Designed and formulated research aims with A. K. Bertram.

• Performed literature research.

• Prepared the writing and all figures in the chapter.

• Additional contributions from co-authors.
  • A. K. Bertram also helped to write the chapter.
# Table of Contents

Abstract ................................................................. ii

Preface ................................................................. iv

Table of Contents ....................................................... viii

List of Tables ............................................................ xii

List of Figures ........................................................... xvi

List of Symbols .......................................................... xxxi

List of Units ............................................................... xxxii

List of Abbreviations .................................................... xxxiii

Acknowledgements ....................................................... xxxiv

Dedication ................................................................. xxxvi

1 Introduction ............................................................. 1

1.1 Atmospheric aerosols .............................................. 1

1.1.1 Formation, sources, and classification of aerosols ... 1

1.1.2 Effects of aerosols ............................................. 3

1.2 Formation of secondary organic material ...................... 5

1.3 Viscosity ............................................................. 7

1.3.1 What is viscosity? .............................................. 7

1.3.2 Types of fluids ................................................ 9

1.3.3 Commercially available methods to measure viscosity 11

viii
# Table of Contents

1.3.4 Potential viscosities of SOM ........................................... 13
1.3.5 The importance of the viscosity of SOM ........................... 14
1.4 Previous research related to the viscosity of SOM .................. 16
1.5 Overview of dissertation .................................................. 16

2 Experimental techniques ................................................... 18
  2.1 Bead-mobility technique .................................................. 18
  2.2 Poke-and-flow technique combined with simulations ............... 23
    2.2.1 Poke-and-flow technique ............................................ 23
    2.2.2 Simulations using COMSOL Multiphysics ...................... 27
    2.2.3 Simulations of particles exhibiting flow ........................ 29
    2.2.4 Simulations of particles that cracked when poked ............. 32
  2.3 Equilibration times ...................................................... 35

3 Viscosity of water-soluble α-pinene derived SOM .................... 37
  3.1 Introduction ............................................................. 37
  3.2 Experimental ............................................................ 39
    3.2.1 Production of secondary organic material ...................... 39
    3.2.2 Bead-mobility technique .......................................... 40
    3.2.3 Poke-and-flow technique .......................................... 40
    3.2.4 Simulations of material flow at 40-70 % RH .................. 40
    3.2.5 Simulations of material flow at 25-30 % RH .................. 43
  3.3 Results ................................................................. 43
    3.3.1 Experiments with the bead-mobility technique ................. 43
    3.3.2 Experiments with the poke-and-flow technique ............... 44
  3.4 Discussion ............................................................. 47
  3.5 Summary ............................................................... 52

4 Additional validation of the poke-and-flow technique ............... 54
  4.1 Introduction ............................................................. 54
  4.2 Experimental ............................................................ 56
    4.2.1 Poke-and-flow technique .......................................... 56
    4.2.2 Simulations of fluid flow ........................................ 57
  4.3 Results and discussion ................................................ 60
# Table of Contents

4.3.1 Sucrose-water particles ........................................ 60  
4.3.2 Particles of polybutene standards .......................... 63  
4.4 Summary ............................................................ 65  

5 Viscosity of α-pinene derived SOM ............................. 67  
5.1 Introduction .......................................................... 67  
5.2 Experimental ......................................................... 68  
  5.2.1 Generation of SOM in an environmental chamber ......... 68  
  5.2.2 Generation of SOM in a flow tube ......................... 69  
  5.2.3 Poke-and-flow technique .................................... 71  
  5.2.4 Simulations of fluid flow .................................. 72  
5.3 Results and discussion ............................................. 74  
  5.3.1 Effect on viscosity of RH ................................... 74  
  5.3.2 Effect on viscosity of production mass concentration 77  
  5.3.3 Effect on viscosity of water-insoluble SOM ............ 84  
5.4 Summary ............................................................ 87  

6 Viscosity of a tetraol and saccharide-water mixtures ...... 89  
6.1 Introduction .......................................................... 89  
6.2 Experimental ......................................................... 91  
  6.2.1 Measurements of viscosity ................................ 91  
  6.2.2 Predictions of viscosity using QSPR models ........... 94  
6.3 Results and discussion ............................................. 95  
  6.3.1 Measured viscosities of saccharides at a range of RHs 95  
  6.3.2 Measured viscosity of a tetraol ............................ 99  
  6.3.3 Predicted viscosities of a tetraol ....................... 101  
6.4 Summary ............................................................ 102  

7 The relationship between viscosity and physical properties 104  
7.1 Introduction .......................................................... 104  
7.2 Methods ............................................................... 107  
  7.2.1 Selection of compounds .................................... 107  
  7.2.2 Parameterisation of data .................................. 108  
7.3 Results ............................................................... 109
### Table of Contents

7.3.1 The relationship between viscosity and O:C  . . . . . 109  
7.3.2 The relationship between viscosity and C*  . . . . . 111  
7.3.3 Relationship between viscosity and both O:C and C* 111  
7.4 The predicted viscosity of products of α-pinene ozonolysis . 113  
7.5 Summary . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 115  

8 Conclusions and future work . . . . . . . . . . . . . . . . . 117  
8.1 Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . . . 117  
8.1.1 Poke-and-flow technique: development and validation 117  
8.1.2 The viscosity of SOM and related compounds . . . . 118  
8.1.3 Predicting the viscosity of SOM . . . . . . . . . . . . 119  
8.2 Directions for future work . . . . . . . . . . . . . . . . . . . 120  

Bibliography . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 122  

Appendices

A Appendix to chapter 3 . . . . . . . . . . . . . . . . . . . . . . . 152  
A.1 Composition of SOM from ozonolysis of α-pinene . . . . . 152  
A.2 Viscosity prediction using mixing rules . . . . . . . . . . . . 152  

B Appendix to chapter 5 . . . . . . . . . . . . . . . . . . . . . . . 154  
B.1 Effect of carrier gas flow on SOM particle properties . . . . 154  
B.2 Particle-to-particle and sample-to-sample variability . . . . 155  
B.3 Calculated viscosity for prior studies of α-pinene derived SOM 155  
B.4 Simulations of fluid flow for particles that exhibit cracking . 157  
B.5 Tables and figures . . . . . . . . . . . . . . . . . . . . . . . . 158  

C Appendix to chapter 7 . . . . . . . . . . . . . . . . . . . . . . . 165  
C.1 Table . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 165
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of literature values of measured slip lengths for water and atmospherically relevant organic compounds.</td>
<td>31</td>
</tr>
<tr>
<td>3.1</td>
<td>Mean bead speeds as a function of RH in water-soluble SOM from α-pinene ozonolysis and corresponding viscosities. Originally published in Renbaum-Wolff et al. (2013a).</td>
<td>44</td>
</tr>
<tr>
<td>3.2</td>
<td>Results from the poke-and-flow experiments. Originally published in Renbaum-Wolff et al. (2013a).</td>
<td>45</td>
</tr>
<tr>
<td>4.1</td>
<td>Experimental parameters used when simulating flow with COMSOL for the sucrose-water experiments. Originally published in Grayson et al. (2015a).</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental parameters used when simulating flow with COMSOL for experiments using polybutene standards. Originally published in Grayson et al. (2015a).</td>
<td>59</td>
</tr>
<tr>
<td>5.1</td>
<td>Conditions used for generating and collecting samples of SOM generated via the ozonolysis of α-pinene. The whole SOM (both water soluble and water insoluble component of the SOM) was collected. Originally published in Grayson et al. (2015b).</td>
<td>70</td>
</tr>
<tr>
<td>5.2</td>
<td>Physical parameters used when simulating particles that exhibited flow with COMSOL. Originally published in Grayson et al. (2015b).</td>
<td>73</td>
</tr>
</tbody>
</table>
5.3 Summary of $\tau_{exp,flow}$ times and viscosities of whole SOM and water-soluble SOM produced in the flow tube at a production mass concentration of 14,000 $\mu$g m$^{-3}$ and studied at <0.5 % RH. Originally published in Grayson et al. (2015b).

6.1 Properties of saccharide and tetraol compounds studied experimentally.

6.2 Physical parameters used to simulate the flow of material during poke-and-flow experiments where a half-torus geometry was formed and the material subsequently observed to flow. $R$ and $r$ represent dimensions of a half-torus, with $R$ representing the radius of the tube of material, and $r$ representing the radius of the hole at the centre of the tube.

6.3 Physical parameters used to simulate a lower limit of viscosity for poke-and-flow experiments where particles cracked when impacted by the needle, and no observable flow of material was observed over the course of the experiment.

6.4 Summary of experimental viscosity measurements using the bead-mobility and poke-and-flow techniques for the tetraol and the saccharide-water particles studied here, with results from individual particles grouped by RH. For experiments using the bead-mobility technique the mean is reported along with the 95 % confidence intervals. For experiments using the poke-and-flow technique lower and upper limits of viscosity are reported, taking account of the 95 % confidence limits of the simulated lower and upper limits of viscosity for the group of particles studied at each RH. N/A is reported for all experiments performed using the poke-and-flow technique, for which no mean viscosity is calculated, and for upper limits of viscosity for experiments with the poke-and-flow technique where the particle cracked, as only a lower limit of viscosity can be calculated.
List of Tables

7.1 A summary of the functional groups featured in the 156 compounds used to determine the relationship between viscosity and either O:C or C*. A compound with multiple oxygen containing functional groups is counted once for each type of functional group it contains, and once in the multiple oxygen containing functional group row. As such, the total sums to >156. ................................................................. [108]

7.2 Summary of the parameterisations used in this study. In each case log(\(\eta / \text{Pa s}\)) is used as the dependent variable, and O:C and log(\(C^* / \mu g \text{m}-3\)) are the independent variables. RMSE refers to the root mean square error between the log(\(\eta / \text{Pa s}\)) predicted by the parameterisation for each of the compounds in the study and the experimental viscosities. ............. [109]

B.1 Summary of \(\tau_{exp,flow}\) times and viscosities of sample analysed after both 1 hour and 45 hours of exposure to a dry (<0.5 \% RH) flow of Nitrogen gas. Originally published in Grayson et al. (2015b). ............................................................... [158]

B.2 Experimentally determined contact angles for each of the samples studied. The range of values represent the 95 \% confidence intervals of the values measured for multiple particles. Originally published in Grayson et al. (2015b). ............... [158]
B.3 Summary of the percent relative standard deviation (% RSD) in $\tau_{\text{exp,flow}}$, lower limits of viscosity, and upper limits of viscosity for particles produced using equivalent conditions and studied via the poke-and-flow technique in combination with simulations of fluid flow at <0.5 % RH. Three samples were studied per production mass concentration in the flow tube. Values prior to parentheses represent the relative standard deviation between all particles studied that were produced at a given mass concentration, whilst the values inside each parenthesis represent the average relative standard deviation between particles on the same substrate. Originally published in Grayson et al. (2015b). 159

B.4 Summary of parameters used to estimate viscosity from literature studies of SOM produced via the ozonolysis of $\alpha$-pinene. Originally published in Grayson et al. (2015b). 160

B.5 Physical parameters when simulating particles that don’t exhibit flow in COMSOL. Originally published in Grayson et al. (2015b). 161

C.1 A list of compounds included in the study, along with selected chemical and physical properties. 165
List of Figures

1.1 A summary of radiative forcing by atmospheric aerosols and other atmospheric constituents between 1750 and 2011. Uncertainties represent the 5-95 % confidence range, with solid error bars representing the uncertainty in the magnitude of effective radiative forcing and dotted bars representing uncertainty in the magnitude of radiative forcing. Also shown is the level of confidence for each source of forcing, based on the current level of scientific knowledge. Figure adapted from Figure TS.6 of Stocker et al. (2013). 5
1.2 Chemical structures of isoprene (left) and (+)-α-pinene (right). 6
1.3 Laminar flow of a fluid between two 2D boundary plates - one stationary and one moving. 8
1.4 The relationship between shear rate and shear stress for types of fluids. 10
1.5 Schematic of two examples of commercially available viscometers. Shown in (a) is an Ostwald viscometer. Sample is added to side 1 until the sample in the capillary is level with line A. Suction is subsequently applied at point 2, and the time taken for the sample to flow between line B and line C is measured. Shown in (b) is a coaxial-cylinder viscometer. The outer cylinder is rotated at a constant speed, and the angular deflection of the inner cylinder is used to determine the viscosity of the sample. 12
List of Figures

1.6 (a) A scale showing part of the viscosity continuum, detailing the regions typically defined to be bound by the solid, semi-solid, and liquid regimes, as well as the viscosities of some common substances (idea to show common substances is borrowed from Koop et al. [2011]). The image of the pitch is a detail of a picture taken from Wikimedia Commons of the pitch drop experiment Wikipedia page (GFDL, John Mainstone, University of Queensland, Australia). (b) A scale showing the ranges of viscosity measurable using commercially available instrumentation for measuring viscosity, as well as the possible range of viscosities spanned by SOM.  

1.7 (a) Effect of particle viscosity on the mechanism of growth of SOM by semivolatile organic compound (SVOC) uptake. (b) Effect of particle viscosity on heterogeneous oxidation by ozone. (c) Climate effects of particles and implications of high particle viscosities on particle growth rates, particle mass, and heterogeneous oxidation by O₃. The implications of particle viscosity on growth and heterogeneous oxidation in (a)-(c) assume a monodisperse particle population. Originally published in Renbaum-Wolff et al. (2013a).  

2.1 Schematic representation of bead-mobility experimental setup. Originally published in Renbaum-Wolff et al. (2013b).  

2.2 Illustration of the flow of the flow gas around a sample particle. Originally published in Renbaum-Wolff et al. (2013b).  

2.3 Internal circulation of beads within a particle of glycerol. The red lines overlaid on the image show the 2-D circulation of three beads within the particle. Originally published in Renbaum-Wolff et al. (2013b).
2.4 Images from the bead-mobility studies. Images in (a) correspond to images recorded at 90 % RH and images in (b) correspond to images recorded at 70 % RH. Indicated in the figure are different beads monitored in the experiments and the x-y coordinates of the beads. Originally published in Renbaum-Wolff et al. (2013a).

2.5 Average bead speed (±1 σ) vs. viscosity for standard compounds. Originally published in Renbaum-Wolff et al. (2013b).


2.7 Deformation and recovery across time of poked SOM particles. Prior to poking (pre-poke), the particle morphology can be approximately described as a spherical cap. At higher RH (40-70 %) (rows a-c), geometries approximately described as half-torus are formed, and flow occurs. By comparison, for low RH (≤30%) (row d) particles shatter and do not flow over a period of 8 h. The ring structures observed in the first and last columns are an optical effect that arises from hemispherical diffraction. Originally published in Renbaum-Wolff et al. (2013a).

2.8 Details of half-torus model used to simulate the flow in experiments: (a) top view, where R and r are the notations used here to describe the dimensions of a half-torus geometry; (b) side view, where surface 1 represents the air-fluid interface, and surface 2 represents the fluid-substrate interface. Originally published in Grayson et al. (2015a).
2.9 The dependence of viscosity as (a) surface tension, (b) slip length, (c) density, (d) contact angle, and (e) $\tau_{\text{model,flow}}$, are varied across a wide range of values for particles of dimensions $R_0 = 16$, $r_0 = 4$ (filled symbols) and $R_0 = 14$, $r_0 = 6$ (open symbols). For each simulation four of the five properties were held constant whilst the fifth was varied. Black squares: surface tension = 75.15 mN m\(^{-1}\), slip length = 10 $\mu$m, density = 1500 kg m\(^{-3}\), contact angle = 98.5 $^\circ$, $\tau_{\text{model,flow}} = 1000$ seconds. Red circles: surface tension = 57.2 mN m\(^{-1}\), slip length = 5 nm, density = 1500 kg m\(^{-3}\), contact angle = 98.5 $^\circ$, $\tau_{\text{model,flow}} = 0.1$ seconds.

2.10 Details of quarter-sphere model used to simulate flow for particles that exhibit cracking behaviour and no discernible flow over subsequent hours of observation. Surfaces 1 and 2 represent the external fluid interfaces, to which a relevant value of surface tension from literature was assigned, and surface 3 represents the particle-substrate interface, which was represented as a Navier-slip boundary with a slip length of 10-17 nm. Originally published in Renbaum-Wolff et al. (2013a).

3.1 Schematic detailing the production of SOM via the ozonolysis of $\alpha$-pinene.

3.2 Calibration line from COMSOL simulations (black solid line). In the simulations used to generate this calibration a surface tension of 75 mN m\(^{-1}\) and contact angle of 90 $^\circ$ were used. The annotation in the figure illustrates how the calibration line would shift if a smaller surface tension, smaller equilibrium contact angle, smaller slip length, and/or surface scratching was included in the model. An example line constructed with lower surface tension (60 mN m\(^{-1}\)) and lower contact angle (70 $^\circ$) is given to display the sensitivity of the model to these parameters (grey dashed line). Originally published in Renbaum-Wolff et al. (2013a).
3.3  **(a)** Summary plot of the SOM viscosities determined by a combination of experiments using the bead-mobility technique (black empty squares and triangles for HEC and PNNL samples, respectively, where the black bars represent the 95% prediction intervals) and experiments using the poke-and-flow technique (where the blue bars represent the bounds of the viscosities). HEC refers to samples collected on quartz fiber filters from the Harvard Environmental Chamber. PNNL refers to samples collected on Teflon filters from the Pacific Northwest National Laboratory Continuous-Flow Environmental Chamber. Various common substances have been placed alongside the diagram, along with their approximate viscosities at room temperature, to provide points of reference following the idea of Koop et al. (2011). The secondary $y$-axes show (1) diffusion coefficients calculated using the Stokes-Einstein relation and (2) mixing times ($\tau_{\text{mixing}}$) of the particles due to bulk diffusion in 100 nm particles of the same viscosity (see main text). The image of the pitch is a detail of an image from the pitch drop experiment (Wikimedia Commons, GFDL, University of Queensland, Australia, John Mainstone).  **(b)** Typical relative humidities observed in the planetary boundary layer (Hamed et al., 2011; Held and Soden, 2000; Martin, 2000) and environmental chambers (Kostenidou et al., 2009; Tillmann et al., 2010). Originally published in Renbaum-Wolff et al. (2013a).
List of Figures

4.1 Optical images of sucrose-water particles poked at RHs of (a) 48.8, (b) 52.7, and (c) 58.8% recorded during typical poke-and-flow experiments. Images a1, b1, and c1 correspond to the particles before they are poked. Images a2, b2, and c2 correspond to the first frame post-poke (i.e., the first frame after the needle has been removed). Images a3, b3, and c3 correspond to images of the experimental flow time, $\tau_{\text{exp,flow}}$, the point at which the equivalent area diameter of the hole at the centre of the particle has decreased to 50% of its original size. Images a4, b4, and c4 correspond to the final frame recorded, at which point each particle has re-attained its original spherical cap geometry. Scale bar: 20 $\mu$m. Originally published in Grayson et al. (2015a).

4.2 (a) $\tau_{\text{exp,flow}}$ as a function of RH for individual sucrose-water particles. (b) Calculated viscosities for the individual sucrose-water particles in (a), where red bars represent the calculated lower and upper limits of viscosity. (c) Lower and upper limits of viscosity for the particles shown in (b), grouped by RH. The error bars on the $x$-axis represent the range of RHs at which particles in the group were poked. Lower and upper limits of viscosity were determined for each particle via simulation, with the bottom of a bar on the $y$-axis representing the lowest lower limit of viscosity for any of the particles in the group, and the top of the bar representing the highest upper limit of viscosity for any of the particles in the group. Literature values (Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958) are provided for comparison, with error bars representing $1\sigma$ for Power et al. (2013) and 95% confidence intervals for Quintas et al. (2006). Originally published in Grayson et al. (2015a).
4.3 Optical images of particles of polybutene standards (a) Standard #1 (N450000), and (b) Standard #2 (N2700000), being poked at 0 % RH recorded during typical poke-and-flow experiments. Images a1 and b1 correspond to particles prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, $\tau_{exp,flow}$, the point at which the equivalent area diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Images a4 and b4 correspond to the final frame recorded of each particle, at which point each particle has re-attained its original spherical cap geometry. Scale bar: 20 $\mu$m. Originally published in Grayson et al. (2015a).

4.4 Viscosity as a function of temperature for experiments with the polybutene standards. Results from standard #1 (N450000) are in black whilst results from Standard #2 (N2700000) are in red. Symbols represent values measured by Cannon Instrument Company using a manual capillary viscometer. Bars represent viscosities determined herein. For the bar that represents each standard the bottom of the bar represents the lowest lower limit of viscosity of all the particles examined, whilst the top of the bar represents the highest upper limit of viscosity of all of the particles examined. Originally published in Grayson et al. (2015a).
5.1 Optical images recorded during typical poke-and-flow experiments of whole SOM produced at a production mass concentration of 520 $\mu$g m$^{-3}$ being poked at (a) <0.5 %, and (b) 50 %, RH. Images a1 and b1 correspond to SOM prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: 20 $\mu$m. Originally published in Grayson et al. (2015b). . . . . . . . . . . . . . . . . . . . . 75

5.2 Summary of poke-and-flow experiments from <0.5 % to 50 % RH performed on samples of whole SOM produced at mass concentrations of 520 $\mu$g m$^{-3}$ (Panels (a) and (c)) and 121 $\mu$g m$^{-3}$ (Panels (b) and (d)). Panels (a) and (b) show box plots of observed $\tau_{exp,flow}$ as a function of RH. Panels (c) and (d) show simulated lower (filled symbols) and upper (open symbols) limits of viscosity. Y-error bars represent 95 % confidence intervals, and x-error bars represent the range of RH at which measurements were made. The shaded regions are included to guide the eye of the reader. The viscosities of common substances at room temperature have been added to (d) to provide points of reference, as per Koop et al., 2011. The image of pitch is part of an image from the pitch drop experiment (image courtesy of Wikimedia Commons, GNU Free Documentation License, University of Queensland, John Mainstone). Originally published in Grayson et al. (2015b). . 76
5.3 Optical images recorded during typical poke-and-flow experiments of particles of the whole SOM produced at production mass concentrations of (a) 14,000 µg m\(^{-3}\), (b) 520 µg m\(^{-3}\), and (c) 121 µg m\(^{-3}\) being poked at <0.5 % RH. Images a1, b1 and c1 correspond to SOM prior to poking. Images a2, b2 and c2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3, b3 and c3 correspond to images of the experimental flow time, \(\tau_{exp,flow}\), the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1, b1 and c1: 20 µm. Originally published in Grayson et al. (2015b).

5.4 Summary of poke-and-flow experiments performed on samples of whole SOM at <0.5 % RH. Black symbols represent results from particles produced in a flow tube, whilst red symbols represent results from particles produced in a chamber. Panel (a) shows box plots of observed \(\tau_{exp,flow}\) times at different production mass concentrations for particles poked <0.5 % RH. Boxes represent the 25, 50, and 75 percentiles, open circles represent median values, and whiskers represent the 5 and 95 percentiles. Panel (b) shows the simulated lower (filled squares) and upper (open squares) limit of viscosity for particles at each production mass concentration poked at <0.5 %. Symbols represent mean values. The y error bars represent 95 % confidence intervals. The shaded regions are included to guide the eye of the reader. Also included in (b) are literature viscosities for SOM produced via the ozonolysis of α-pinene (Renbaum-Wolff et al., 2013a; Zhang et al., 2015). Originally published in Grayson et al. (2015b).
5.5 Summary of poke-and-flow experiments performed on particles of whole SOM at 30 % RH. Black symbols represent results from particles produced in a flow tube, whilst red symbols represent results from particles produced in a chamber. Panel (a) shows box plots of observed $\tau_{exp,flow}$ times as a function of SOM mass concentrations for particles studied using the poke-and-flow technique at 30 % RH. Panel (b) shows the simulated lower (filled squares) and upper (open squares) limit of viscosity for particles at each SOM mass concentration studied using the poke-and-flow technique at 30 % RH. Symbols represent mean values, whilst the y error bars represent 95 % confidence intervals. The shaded region is included to guide the eye of the reader. Also included in (b) are literature viscosities from Renbaum-Wolff et al. (2013a) and Zhang et al. (2015), for SOM produced via the ozonolysis of $\alpha$-pinene and studied at 30 % RH. Originally published in Grayson et al. (2015b).
5.6 Optical images recorded during poke-and-flow experiments using particles consisting of (a) the water-soluble component of the SOM and (b) the whole SOM (i.e., both the water-soluble and the water-insoluble components). In both experiments the SOM was produced using a mass concentration of 14,000 $\mu$g m$^{-3}$ and was poked at $<0.5$ % RH. Images a1 and b1 correspond to the SOM prior to being poked. The brightness in Image a1 is due to reflection of the source light by the needle positioned just above the particle. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). The particle comprised of the water-soluble component of SOM exhibited cracking behaviour and, as shown in Image a3, no change in the size or shape of the cracks can be observed 14 hours after the particle has been poked. The particle comprised of whole SOM exhibited flow, and Image b3 corresponds to an image of the particle at its experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: 20 $\mu$m. Originally published in Grayson et al. (2015b).
List of Figures

6.1 Figure 1: Optical images recorded during poke-and-flow experiments using particles of (a) maltohexaose and (b) raffinose. Images a1 and b1 correspond to the particles prior to being poked, with the white haloes being an optical effect. Images a2 and b2 correspond to the first frame after the needle has been remover. The particle composed of maltohexaose and studied at 50 % RH exhibited cracking behaviour and, as shown in Image a3, no change in the size or shape of the cracks can be observed 3 h after the particle has been poked. The particle comprised of raffinose and studied at 54 % RH exhibited flow, and Image b3 corresponds to an image of the particle at its experimental flow time, $\tau_{\text{exp,flow}}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. The scale bar in images a1 and b1 corresponds to 20 $\mu$m.

6.2 Plots of log$_{10}$ (viscosity) vs. (a) relative humidity and (b) both molar mass and number of saccharide units for glucose, sucrose, raffinose, and maltohexaose. Results determined in the current study using the bead-mobility technique are shown using circle symbols, and those determined using the poke-and-flow technique are shown using squares, with filled squares representing upper limits of viscosity and open squares representing lower limits of viscosity, with $y$-error bars representing 95 % confidence intervals for both techniques, as detailed for Table 3. Also included are literature viscosity values for sucrose (Förrst et al., 2002; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007) and glucose (Achard et al., 1992; Barbosa-Canovas et al., 2007; Haynes, 2015), with the viscosity of glucose at 47 % shown in (b) being determined using a polynomial fit of the literature data. The viscosity of water is added to (a), and shaded regions are added to (a) and (b) to guide the readers eye.
6.3 A plot of log(viscosity) vs. number of hydroxyl functional groups added to 2-methylbutane. The symbols correspond to 2-methylbutane (square), 1-hydroxy-2-methylbutane (upward pointing triangle), and 2-methyl-1,2,3,4-tetraol (leftward pointing triangle). The solid line is a fit of the data for 2-methylbutane and 1-hydroxy-2methylbutane.

6.4 Plot of log(viscosity) vs. number of hydroxyl groups added to C\textsubscript{3}-C\textsubscript{8} alkanes. Symbols correspond to alkanes (squares), monoalcohols (upward pointing triangles), diols (downward pointing triangles), and triols (diamonds), with lines drawn between compounds with the same number of carbons.

6.5 Plot of experimental vs. predicted log(viscosity) of C\textsubscript{3}-C\textsubscript{8} alkanes, monoalcohols, and polyols for the models derived by (a) Sastri and Rao (1992) and (b) Marrero-Morejón and Marrero-Morejón and Pardillo-Fontdevila (2000). Dashed 1:1 lines are shown on each plot to guide the readers eye.

7.1 Plots detailing the relationship between viscosity (log(\(\eta / \text{Pa s}\))) and ((a) and (b)) O:C, and ((c) and (d)) log saturation vapour concentration (log(C*)) for a range of compounds comprised only of carbon and hydrogen or carbon, hydrogen, and oxygen atoms, and containing atmospherically relevant functional groups. Lines of best fit are included on plots (a) and (c). 1:1 lines are included on plots (b) and (d) to guide the eye of the reader. Statistical values from the plots are reported in Table 7.2.
List of Figures

7.2 (a) is a 3-D contour plot with O:C and \( \log_{10}(C^* / \mu g m^{-3}) \) on the \( x \)- and \( y \)-axes, respectively, and the colour scale on the plot indicating the viscosity predicted using an MLR with experimental \( \log(\eta / Pa s) \) as the dependent variable and O:C and \( \log(C^* / \mu g m^{-3}) \) as the independent variables. (b) is a residual plot showing the difference for each compound between its experimental viscosity and the viscosity predicted by the regression. (c) is a plot of the predicted viscosities for each of the compounds vs. their experimental viscosities, with a 1:1 line to guide the readers eye.

7.3 Plot of \( \log(\eta / Pa s) \) vs. \( \log(C^* / \mu g m^{-3}) \) for the compounds detailed in Table C.1. The shaded pink region represents the 95 % prediction interval of the linear regression between \( \log(C^* / \mu g m^{-3}) \) vs. \( \log(\eta / Pa s) \). Shown on the \( x \)-axis are the regions of the \( \log(C^*) \) scale attributed to semivolatile organic compounds (SVOCs), intermediate volatility organic compounds (IVOCs), and volatile organic compounds (VOCs). Also shown is the position of \( \alpha \)-pinene (dark blue circle) (per Donahue et al., 2009), as well as first generation products from \( \alpha \)-pinene ozonolysis, cis-pinic acid (green), cis-pinonic acid (red), and pinonaldehyde (cyan) (\( C^* \) values calculated from Hartonen et al., 2013).

B.1 A plot of particle volume vs. time for five particles exposed to a dry (<0.5 % RH) N\(_2\) gas flow. Dotted lines represent the measured mean size of a particle. Error bars on the \( y \)-axis represent the uncertainty in measuring both the area of the particle, and the equilibrium contact angle, at the particle-substrate interface. Originally published in Grayson et al. (2015b).
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.2</td>
<td>(a) Schematic representation of instrumental setup for contact angle images. (b) Fluorescence image obtained of an SOM particle. The green overlay is used to determine the contact angle of the particle, in this case 60°, and was produced using the LB-ADSA plugin for ImageJ. Originally published in Grayson et al. (2015b).</td>
</tr>
<tr>
<td>B.3</td>
<td>Plot of production mass concentration vs. viscosity for whole SOM produced via the ozonolysis of α-pinene and studied at &lt;5 % RH. Shown are the results determined here along with those previously reported in literature (Abramson et al., 2013; Cappa and Wilson, 2011; Perraud et al., 2012; Renbaum-Wolff et al., 2013a; Robinson et al., 2013; Saleh et al., 2013; Zhang et al., 2015). Originally published in Grayson et al. (2015b).</td>
</tr>
</tbody>
</table>
## List of Symbols

<table>
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<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
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</tr>
<tr>
<td>( C^* )</td>
<td>saturation vapour concentration</td>
</tr>
<tr>
<td>( D )</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>( \eta )</td>
<td>dynamic viscosity</td>
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<td>( F )</td>
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<td>( k_B )</td>
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<td>( l )</td>
<td>grid spacing in COMSOL simulations</td>
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<td>( \nu )</td>
<td>kinematic viscosity</td>
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<td>( P )</td>
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<td>( \tau_{model_flow} )</td>
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<td>( u )</td>
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<tr>
<td>( v )</td>
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# List of Units

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<td>Pascal seconds</td>
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</tr>
<tr>
<td>sLpm</td>
<td>standard Litres per minute</td>
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<td>Tg</td>
<td>terragrams</td>
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</table>
List of Abbreviations

DRH  deliquescence relative humidity
ELVOCs extremely low volatility organic compounds
IVOCs intermediate volatility organic compounds
MLR  multiple linear regression
O:C  elemental oxygen-to-carbon ratio
PM$_{2.5}$ particulate matter of diameter <2.5 µm
RH   relative humidity
SOM  secondary organic material
SVOCs semivolatile organic compounds
VOCs volatile organic compounds
Acknowledgements

The work presented in this thesis is as much a reflection of the support of the people around me as it is of me.

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To my parents, Richard and Helen, my brother, Mark, and my partner, Amy
Chapter 1

Introduction

1.1 Atmospheric aerosols

1.1.1 Formation, sources, and classification of aerosols

Atmospheric aerosols are liquid or solid particles suspended in the Earth’s atmosphere. The formation of atmospheric aerosols may be primary, via the direct emission of solid or liquid particulate matter from the Earth’s surface, or secondary, as a result of gases reacting in situ in the atmosphere, eventually forming products of low volatility, which undergo gas-to-particle conversion (Seinfeld and Pandis, 2006).

Aerosols range in diameter from nanometers to hundreds of microns, and are typically classified into four size modes (Seinfeld and Pandis, 2006, p.369). The smallest aerosols, of diameter $< 10$ nm, belong to the nucleation mode, which is comprised of secondary aerosols. The Aitken mode, comprised of particles ranging in diameter from 10 - 100 nm, is comprised of primary aerosols recently emitted to the atmosphere and secondary aerosols recently produced via gas-to-particle conversion. Both nucleation and Aitken mode aerosols rapidly coagulate to form accumulation mode particles, and have atmospheric lifetimes on the order of tens of minutes. Ranging in diameter from 100 nm - 2.5 µm, accumulation mode particles also include primary aerosols emitted directly into the atmosphere, and have an atmospheric lifetime on the order of a week. Collectively, nucleation, Aitken, and accumulation mode aerosols are known as fine particles. The largest aerosols, those of diameter $> 2.5$ µm, belong to the coarse mode, which typically consists mainly of primary particulate matter including dust from natural and anthropogenic sources, and salt particles produced by sea-spray.
1.1. Atmospheric aerosols

Due to their size, only a small fraction of coarse-mode particles are entrained into the atmosphere and, as such, their lifetime is typically on the order of hours to a few days.

Aerosols are also often classified based on whether their emissions source is natural or anthropogenic. Natural sources include sea spray from oceans, mineral dust from deserts, and gaseous emissions from forests, whilst anthropogenic sources include both industrial and agricultural activities, and the combustion of fossil fuels. Sea spray and mineral dust combined account for the majority of the total mass of aerosols and aerosol precursors emitted to the atmosphere (≈45% and ≈30%, respectively) (Stocker et al., 2013), and all natural sources combined account for >90% of the mass of aerosols and aerosol precursors emitted. The single largest source of anthropogenic emissions is dust produced during industrial activities (Seinfeld and Pandis, 2006, p.61).

Vast spatial and temporal variations are observed in aerosol number concentrations, which can range from \(10^2\) - \(10^8\) cm\(^{-3}\) (Seinfeld and Pandis, 2006, p.350), although they typically fall between \(10^3\) and \(10^5\) cm\(^{-3}\) (Pruppacher and Klett, 2010, p.252). Spatially, this dramatic spread is the result of the short lifetime of Aitken mode particles that dominate aerosol number concentrations in the atmosphere. Areas located far from the emission sources of Aitken mode particles, such as remote regions at the Earth’s high latitudes, have the lowest number concentrations (Ottar, 1989), with urban regions close to industrial activity and transportation networks typically having the highest concentrations (e.g. Hussein et al., 2005). Temporal variations may be observed diurnally as a result of traffic patterns (e.g. Du et al., 2012, and references therein) and seasonally as a result of agricultural activities (e.g. Rastogi et al. 2016; Urban et al., 2016). Huge quantities of coarse mode mineral dust particles can be entrained during dust storms, also leading to short term temporal variations in particle number concentrations (e.g. Welner et al., 2004).
1.1. Atmospheric aerosols

1.1.2 Effects of aerosols

The presence, composition, and concentration of atmospheric aerosols impact the organisms inhabiting the Earth’s surface, and both directly and indirectly affect its atmosphere and climate.

Aerosols can have numerous effects on health. For example, aerosols from diesel soot, welding fumes, black carbon, and coal fly ash that reach the lungs have the potential to cause oxidative stress, inflammation, and cancer (Donaldson et al., 2005), whilst prenatal exposure to polyaromatic hydrocarbons present in fossil fuels and released during incomplete combustion of wood, coal, and diesel, has been linked to both lower IQ and asthma in infants, as well as an increase in the incidence of childhood anxiety and depression (Perera et al., 2009, 2012). Farm workers have also reported coughing, wheezing, and breathlessness during grain harvesting, when concentrations of fungal spores are elevated (Darke et al., 1976). Further, exposure to secondary organic aerosols has been observed to result in an increase in the time needed to repair mammalian epithelial cells (Gaschen et al., 2010), as well as an increase in premature cell death (Baltensperger et al., 2008).

Aerosols affect the atmosphere directly through interactions with incoming solar radiation, and indirectly by acting as cloud condensation nuclei (Seinfeld and Pandis, 2006, p.1055). The direction and magnitude of these effects is quantified using radiative forcing. Radiative forcing, which is reported in Watts per metre squared (W m\(^{-2}\)) and typically quantified at the tropopause, refers to a change in energy per unit area of the Earth due to a change in the concentration of a climate forcing agent. Effective radiative forcing is also used. Effective radiative forcing is similar to radiative forcing, however, it determines the change in energy per unit area of the Earth caused by the change in concentration of a climate forcing agent after allowing for atmospheric temperatures, water vapour, and clouds to adjust to the change in concentration of the climate forcing agent.

The direct effects incorporate aerosol-radiation interactions, whereby incoming solar radiation may be scattered and directed back into space by
1.1. Atmospheric aerosols

compounds such as sulfates, or may be absorbed by black carbon, trapping the energy of the radiation in the atmosphere (Stocker et al., 2013). Black carbon also covers the Earth’s surface at polar regions, absorbing incoming solar radiation and accelerating the melting of snow and ice (Bond et al., 2013).

The indirect effects of aerosols are more complex, with aerosols influencing cloud formation, as well as the microphysical properties, amount, and lifetime of clouds in the atmosphere (Haywood and Boucher, 2000; Twomey, 1991). Clouds are composed of droplets that scatter incoming radiation. An increase in the emission of aerosols from anthropogenic sources may lead to an increase in aerosol number concentration, which increases the concentration of cloud condensation nuclei in the atmosphere and affects the composition of clouds. For example, clouds formed in regions of elevated aerosol concentrations can contain a greater concentration of smaller droplets compared with clouds of equivalent water and ice content formed in regions of lower aerosol concentration. Of the two, the cloud formed under a higher aerosol concentration will scatter a greater proportion of incoming solar radiation. This increase in scattered solar radiation is referred to as the albedo effect, or the first indirect effect (Twomey, 1991). A second indirect effect, known as the cloud lifetime effect, arises as a result of the reduced propensity of these smaller droplets to precipitate, increasing cloud lifetime in the atmosphere (Seinfeld and Pandis, 2006).

The extent of the radiative forcing attributed to direct and indirect forcing is detailed in Figure 1.1, along with the radiative forcing of other anthropogenic and natural atmospheric constituents (Stocker et al., 2013). Both the direct and indirect effects of aerosols are observed to give rise to a negative radiative forcing, or a net cooling effect on the Earth-atmosphere system. However, there are large uncertainties associated with each effect, along with a low level of scientific understanding, which suggests there is much to benefit from an improved understanding of the climate effects of aerosols.
1.2. Formation of secondary organic material

This thesis focuses on atmospheric aerosols consisting of secondary organic material (SOM). SOM forms as a result of the oxidation of gaseous volatile organic compounds (VOCs) emitted from the Earth’s surface by both anthropogenic and natural sources. Once in the atmosphere, highly volatile organic compounds readily react with atmospheric oxidants such as ozone (O₃), hydroxyl radicals (•OH), and nitrous oxides (NO or NO₂, commonly referred to collectively as NOₓ), leading to the formation of semivolatile reaction products (Hallquist et al., 2009; Kanakidou et al., 2005; Seinfeld and Pankow, 2003). Following numerous successive oxidation reactions, these
1.2. Formation of secondary organic material

Semivolatile compounds have a sufficiently low vapour pressure to partition to the particle phase (Donahue et al., 2011; Ehn et al., 2014; Jimenez et al., 2009; Schobesberger et al., 2013). SOM is estimated to account for 30 to 70% of the mass concentration of suspended submicron particles in most regions of the atmosphere (Kanakidou et al., 2005).

Anthropogenic sources of VOCs include industrial and agricultural activities, as well as the intentional burning of biomass (e.g., Hodzic et al., 2009), and annual anthropogenic emissions of VOCs are estimated to exceed 100 Tg (Stocker et al., 2013). By far the largest natural sources of VOCs are the Earth’s biogenic regions (Stocker et al., 2013), with annual emissions from forested areas estimated to range from 500 to 820 Tg (Arneth et al., 2008), and inventories of biogenic sources suggesting they emit at least as great an amount of mass of VOCs into the Earth’s atmosphere as all anthropogenic activities (Guenther et al., 2000). One class of compounds that account for a significant fraction of VOC emissions are terpenes (e.g., Guenther et al., 2000). Terpenes are emitted by biogenic sources for an array of reasons, such as in response to insect damage in order to both attract insect predators to their surface and communicate the damage to neighbouring plants (Paré and Tumlinson, 1999). The structures of isoprene and α-pinene, which account for the majority of biogenic VOC emissions (Kanakidou et al., 2005), are shown in Figure 1.2.

The number of competing oxidation pathways for VOCs and their oxidation products result in the formation of thousands of individual components that have been observed in field studies to be largely comprised of carbon, hydrogen, and oxygen atoms (Farmer et al., 2010; Russell et al., 2011), and contain a wide range of functional groups including alkanes, alkenes,

Figure 1.2: Chemical structures of isoprene (left) and (+)-α-pinene (right).
1.3. Viscosity

alcohols, carboxylic acids, aldehydes, ketones, esters, ethers, and acid anhydrides, as well as both aromatic and non-aromatic cyclic molecules (Aschmann and Atkinson, 1998; Chan et al., 2010; Chen et al., 2011a; Christoffersen et al., 1998; Day et al., 2009; Russell et al., 2011; Surratt et al., 2006). As a result of this complexity only \( \approx 10 \% \) of the individual components of SOM have been identified (Hallquist et al., 2009). The average oxygen-to-carbon elemental ratio (O:C) of SOM ranges from approximately 0.25-1.0 (Jimenez et al., 2009), though the O:C of individual compounds can exceed 1.0 (Chen et al., 2011a; Ehn et al., 2014; Praplan et al., 2015), and whilst a wide range of molar mass is observed for individual components, the vast majority are of molar mass \(<1000 \text{ g mol}^{-1}\) (Hallquist et al., 2009; Praplan et al., 2015; Schobesberger et al., 2013).

Due to the complexity of SOM, explicit description of its formation, evolution, and physical properties of SOM cannot currently be incorporated into large-scale models (Hallquist et al., 2009). As a result, researchers have used simple methods to describe these processes and properties.

1.3 Viscosity

1.3.1 What is viscosity?

The viscosity of a material is a measure of its resistance to deformation under stress, with the resistance caused by the materials’ intermolecular forces, and the local structures they produce (Viswanath et al., 2007).

Two measures of viscosity are commonly used, dynamic viscosity \( (\eta) \) and kinematic viscosity \( (\nu) \), with kinematic viscosity incorporating both a materials dynamic viscosity and its density \( (\sigma) \) (Equation 1.1),

\[
\nu = \frac{\eta}{\sigma}
\]  

(1.1)

Dynamic viscosity is the measure of the tangential force required to slide one layer of fluid against another (Viswanath et al., 2007), which produces a mechanical non-equilibrium system, and is measured in Pascal seconds (Pa s). The force is required to overcome intermolecular interactions between
neighbouring molecules, which may be electrostatic and/or steric in nature. This may be visualised as shown in Figure 1.3 for a sample between two boundary plates, separated by a distance of $y$. One plate remains stationary whilst the second plate moves, with velocity $v$, imparting a shear stress, $\tau$, on the fluid. Resistance to this stress results in layers closer to the moving plate travelling with greater velocity than those far from the moving plate. From this picture, dynamic viscosity may be expressed mathematically as,

$$\eta = \frac{\tau}{\delta v}$$

(1.2)

Dynamic viscosity, rather than kinematic viscosity, is used throughout this thesis, and further mentions of viscosity in this thesis refer exclusively to dynamic viscosity. This is for two main reasons. Firstly, diffusion is an atmospherically important process, and diffusion and dynamic viscosity may be readily converted using the Stokes-Einstein equation,

$$\eta = \frac{k_B T}{6\pi D r}$$

(1.3)

where $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), $T$ is temperature (K), $D$ is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), and $r$ is the hydrodynamic radius (m) of the diffusing molecule. Secondly, the density of the material under investigation is not always known accurately.

Figure 1.3: Laminar flow of a fluid between two 2D boundary plates - one stationary and one moving.
1.3. Viscosity

That the Stokes-Einstein relationship successfully relates diffusion, which is relevant on a molecular length scale, and viscosity, which is relevant on a macroscopic scale, may be surprising. However, whilst it is known to break down under certain conditions, such as close to a compounds glass transition temperature, it is nevertheless successful in correlating the temperature and density variations of diffusion and viscosity across a wide range of values for liquids (Corti et al., 2008; Stillinger and Debenedetti, 2005). An alternative method by which the transport of momentum, which gives to viscosity, may be studied, is on the microscopic level via the Green-Kubo formalism. The formalism may be expressed as,

\[
\eta = \frac{1}{k_B T V} \int_0^\infty \langle J^{xy}(0) J^{xy}(t) \rangle dt \tag{1.4}
\]

where \( k_B \) and \( T \) are as for Equation 2.6, \( V \) is the macroscopic system volume, the brackets \( \langle ... \rangle \) denote the ensemble average, and \( J^{xy} \) is the \( x,y \) component of a momentum flux tensor, which is expressed as:

\[
J^{xy} = \sum_{j=1}^{N} \left( \frac{p_j x_j p_j y_j}{m} + x_j F_{jy} \right) \tag{1.5}
\]

where \( p \) represents the momentum of particle \( j \), \( m \) represents the particle’s mass, and \( F_{jy} \) represents the \( y \) component of the force experienced by particle \( j \).

Whilst the Kubo-Green expressions provide an overview of the forces experienced by particles at the microscopic level, the more granular Stokes-Einstein equation is used throughout this thesis due to both the experimental observation that many liquids conform closely to Stokes-Einstein behaviour (Stillinger and Debenedetti, 2005) and its comparative simplicity.

1.3.2 Types of fluids

The relationship between shear rate and shear stress is used to broadly divide fluids into those that are Newtonian and those that are non-Newtonian.
1.3. Viscosity

(Viswanath et al., 2007). Whilst Newtonian fluids exhibit a linear relationship between shear rate and applied shear stress, and thus have viscosities that are independent of applied shear stress, non-Newtonian fluids exhibit a non-linear relationship between shear rate and applied shear stress, meaning their viscosities are dependent upon applied shear stress. Examples of types of non-Newtonian fluids include pseudoplastic, or shear-thinning, fluids that exhibit a decrease in viscosity as shear rate is increased, and dilatant, or shear-thickening, fluids, that exhibit an increase in viscosity as shear rate is increased. The relationship between shear rate and applied shear stress is shown in Figure 1.4 for Newtonian, pseudoplastic, and dilatant fluids.

Though the relationship between shear rate and applied shear stress for secondary organic material (SOM), which is the main focus of this thesis, has yet to be determined, a linear relationship between shear rate and applied shear stress has been determined for compounds that are typically used as proxies for SOM, including glycerol/water solutions (Hosny et al., 2013) and sucrose/water solutions (Saggin and Coupland, 2004). As such, SOM is assumed to be Newtonian in nature.

Figure 1.4: The relationship between shear rate and shear stress for types of fluids.
1.3. Viscosity

1.3.3 Commercially available methods to measure viscosity

Two commonly used families of commercially available viscometers are those typically classified as capillary viscometers and rotational viscometers.

Capillary viscometers use either gravity or an applied pressure as the force used to push or pull a sample through a capillary of known diameter. A schematic of an Ostwald viscometer, an example of a capillary viscometer, is shown in Figure 1.5(a). A known volume of sample is added to the capillary (at point 1, filling the capillary to line A), and suction applied (at point 2). The time taken for the sample to flow between specified points (lines B and C) inside the capillary is measured, with the viscosity being calculated using the general equation,

$$\eta = kt$$  \hspace{1cm} (1.6)

where \(k\) is a constant that takes account of the capillary dimensions and the suction applied to pull the sample through the capillary, and \(t\) is the time taken for the sample to flow between lines B and C.

Rotational viscometers determine the amount of rotational force that must be applied to a sample held in an outer cylinder in order to rotate an inner solid cylinder at the centre of the sample. One such design is the coaxial-cylinder viscometer, a schematic of which is shown as Fig. 1.5(b). The angular deflection of the inner cylinder is a function of the viscosity of the sample, the dimensions of the inner and outer cylinders, and the speed of rotation of the outer cylinder.

Figure 1.6(a) shows a scale outlining part of the viscosity continuum. Viscosity spans an enormous range for common substances, with at least 15 orders of magnitude separating that of water from that of a glass.

Commercially available viscometers are capable of measuring materials with viscosities ranging from \(<10^{-3} \approx 10^6\) Pa s, which corresponds to materials less viscous than water up to those of viscosity between that of window putty and tar pitch (Fig. 1.6(b)).

The design of many commercially available instruments such as capillary
1.3. Viscosity

Figure 1.5: Schematic of two examples of commercially available viscometers. Shown in (a) is an Ostwald viscometer. Sample is added to side 1 until the sample in the capillary is level with line A. Suction is subsequently applied at point 2, and the time taken for the sample to flow between line B and line C is measured. Shown in (b) is a coaxial-cylinder viscometer. The outer cylinder is rotated at a constant speed, and the angular deflection of the inner cylinder is used to determine the viscosity of the sample.

and rotational viscometers require samples on the order of grams or tens of grams of material in order to determine viscosities, though SOM is typically only produced on the microlitre (µL) scale. Whilst methods are available for measuring viscosities on this scale, such as microfluidic capillary devices similar but smaller in design compared to their macro counterparts (Han et al., 2007; Lin et al., 2007; Pipe and McKinley, 2009; Srivastava et al., 2005), the range of viscosities they can measure is limited to viscosities $<10^{-1}$ Pa s, approximately equivalent to that of olive oil (Renbaum-Wolff et al., 2013b). The range of viscosities that may be measured for techniques utilizing µL of material is illustrated in Fig. 1.6(b).
1.3. Viscosity

Figure 1.6: (a) A scale showing part of the viscosity continuum, detailing the regions typically defined to be bound by the solid, semi-solid, and liquid regimes, as well as the viscosities of some common substances (idea to show common substances is borrowed from Koop et al., 2011). The image of the pitch is a detail of a picture taken from Wikimedia Commons of the pitch drop experiment Wikipedia page (GFDL, John Mainstone, University of Queensland, Australia). (b) A scale showing the ranges of viscosity measurable using commercially available instrumentation for measuring viscosity, as well as the possible range of viscosities spanned by SOM.

1.3.4 Potential viscosities of SOM

The initial studies related to the viscosity of SOM have focused on discussion of the phase of the SOM, i.e., whether it is liquid, semi-solid, or solid, with the terms solid and glass often being used interchangeably, as opposed to a numerical measure of its viscosity. As illustrated in Fig. 1.6(a), liquids are of viscosity $<10^2$ Pa s, semi-solids are of viscosities between $10^2$ and $10^{12}$ Pa s, and solids are of viscosity $>10^{12}$ Pa s (Angell, 1995; Shiraiwa et al., 2011a).

Initial studies by Virtanen et al. (2010) concluded SOM particles can adopt an amorphous solid - most probably glassy - state. As such, the viscosity of SOM may range from that of water ($\approx 10^{-3}$ Pa s) to that of a
solid (>10^{12} \text{ Pa s}) as illustrated in Fig. 4(b). Given the limited quantity of SOM that can be generated on a reasonable timescale in the laboratory (on the order of a few milligrams), currently available techniques for measuring viscosity are unlikely to be able to measure the full range of viscosities exhibited by laboratory generated SOM.

1.3.5 The importance of the viscosity of SOM

The viscosity of SOM is important for a number of reasons. First, the viscosity of SOM governs the rate at which organic molecules can diffuse through particles, and knowledge of the viscosity is thus required to predict the mechanism, rate of growth, total mass, and size of modelled particles (Figure 1.7(a)) (Riipinen et al., 2011, Shiraiwa and Seinfeld, 2012, Shiraiwa et al., 2011a, 2013; Zaveri et al., 2014). The reaction of oxidants within particles comprised of SOM may also be inhibited at high viscosities (Fig. 1.7(b)) (Shiraiwa et al., 2011a), as well as rates of both heterogeneous and photochemical processes (Houle et al., 2015, Kuwata and Martini, 2012, Lignell et al., 2014, Zhou et al., 2013).

In addition, high viscosities in particles containing SOM may alter their physical properties after ice cloud processing (Adler et al., 2013, Robinson et al., 2014), and high viscosities may also inhibit crystallization of inorganic salts (Bodsworth et al., 2010, Murray and Bertram, 2008, Song et al., 2012), and the hygroscopic properties of particles (Bones et al., 2012, Hawkins et al., 2014, Lu et al., 2014, Price et al., 2014, Tong et al., 2011). Furthermore, if SOM particles are solid or ‘glassy’ in phase under atmospheric conditions they may provide a surface for ice nucleation (Baustian et al., 2013, Berkemeier et al., 2014, Knopf and Rigg, 2011, Ladino et al., 2014, Murray et al., 2010, Schill et al., 2014, Wang et al., 2012), modifying their ability to promote cloud formation. Viscosity in SOM particles is also important for predicting the long range transport of polycyclic aromatic hydrocarbons, which are known to have a detrimental effect on human health (Zelenyuk et al., 2012, Zhou et al., 2012).
1.3. Viscosity

Figure 1.7: (a) Effect of particle viscosity on the mechanism of growth of SOM by semivolatile organic compound (SVOC) uptake. (b) Effect of particle viscosity on heterogeneous oxidation by ozone. (c) Climate effects of particles and implications of high particle viscosities on particle growth rates, particle mass, and heterogeneous oxidation by O$_3$. The implications of particle viscosity on growth and heterogeneous oxidation in (a)-(c) assume a monodisperse particle population. Originally published in Renbaum-Wolff et al. (2013a).
1.4 Previous research related to the viscosity of SOM

Researchers have traditionally assumed particles containing SOM to be of low viscosity when modeling particle growth (Hallquist et al., 2009). However, recent measurements have suggested that this may not be the case under certain conditions. Measurements that have suggested SOM can have high viscosities include (1) direct measurements of viscosity of SOM or proxies for SOM (Booth et al., 2014; Pajunen et al., 2014; Song et al., 2015; Zhang et al., 2015), (2) measurements of diffusion rates and mixing times in SOM (Abramson et al., 2013; Loza et al., 2013; Perraud et al., 2012), (3) bounce measurements off surfaces (Bateman et al., 2015; Kidd et al., 2014; Saukko et al., 2012; Virtanen et al., 2010, 2011), (4) measurements of the flatness of particles after impaction (O’Brien et al., 2014), (5) measurements of rates of evaporation from SOM (Cappa and Wilson, 2011; Vaden et al., 2011), and (6) measurements of reactivity of SOM (Kuwata and Martin, 2012; Wang et al., 2012, 2015). Nevertheless, the viscosities and diffusion rates of SOM are still a matter of debate (Price et al., 2015; Robinson et al., 2013; Saleh et al., 2013; Yatavelli et al., 2014).

Given this array of observations, and the range of atmospheric processes affected by the viscosity of SOM, it is important to determine the viscosity of SOM in order to improve our ability to predict the climate effects of SOM.

1.5 Overview of dissertation

Chapter 1 (this chapter) provides an introduction to atmospheric aerosols and secondary organic material as well as a motivation for the rest of the thesis. Chapter 2 details two novel techniques used to measure a wide range of viscosities in small samples of organic compounds, the bead-mobility and the poke-and-flow technique combined with simulations of fluid flow. Chapter 3 describes initial measurements of the viscosity of the water-soluble component of the SOM produced via the ozonolysis of α-pinene. Chapter 4 details further validation of the poke-and-flow technique, which is subse-
1.5. Overview of dissertation

Subsequently utilised in Chapter 5 to determine the viscosity of the total SOM (water-soluble and water-insoluble fractions) produced via the ozonolysis of α-pinene, and in Chapter 6 to determine the viscosity of highly oxidized compounds that have been previously identified as components of SOM, and are used as proxies for highly oxidized SOM found in the atmosphere. In Chapter 7 the relationship between viscosity, elemental oxygen-to-carbon ratio (O:C), molar mass, and saturation vapour concentration, the mass based equivalent of saturation vapour pressure, is investigated.
Chapter 2

Experimental techniques

The experimental results in this thesis are predominantly determined using two novel techniques for measuring high viscosities in small samples, a bead-mobility technique and a poke-and-flow technique. These new techniques for measuring viscosities were needed because conventional viscometers are not able to accommodate the small sample volumes associated with laboratory or atmospheric sampling of SOM particles (typically on the order of 1 µL) (see Section 1.3.3), and because microviscometers that can accommodate small sample sizes are often limited to measurements of low viscosities (<0.1 Pa s) (Han et al., 2007; Lin et al., 2007; Silber-Li et al., 2004; Srivastava and Burns, 2006), whereas SOM is anticipated to have considerably higher viscosity, at least at low RH. These newly introduced techniques may also find broader future use in other disciplines that require viscosity measurements of small sample volumes, e.g., due to cost or availability such as biological samples. The bead-mobility technique is used in Chapters 3 and 6, and the poke-and-flow technique is used in Chapters 3, 4, 5, and 6. Both of the techniques are described in detail here, and these descriptions referred to in the relevant places in further Chapters.

2.1 Bead-mobility technique

The bead mobility technique was first described, and validated, in Renbaum-Wolff et al. (2013b).

Super-micron sized particles, typically 20-50 µm in diameter, were generated on a hydrophobic slide surface by using a nebuliser (Meinhard, model TR-30-A1, USA) to nebulise dilute aqueous solutions onto a hydrophobic glass slide or a Teflon slide. The glass slides used during experiments in
2.1. Bead-mobility technique

Chapters [3, 4] and [6] were siliconised glass slides obtained commercially (12mm, Hampton Research, USA), whilst the glass slides used during experiments in Chapter [5] were produced by cleaning plain circle glass cover slides (12mm, Hampton Research, USA) using Piranha solution (three parts concentrated sulfuric acid to one part 30% hydrogen peroxide solution), and subsequently coating the slides using a fluorinating agent (Trichloro-(1H, 1H, 2H, 2H-perfluorooctyl) silane, Sigma Aldrich). A dilute aqueous suspension of 1 µm hydrophilic melamine beads (actual diameter 930 ± 50 nm (Sigma Aldrich, Cat# 86296)) was then nebulised over the slide containing the super-micron sized particles, resulting in beads being incorporated into the bulk of the particle. Melamine beads were chosen as they are prepared by the manufacturer without the use of surfactants and are not susceptible to swelling or aggregation in solution. The slide containing the super-micron sized particles with bead inclusions was then placed in a flow cell with relative humidity control.

A schematic of the flow cell is shown as Figure [2.1]. The flow cell was mounted to an optical microscope (Zeiss, Axio Observer), and relative humidity inside the cell was controlled by passing a flow gas (N2) through a water bubbler located in a controlled-temperature bath. The dew point temperature of the gas was measured after the flow cell using a hygrometer (General Eastern, Model 1311DR). The temperature of the flow cell was measured using a thermocouple probe. The hygrometer was calibrated at the beginning of each set of experiments using the deliquescence of ammonium sulfate particles, with the uncertainty (1σ) of the hygrometer after calibration typically ± 0.5 % RH at 80.3 % RH. The flow gas (linear flow velocity of 100 cm s\(^{-1}\)), produced a shear stress on the particle surface (Figure [2.2]), which resulted in internal circulations of material within the particle. These circulations also carried the beads. Examples of the paths travelled by the beads are shown in Figure [2.3], and observed to be roughly hemispherical in nature, with the shear stress of the gas causing the beads to travel around the outside of the particle, before travelling back through its centre.
2.1. Bead-mobility technique

Figure 2.1: Schematic representation of bead-mobility experimental setup. Originally published in Renbaum-Wolff et al. (2013b).

Figure 2.2: Illustration of the flow of the flow gas around a sample particle. Originally published in Renbaum-Wolff et al. (2013b).

Figure 2.3: Internal circulation of beads within a particle of glycerol. The red lines overlaid on the image show the 2-D circulation of three beads within the particle. Originally published in Renbaum-Wolff et al. (2013b).
2.1. Bead-mobility technique

Optical microscopy was used to track the movement of the beads over time, with a frame collected every 0.2-40 s, depending on the rate of movement of the beads within the particles. In total a time series of 50 to 100 optical images were recorded, and the movement of the beads was tracked as they travelled all the way around the particle. Examples of optical images that show the change over time in the $x$ and $y$ co-ordinates of beads within a particle are included in Figure 2.4.

Figure 2.4: Images from the bead-mobility studies. Images in (a) correspond to images recorded at 90% RH and images in (b) correspond to images recorded at 70% RH. Indicated in the figure are different beads monitored in the experiments and the x-y coordinates of the beads. Originally published in Renbaum-Wolff et al. (2013a).
2.1. Bead-mobility technique

Given the microscope was focused on a single plane in the $z$-axis, movement of beads in the $z$ plane could not be quantified. Further, there is likely some variation of bead speed at different heights within the particle and thus effort was made to focus at the mid-height of each particle studied. Each of these processes are potential sources of error for the technique. Above a certain viscosity the movement of the beads became too slow to quantify. The bead speed was converted to viscosity using a calibration curve such as that shown in Figure 2.5. Such calibration curves typically gave rise to 95% prediction limits that had lower/upper limits of viscosity that were within a factor of two of the best-fit function.

The organic molecules used to generate Fig. 2.5 are listed on the figure, and had O:Cs ranging from 0.1-1.0, molar masses ranging from 92-600 g mol$^{-1}$, surface tensions ranging from 32-75 mN m$^{-1}$, and contact angles with the slide substrate ranging from 58-95°. The diameter of the particles studied ranged from 20-50 µm. Within experimental uncertainty, the relationship between bead speed and viscosity was determined to be in-

![Figure 2.5: Average bead speed ($\pm 1\, \sigma$) vs. viscosity for standard compounds. Originally published in Renbaum-Wolff et al. (2013b).](image)
dependent of these parameters within the ranges studied (Renbaum-Wolff et al., 2013b).

The range of these physical properties is expected to extend beyond the range of that exhibited by SOM. For example, secondary organic particles generated from the ozonolysis of α-pinene in environmental chambers have an average O:C of 0.3-0.4 (Aiken et al., 2008; Chen et al., 2011a; Heaton et al., 2007; Putman et al., 2012; Shilling et al., 2009). Although the surface tension of secondary organic material collected in environmental chambers is largely unmeasured for the subsaturated RH regime, estimates of 40-75 mN m$^{-1}$ have been made based on model compounds (Huff-Hartz et al., 2006; Hyvärinen et al., 2006; Tuckermann and Cammenga, 2004). The myriad compounds present in the SOM have been estimated to have molar mass largely less than 600 g mol$^{-1}$ (Gao et al., 2004, 2010; Putman et al., 2012).

Measurements in Chapter 3 that were made using the bead-mobility technique used the calibration curve shown in Fig. 2.5. Measurements in Chapter 6 that were made using the bead-mobility technique occurred more than a year after those in Chapter 3 and so a new calibration curve was produced to ensure any change in the instrumentation was accounted for. This calibration curve comprised of measurements of sucrose and glycerol, as it was demonstrated in Renbaum-Wolff et al. (2013b) that a calibration curve produced using just sucrose and glycerol predicted the same viscosity for olive oil as the combination of all nine compounds included in Fig. 2.5.

### 2.2 Poke-and-flow technique combined with simulations of fluid flow

#### 2.2.1 Poke-and flow technique

The qualitative method of poking a particle to determine the particle phase (i.e., solid/semisolid vs. liquid) was introduced by Murray et al. (2012). This approach is expanded upon in this thesis by quantifying flow rates after poking and determining viscosities from simulations of flow.

Super-micron sized particles were generated on a hydrophobic glass slide
2.2. Poke-and-flow technique combined with simulations

(Hampton Research, Canada) and the slide containing the super-micron sized particles was then placed in a flow cell with relative humidity control. A schematic of the flow cell is shown as Figure 2.6. The flow cell is similar to those described previously (Koop et al., 2000; Song et al., 2012; You et al., 2012), but with a small hole added at the top through which a needle could be inserted (Fig. 2.6). The flow cell was mounted to an optical microscope (Zeiss, Axio Observer), and relative humidity inside the cell was controlled by passing a flow gas (N₂) through a water bubbler located in a controlled-temperature bath. The dew point temperature of the gas was measured after the flow cell using a hygrometer (General Eastern, Model 1311DR). The temperature of the flow cell was measured using a thermocouple probe. The hygrometer was calibrated at the beginning of each set of experiments using the deliquescence of ammonium sulfate particles, with the uncertainty (1σ) of the hygrometer after calibration typically ± 0.5 % RH at 80.3 % RH. The presence of the hole at the top of the flow cell upon RH in the cell was determined by studying the deliquescence relative humidity of ammonium sulfate and potassium carbonate particles with the hole open and the hole closed. The DRH of ammonium sulfate particles differed by <0.2 % RH at 80 % RH, whilst the DRH of potassium carbonate particles differed by <0.4 % RH at 43 % RH.

![Schematic representation of poke-and-flow experimental setup. Originally published in Grayson et al. (2015a).](image-url)
2.2. Poke-and-flow technique combined with simulations

Needles were used to poke the particles, with two different types of needles used. Both types of needle had tips that were circular in geometry. For particles of lower viscosities a sterilized, sharp needle (0.9 mm x 40 mm) (Becton-Dickson, USA), with a tip diameter of \( \approx 20 \, \mu m \), was used. However, at higher viscosity particles stuck to the needle and as a result were removed from the substrate. As such, a second set of needles (RS-6063, Roboz Surgical Instrument Co., USA), with a tip diameter of \( \approx 10 \, \mu m \), was occasionally used. These needles were coated with a hydrophobic Dursan coating (SilcoTek, USA) to prevent material sticking to the needles. In each case the needles were mounted to a micromanipulator (Narishige, model MO-202U, Japan) and inserted through the hole at the top of the flow-cell. The micromanipulator was used to move the needle in the \( x \)-, \( y \)-, and \( z \)-, axes.

For a given experiment, the tip of the needle was aligned vertically above the centre of a particle, and then moved down in the z direction, impacting the particle at the peak of its spherical cap geometry. The poking and subsequent behaviour of the particles was monitored during experiments using a reflectance optical microscope (Zeiss, Axio Observer), and recorded using a CCD camera.

For particles of lower viscosity, the needle penetrated the particle and subsequently came in contact with the substrate beneath. After the needle was removed the material of the particle was present in a non-equilibrium, half-torus, geometry, and began to flow in order to minimize the surface energy of the system. Eventually the hole at the centre of the half-torus completely closed, and the particle returned to its original, spherical cap, morphology. Shown in Figure 2.7(a-c) are examples of particles before and after being poked that exhibit this behaviour.

Analysis of optical images captured during each experiment was performed using Zen software (Zeiss). The hole at the centre of the half-torus was traced and the area of the hole calculated. An equivalent area diameter of the hole was calculated via the relationship \( d = (4A/\pi)^{1/2} \), where \( d \) is the equivalent area diameter of a hole of area, \( A \) (Reist, 1992). The experimental flow time, termed \( \tau_{exp,flow} \), was assigned as the time taken for
2.2. Poke-and-flow technique combined with simulations

<table>
<thead>
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<th>a) 70% RH (HEC)</th>
<th>pre-poke</th>
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<th>50 seconds</th>
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Figure 2.7: Deformation and recovery across time of poked SOM particles. Prior to poking (pre-poke), the particle morphology can be approximately described as a spherical cap. At higher RH (40-70 %) (rows a-c), geometries approximately described as half-torus are formed, and flow occurs. By comparison, for low RH (≤30%) (row d) particles shatter and do not flow over a period of 8 h. The ring structures observed in the first and last columns are an optical effect that arises from hemi-spherical diffraction. Originally published in Renbaum-Wölf et al. (2013a).

the equivalent area diameter to decrease to 50 % of its original value. This definition of experimental flow time was chosen as it allows experimental flow time of more viscous particles, the holes of which may not fully close on a laboratory timescale, to be measured.

In some of the experiments a point around the inner edge of the half-torus appeared to be pinned to the hydrophobic surface. This behaviour may suggest that in some cases the needle scratched the surface. Particles that exhibited this pinning behaviour were excluded from analysis in order
to avoid influencing the results. Pinning affected <20 % of all the particles that formed a torus geometry after poking.

Particles of higher viscosity cracked when impacted by the needle, forming pieces with sharp, distinct edges. These particles were observed over a period of hours, with no flow discernible at the edges. An example of a particle exhibiting this behaviour after upon and after being poked is shown in Figure 2.7(d).

### 2.2.2 Simulations using COMSOL Multiphysics

Simulation of particles exhibiting flow during poke-and-flow experiments was carried out using the laminar two-phase flow moving mesh mode within the Micro-fluidics module of COMSOL Multiphysics (version 4.3a), a finite element analysis software package.

Finite element analysis employs the calculus of variations in order to determine approximate solutions to boundary value problems for differential equations. The method involves deducing simple equations to describe small, finite, regions, which are subsequently used to determine a more complex equation that approximates a larger domain.

The Navier-Stokes equation, including surface tension, was used to describe the transport of mass and momentum. The Navier-Stokes equations describe viscous flow by applying Newton’s second law to fluid motion, whilst also assuming that the stress in a fluid is the sum of a diffusing viscous term and a pressure term.

Newton’s second law,

\[ F = \frac{dp}{dt} = \frac{d(mv)}{dt} \] (2.1)

states that the force \( F \) on an object is equal to the rate of change of its linear momentum \( p \), where momentum = mass \( m \) multiplied by velocity \( v \). As well as Newton’s first law, this relationship also implies a conservation of momentum whereby an object in motion will be of constant momentum if no external forces are acting upon it.
2.2. Poke-and-flow technique combined with simulations

In an inertial frame of reference Newton’s second law can be applied to produce a general form of the Navier-Stokes equations, which may be expressed as:

\[
\rho \left( \frac{du}{dt} + u \nabla u \right) = -\nabla p + \nabla \tau + f
\]  

(2.2)

where \( \rho \) represents density, \( u \) represents the flow velocity, \( p \) represents pressure, \( \tau \) represents a stress tensor, and \( f \) represents other forces acting on the material. For the simulations used herein one of these other forces is a frictional boundary force that arises at the fluid-substrate interface, and may be expressed as:

\[
F_{fr} = -\frac{\eta}{\beta} u
\]  

(2.3)

where \( \beta \) represents slip length. The greater the slip length, the weaker the frictional force at the fluid-substrate interface. Incompressible flow is assumed for the poke-and-flow experiments due to the low flow rate of the particles with respect to the gas flow around them. In such instances the his allows the Navier-Stokes equations to be expressed as:

\[
\rho \left( \frac{du}{dt} + u \nabla u \right) = -\nabla p + \eta \nabla^2 u + f
\]  

(2.4)

Division by \( \rho \) followed by rearrangement gives rise to the equation,

\[
\frac{du}{dt} = u \nabla u - \frac{\nabla p}{p} + \frac{f}{p} + \eta \nabla^2 u
\]  

(2.5)

which is of the form momentum/mass = mass + pressure + body force + viscosity, consistent with the conservation of momentum.

The evolution of the fluid as it flowed over time was tracked using the Arbitrary Lagrangian Eularian (ALE) method. Within ALE, the initial flow is Lagrangian, whereby the mesh used to describe the materials initial geometry moves with the material. However, over time this can lead to significant distortion of the mesh. In such instances a simulation using an
2.2. Poke-and-flow technique combined with simulations

ALE method will re-position distorted portions of the mesh. ALE provides a compromise between the large expense of models utilising a pure Lagrangian approach whilst providing a more accurate solution than a pure Eularian approach.

2.2.3 Simulations of particles exhibiting flow

Simulations were performed with a mesh that consisted of \( \approx 5800 \) elements and had a mesh spacing of 3.92-337 nm. A top view of the half-torus geometry used to simulate the experimental observations is shown in Figure 2.8(a), where the dotted line is at the midpoint between the inner and outer edges of the ring of material forming the torus. The initial radius of the hole at the centre of the half-torus is denoted as \( R_0 - r_0 \), where \( R_0 \) represents the distance from the centre of the hole to the midpoint of the ring of material that creates the torus, whilst \( r_0 \) represents the radius of the ring of material. The half-torus had two distinct surfaces (Figure 2.8(b)). Surface 1 represents the air-fluid interface, which was allowed to undergo free deformation in all dimensions. Surface 2 is the fluid-substrate interface, which was allowed to undergo free deformation in the horizontal x-y plane, but not in the vertical, z, direction. In the simulations, the size of the hole in the half-torus geometry decreases in an axi-symmetric manner, as the material flowed to attain a spherical cap geometry and thus minimize the surface energy of the system. The time taken for \( R_0 - r_0 \) to decrease to 50 % of the initial value was assigned \( \tau_{\text{model,flow}} \). Flow occurred in the simulations in a way that minimized the total surface energy.

For a given simulation, values of \( R_0, r_0, \) surface tension, slip length, and density were required. The dimensions \( R_0 \) and \( r_0 \), and the equilibrium contact angle, were determined from measurements, and the values of surface tension (Surface 1, Fig. 2.8(b)), slip length (which describes the interaction at Surface 2 in Fig. 2.8(b)), and the density of the material were determined based on literature values. A summary of literature values for the slip length of water, as well as some atmospherically relevant compounds, is included as Table 2.1. Included as Figure 2.9 are the results from a range of
2.2. Poke-and-flow technique combined with simulations

Figure 2.8: Details of half-torus model used to simulate the flow in experiments: (a) top view, where R and r are the notations used here to describe the dimensions of a half-torus geometry; (b) side view, where surface 1 represents the air-fluid interface, and surface 2 represents the fluid-substrate interface. Originally published in Grayson et al. (2015a).

Simulations, where surface tension, slip length, density, contact angle, and $\tau_{\text{model,flow}}$ are varied across a range greater than that expected for poke-and-flow experiments. The viscosities determined via simulation suggest that the largest uncertainty associated with the technique is that due to slip length, with simulated viscosities varying by approximately two orders of magnitude across the range of slip lengths outlined in Table 2.1. Across the range of values studied the simulated viscosities were determined to be less dependent on surface tension and contact angle, and determined to be independent of the density of the particle. As expected a linear relationship was observed between viscosity and $\tau_{\text{model,flow}}$. The viscosity of each particle that was poked and formed a half-torus geometry, and was not significantly influenced by scratches (determined visually, as discussed above), was determined via simulations. Further details are provided in individual Chapters.

In Chapter 3, experimental flow times, $\tau_{\text{exp,flow}}$, were converted to viscosities using the linear relationship between the modeled flow time, $\tau_{\text{model,flow}}$, and viscosity for a particle of $R_0 = 20 \ \mu m$ and $r_0 = 7.5 \ \mu m$, representative of the size of particles studied, whilst simulations of particles
Table 2.1: Summary of literature values of measured slip lengths for water and atmospherically relevant organic compounds.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Solution</th>
<th>Surface</th>
<th>Slip length / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schnell (1956)</td>
<td>Water</td>
<td>Siliconised glass</td>
<td>2000-8000 (^{a})</td>
</tr>
<tr>
<td>Watanabe and Udagawa (1999)</td>
<td>Water and glycerin</td>
<td>Acrylic resin treated with hydrophobic silica</td>
<td>200-450 (^{a})</td>
</tr>
<tr>
<td>Baudry et al. (2001)</td>
<td>Glycerol</td>
<td>Gold and thiol</td>
<td>38</td>
</tr>
<tr>
<td>Craig et al. (2001)</td>
<td>Sucrose-water</td>
<td>Glass coated with 11-mercapto-1-undecanol and 1-dodecanethiol</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Jin et al. (2004)</td>
<td>Water</td>
<td>Polydimethylsiloxane microchannel</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Joly et al. (2006)</td>
<td>Water</td>
<td>BK7 glass</td>
<td>8-9</td>
</tr>
<tr>
<td>Zhu et al. (2012)</td>
<td>di-n-octyl phthalate</td>
<td>Silanised silicon</td>
<td>&lt;400</td>
</tr>
<tr>
<td>Li et al. (2014)</td>
<td>Water</td>
<td>Silicon</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

\(^{a}\) Slip lengths inferred by Lauga et al. (2003) from reported experimental data
2.2. Poke-and-flow technique combined with simulations

Figure 2.9: The dependence of viscosity as (a) surface tension, (b) slip length, (c) density, (d) contact angle, and (e) $\tau_{\text{model,flow}}$, are varied across a wide range of values for particles of dimensions $R_0 = 16$, $r_0 = 4$ (filled symbols) and $R_0 = 14$, $r_0 = 6$ (open symbols). For each simulation four of the five properties were held constant whilst the fifth was varied. Black squares: surface tension = 75.15 mN m$^{-1}$, slip length = 10 $\mu$m, density = 1500 kg m$^{-3}$, contact angle = 98.5 o, $\tau_{\text{model,flow}}$ = 1000 seconds. Red circles: surface tension = 57.2 mN m$^{-1}$, slip length = 5 nm, density = 1500 kg m$^{-3}$, contact angle = 98.5 o, $\tau_{\text{model,flow}}$ = 0.1 seconds.

In Chapters 4-6 used the dimensions of each particle. The viscosity used in the simulations of a particle was varied until $\tau_{\text{model,flow}}$ agreed with the particles $\tau_{\text{exp,flow}}$ (to within 1 %). Further details are provided in individual Chapters.

2.2.4 Simulations of particles that cracked when poked

Simulation of particles that cracked when poked, and exhibited no discernible flow during subsequent observations was also carried out using the laminar two-phase flow moving mesh mode within the Micro-fluidics module.
2.2. Poke-and-flow technique combined with simulations

For the initial conditions a quarter of a sphere was used (radius = 10 µm) with one of the flat faces in contact with a solid substrate (see Figure 2.10). In this case, there are three interfaces, labeled 1-3 in Fig. 2.10. Interfaces 1 and 2 represent external fluid interfaces and were assigned a surface tension that represented the lower limit of the estimated surface tension of the particle and allowed to undergo free deformation. Interface 3 represents the interface between the fluid and the solid slide substrate. This interface was allowed to deform in the X-Y plane but not in the Z direction, and the equilibrium contact angle between the surface and the fluid was assigned a value of 90° (see below for implications).

The extent of movement of the sharp edge of the particle was independent of the equilibrium contact angle between 20° and 100°. Interactions between the fluid and the solid surface were described with a Navier slip wall boundary condition, with a slip length of 0.01*l, where l is the grid spacing of the mesh which ranged from 1-1.7 µm. Thus, the slip length was typically between 10-17 nm, consistent with experiments of water on hydrophobic substances at low shear rate (Churaev et al., 1984). The amount of movement of the sharp edge of the particle was only weakly dependent

Figure 2.10: Details of quarter-sphere model used to simulate flow for particles that exhibit cracking behaviour and no discernible flow over subsequent hours of observation. Surfaces 1 and 2 represent the external fluid interfaces, to which a relevant value of surface tension from literature was assigned, and surface 3 represents the particle-substrate interface, which was represented as a Navier-slip boundary with a slip length of 10-17 nm. Originally published in Renbaum-Wolff et al. (2013a).
2.2. Poke-and-flow technique combined with simulations

on the slip length used, leading to less than a 10% change in the observed movement when the slip length was varied from 1 nm to 10 µm. A relevant value for density was assumed based on literature values. The viscosity of the fluid was adjusted until the sharp edge at the top of the particle, (viewed from above the quarter-sphere) moved by ≈ 0.5 µm over 8 h, a typical experimental time (see Fig. 2.7(b) and Fig. 2.10). The extent of movement, 0.5 µm, was chosen because if movement of this magnitude occurs it is clearly detectable in the microscope images.

The viscosity determined as described above is a lower bound to viscosity for the following reasons: (a) movement of 0.5 µm is an upper limit to the movement observed in our experiments, (b) if a higher surface tension were used in the simulations the result would be a higher prediction of the viscosity.

Simulations were initialized as a quarter sphere having one flat face in contact with a substrate. In a set of stepwise simulations, the viscosity was decreased until the maximum displacement at the corners of the quarter-sphere was 0.5 µm in 8 h, establishing a lower limit for viscosity of 5 × 10^8 Pa s for a particle that cracks and exhibits no discernible flow over the course of 8 h (see Section 3.2.5).

Further simulations were also carried out using other geometries to determine if the predicted lower bounds of the viscosities were sensitive to the initial geometry. For example, simulations included using a) a 2-D square as the initial geometry with lengths for the sides set to 20 µm and b) a 3-D cylinder with a height and radius of 20 µm and 10 µm, respectively. In these two cases no interactions with a stationary surface were considered. Both the 2-D square model and the 3-D cylinder model resulted in 0.5 µm movement in 8 h when a viscosity of 1 × 10^9 Pa s was used, suggesting the quarter-sphere model used herein provides the most conservative lower limit to the viscosity of these models.
2.3 Equilibration times

For experiments using both the bead-mobility and poke-and-flow techniques, the RH inside the flow cell was initially set at 90 % for 30 min, after which the RH was decreased (at a rate of $<0.5 \text{ % RH min}^{-1}$) to the experimental value, at which point the RH was held constant to allow the particles to equilibrate once more. To estimate the time for particles to come to equilibrium with the water vapour the procedure outlined by Shiraiwa et al. (2011a) was followed, which is based on percolation theory. Equilibration times for water are expected to be significantly faster than equilibration times for larger organic molecules because small molecules like water percolate (i.e., diffuse) more rapidly though the host matrix (Shiraiwa et al., 2011a).

When calculating equilibration times, diffusion coefficients from Table 1 in Shiraiwa et al. (2011a) and the particle diameters used in the poke-and-flow experiments were used with the equation,

$$\tau_{mixing} = \frac{d_p^2}{4\pi^2 D}$$

where $d_p$ is the particle diameter, $D$ is the diffusion coefficient, and $\tau_{mixing}$ is the time taken for the concentration of a representative molecule anywhere in the particle to deviate by less than $1/e$ from the initial disequilibrium concentration. The particle size studied of 20-70 $\mu$m was used in the poke-and-flow experiments, although this full range was not used at each RH. Using this methodology, an estimate of the equilibration time was determined to be $<1$ s for particles with a viscosity of $10^{-3}$ Pa s (roughly equivalent to that of water), $<1$ minute for particles with a viscosity of $10^2$ Pa s (roughly equivalent to that of ketchup), and $<20$ minutes for particles with a viscosity of $10^{12}$ Pa s (greater than that of tar pitch).

Particles were allowed to equilibrate at a given RH for at least 30 minutes at all RHs for experiments performed using both the bead-mobility and poke-and-flow techniques. For poke-and-flow experiments the equilibration time was extended as RH was decreased, reaching 120 minutes in some cases. As such, the equilibration times suggest the particles were in equilibrium...
2.3. Equilibration times

with the surrounding water vapour when they were studied. Even if the equilibration time is longer than predicted by percolation theory (Bones et al., 2012), it is unlikely that the particles are far from equilibrium in the poke-and-flow experiments considering both the slow RH ramp down time and long equilibration times used in the experiments. Further, no strong dependence of the results on particle size was observed, suggesting that non-equilibration between the gas and the particle was not an issue.
Chapter 3

Viscosity of \(\alpha\)-pinene secondary organic material and implications for particle growth and reactivity

3.1 Introduction

Biological sources (e.g., vegetation) emit copious quantities of volatile organic compounds, such as \(\alpha\)-pinene (Hallquist et al., 2009; Kanakidou et al., 2005). In the atmosphere, a complex series of chemical reactions oxidizes these volatile compounds, to form semivolatile organic compounds (SVOCs) that condense to the particle phase (Hallquist et al., 2009; Kanakidou et al., 2005). These particles can influence climate by scattering and absorbing solar radiation (direct climate effect) and by serving as nuclei for cloud formation (indirect climate effect), among other mechanisms (Solomon et al., 2007). They can also influence air quality and health (Baltensperger et al., 2008; Jang et al., 2006; US Environmental Protection Agency, 2008).

Recently, molecular diffusion within SOM particles has become an area of intense scientific interest (see Chapter 1). In many large-scale modelling studies, it is often assumed that equilibrium is rapidly achieved between gas-phase organic compounds and the bulk of SOM particles (Hallquist et al., 2009; Kamens et al., 1999; Odum et al., 1994; Rounds and Pankow, 1990). This assumption implies that diffusion within the particles is fast when compared to accommodation (Shiraiwa and Seinfeld, 2012). More recently,
strong evidence emerged that some SOM particles, including but not limited to SOM from α-pinene ozonolysis, can behave as semisolids or solids under some conditions, such as low relative humidity (Abramson et al., 2013; Cappa and Wilson, 2011; Kuwata and Martin, 2012; Perraud et al., 2012; Säikkonen et al., 2012; Vaden et al., 2010, 2011; Virtanen et al., 2010, 2011). Prior to this research, however, estimates available in the literature for molecular diffusivity inside SOM are limited to dry conditions (RH <3%) (Cappa and Wilson, 2011; Perraud et al., 2012) whereas atmospheric conditions may cover the full range of RH, with typical values ranging from approximately 20-100 % in the planetary boundary layer (Hamed et al., 2011; Held and Soden, 2000; Martin, 2000). As a result, diffusion rates within SOM particles under typical atmospheric conditions are uncertain, and this uncertainty implies concomitant uncertainty for predicting the impacts of SOM particles on air quality, visibility and climate (Koop et al., 2011).

Our strategy for quantification of molecular diffusivity is to make experimental measurements of viscosity, \( \eta \). Viscosity and molecular diffusion rates are related by the Stokes-Einstein equation in the case of self-diffusion (i.e., similarly sized molecules) if the viscosity is not too near that of a glass, or by other approaches such as percolation theory for a diffusion of a small molecule in host matrix of large molecules (Koop et al., 2011; Zobrist et al., 2008). As is the case for molecular diffusivity, quantitative determination of SOM viscosity is lacking for the range of relative humidity typical of the atmosphere.

Herein, two newly developed techniques are used to measure at room temperature (293-295 K) the RH-dependent viscosity of the water-soluble component of SOM particles produced by α-pinene ozonolysis, a major source of SOM particles in the atmosphere, especially over boreal forests (Cavalli et al., 2006). The water-soluble component makes up the major fraction of SOM particles from α-pinene ozonolysis (see Section A.1).
3.2 Experimental

3.2.1 Production of secondary organic material

Secondary organic material was formed via homogeneous nucleation during the dark ozonolysis of α-pinene in continuous-flow environmental chambers at Harvard University and Pacific Northwest National Laboratory (PNNL). A schematic detailing the steps during the production of SOM is included as Figure 3.1, and the setup and experimental conditions were similar to those employed by Shilling et al. (2008). The α-pinene (80-100 parts-per-billion by volume (ppbv)), ozone (300 ppbv), and 2-butanol (used as an OH scavenger) were introduced continuously to the chambers in a total flow of 20 to 25 sLpm. The temperature and relative humidity inside the chambers were maintained at 298 K and <5 %, respectively. The secondary organic material was collected at the outlet of the Harvard University environmental chamber on a quartz fiber filter (Whatman; 1851-047) and at the outlet of the PNNL chamber on a Teflon filter (Pall; R2PL037). During collection the composition of the SOM was monitored continuously and found to be constant. The collection time for sampling was 48 h at a flow rate of 8.0 sLpm.

After collection, filters were stored at 263 K under dry conditions until they were extracted. The water-soluble species were extracted from the filters through the addition of 20 mL of ultra-pure Millipore water (18.2 MΩ cm). The extract solution was used within 14 days, and stored at 278 K when not in use. Viscosities measured immediately after filter extraction

Figure 3.1: Schematic detailing the production of SOM via the ozonolysis of α-pinene.
3.2. Experimental

and 14 days after filter extraction were the same within experimental un-
certainty. Super-micron sized particles were produced for the bead-mobility
and poke-and-flow experiments in this Chapter by nebulising the extracted
SOM solution.

3.2.2 Bead-mobility technique

The bead mobility technique is described in Section 2.1. The bead speeds
determined here for the SOM were converted to viscosities using the cali-
bbration curve shown in Fig. 2.5.

3.2.3 Poke-and-flow technique

The experimental procedure for experiments with the poke-and-flow tech-
nique combined with simulations of fluid flow is detailed in Section 2.2.1.

3.2.4 Simulations of material flow at 40-70 % RH

Between 40-70 % RH the needle penetrated the particle and caused the
material to take on a half-torus geometry. Upon removal of the needle the
hole at the centre of the half-torus was observed to decrease in size as the
material flowed to re-attain a hemispherical geometry (see Fig. 2.7(a-c)
for examples). This behaviour was simulated to determine upper limits of
viscosity as detailed in Section 2.2.3. Lower limits of viscosity were not
determined.

For the initial conditions a half-torus with fixed dimensions (R₀ = 20 µm,
r₀ = 7.5 µm) was used, representative of the size of the particles studied.
A surface tension of 75 mN m⁻¹ was assigned to Interface 1 of Fig. 2.8,
whilst a particle-substrate contact angle of 90 ° was assigned to Interface
2 (see below for implications). Interactions between the fluid and the solid
surface were described with a Navier slip wall boundary condition, with a
slip length of more than an order of magnitude greater than the particle
height. The effect of the slip length on the simulations is discussed below.
For the fluid a density of 1.3 g cm⁻³ was assumed (Chen and Hopke 2009;
Nga et al. 2006; Saathoff et al., 2003).
3.2. Experimental

Simulations were performed as a function of viscosity to create a calibration curve between viscosity and $\tau_{(model,flow)}$ (Figure [3.2]). This calibration curve was then used to convert values of $\tau_{(exp,flow)}$ into viscosities.

Viscosities determined as described above are upper limits for the following reasons: (a) The calibration curve was generated with a surface tension of 75 mN m$^{-1}$, which is most likely an upper limit to the surface tensions in our experiments [Huff-Hartz et al., 2006; Hyvärinen et al., 2006; Tuckermann and Cammenga, 2004]. If lower surface tensions were used in the simulations the results would be lower predictions of viscosities for a given $\tau_{(exp,flow)}$. (b) The calibration curve was generated using a contact angle of 90°, which is greater than the upper limit to the contact angle measured.

![Figure 3.2: Calibration line from COMSOL simulations (black solid line). In the simulations used to generate this calibration a surface tension of 75 mN m$^{-1}$ and contact angle of 90° were used. The annotation in the figure illustrates how the calibration line would shift if a smaller surface tension, smaller equilibrium contact angle, smaller slip length, and/or surface scratching was included in the model. An example line constructed with lower surface tension (60 mN m$^{-1}$) and lower contact angle (70°) is given to display the sensitivity of the model to these parameters (grey dashed line). Originally published in Renbaum-Wolff et al. (2013a).](image-url)
3.2. Experimental

with a confocal microscope. If a smaller contact angle is used in the simulations, the result would be lower viscosity predictions for a given \( \tau_{\text{(exp,flow)}} \).

(c) A large slip length was used in the calculations (more than an order of magnitude greater than the height of the modelled particles). This is likely an upper limit to the slip length in our experiments (Churaev et al., 1984). If a smaller slip length was used, the result would be lower predictions of viscosities for a given \( \tau_{\text{(exp,flow)}} \).

(d) In some experiments the needle scratches the surface resulting in reduced flows of the particle on the scratched regions (observed visually). If this process was included in the model, then the result would be lower predictions of viscosity for a given \( \tau_{\text{(exp,flow)}} \). See annotations in Fig. 3.2 for the effect of decreased surface tension, decreasing contact angle, decreasing slip length and effect of surface scratching on the calibration curve that relates flow times to viscosities. The sensitivity of the model to changes in surface tension and contact angle was tested by comparing the \( \tau_{\text{(model,flow)}} \) values calculated for a contact angle of 90° and a surface tension of 75 mN m\(^{-1}\) (Fig. 3.2, solid line) to \( \tau_{\text{(model,flow)}} \) calculated for a contact angle of 70° and a surface tension of 60 mN m\(^{-1}\) (Fig. 3.2, dashed line). The small (20 - 30%) change in the predicted \( \tau_{\text{(model,flow)}} \) values are predominantly due to the change in the surface tension.

The upper limits to viscosity at 70 % RH estimated from the poke-and-flow results are consistent with the results obtained with the bead-mobility technique (compare Tables 3.1 and 3.2). As a further test, poke-and-flow experiments were performed using particles of sucrose. When sucrose particles were poked at 56 and 60 % RH and half-torus geometries were formed, the resulting \( \tau_{\text{(exp,flow)}} \) values were 5 and 0.8 seconds, respectively. Using these experimental flow times and the calibration curve in Fig. 3.2, upper limits to the viscosity of the sucrose particles were estimated to be \( 1 \times 10^4 \) and \( 6 \times 10^4 \) Pa s, at 60 % and 56 % RH respectively. At 60 % RH, the literature viscosity of the sucrose/water mixture is approximately \( 9 \times 10^2 \) Pa s. At 56 % RH, the viscosity of the sucrose/water mixture is estimated to be \( 8(^{+3}_{-2}) \times 10^3 \) Pa s, based on an extrapolation of literature data using a third degree polynomial function (see Renbaum-Wolff et al., 2013b).
3.3 Results

3.2.5 Simulations of material flow at 25-30 % RH

At 25 and 30 % RH the particles were observed to crack upon impaction of the needle, forming pieces with sharp, distinct edges. No detectable flow was discerned in the material during observations over the subsequent eight hours.

Flow in these experiments was simulated as detailed in Section 2.2.4. To test the approach for determining lower limits to viscosities, particles of raffinose were studied at 30 % RH using the poke-and-flow technique. According to Zobrist et al. (2008), raffinose passes through a relative humidity induced glass transition at \( \approx 53 \) % RH at room temperature. At 30 % RH, therefore, raffinose particles are expected to be in a glass state, with viscosities \( \geq 10^{12} \) Pa s. The poke-and-flow experiment was performed on raffinose particles at 30 % RH and the particles shattered into well-defined pieces with sharp edges. Movement was less than 0.5 \( \mu \text{m} \) over 8 h. The lower limit of the viscosity estimated with the quarter-sphere COMSOL model discussed in Section 2.2.4 was \( 5 \times 10^8 \) Pa s, which is consistent with the established viscosity \( (\geq 10^{12} \) Pa s) for this material.

3.3 Results

3.3.1 Experiments with the bead-mobility technique

Shown in Fig. 2.4 are examples of optical images showing the change over time in the position of beads within a particle. The average bead speeds and associated viscosities determined between 70 % and 90 % RH are summarised in Table 3.1 and plotted in Figure 3.3. At 70 % RH the viscosity (\( \pm 95 \% \) prediction limits) of the SOM was \( 791^{\pm 1520} \) Pa s, comparable to that of peanut butter. At 90 % RH the viscosity of the SOM was \( 6.25^{\pm 11.8} \) Pa s, comparable to that of honey. Bead speeds were not determined for RH <70 % because the rate of circulation became too slow to readily observe.
Table 3.1: Mean bead speeds as a function of RH in water-soluble SOM from α-pinene ozonolysis and corresponding viscosities. Originally published in Renbaum-Wolff et al. (2013a).

<table>
<thead>
<tr>
<th>Chamber sample a</th>
<th>RH / %</th>
<th>Mean bead speed / µm ms⁻¹</th>
<th>Viscosity (± 95 % prediction limits) / Pa s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEC</td>
<td>90</td>
<td>4.75 × 10⁻⁵</td>
<td>6.25⁺⁻11.8 3.35</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>5.33 × 10⁻⁶</td>
<td>61.8⁺⁻117.7</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>4.67 × 10⁻⁷</td>
<td>791⁺⁻1520 413</td>
</tr>
<tr>
<td>PNNL</td>
<td>87</td>
<td>1.90 × 10⁻⁵</td>
<td>16.3⁺⁻30.7 8.67</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>9.22 × 10⁻⁶</td>
<td>34.8⁺⁻66.7 18.5</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>3.90 × 10⁻⁶</td>
<td>85.7⁺⁻163 45.3</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.40 × 10⁻⁶</td>
<td>251⁺⁻481 132</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>7.41 × 10⁻⁷</td>
<td>488⁺⁻938 256</td>
</tr>
</tbody>
</table>

a HEC refers to samples collected on quartz fiber filters from the Harvard Environmental Chamber. PNNL refers to samples collected on Teflon filters from the Pacific Northwest National Laboratory Continuous-Flow Environmental Chamber.

3.3.2 Experiments with the poke-and-flow technique

In experiments at RH ≥40 %, the needle penetrated the particle, resulting in a half-torus shape being generated after the needle was retracted (e.g. Fig. 2.7(a)-(c)). The half-torus reformed at an observable rate into a spherical cap, minimizing the surface energy of the system (e.g. Fig. 2.7(a)-(c)). The experimental flow time, \( \tau_{(exp,flow)} \), required for the inner diameter of the half-torus to decrease to 50 % of its initial diameter was determined by analysis of a time series of images. The flow time increased from approximately 10 s at 70 % RH to 4000 s at 40 % RH (Table 3.2).
3.3. Results

Table 3.2: Results from the poke-and-flow experiments. Originally published in Renbaum-Wolff et al. (2013a).

<table>
<thead>
<tr>
<th>Chamber sample</th>
<th>RH / %</th>
<th>$\tau_{\text{exp,flow}}$ / s</th>
<th>Limits of viscosity / Pa s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>50.9</td>
<td>378</td>
<td>9.92 x 10^4</td>
</tr>
<tr>
<td>68</td>
<td>8.98</td>
<td>378</td>
<td>1.29 x 10^6</td>
</tr>
<tr>
<td>60</td>
<td>116.5</td>
<td>378</td>
<td>5.08 x 10^5</td>
</tr>
<tr>
<td>55</td>
<td>46.0</td>
<td>378</td>
<td>5.19 x 10^5</td>
</tr>
<tr>
<td>50</td>
<td>47.0</td>
<td>378</td>
<td>3.37 x 10^6</td>
</tr>
<tr>
<td>45</td>
<td>305</td>
<td>378</td>
<td>4.53 x 10^7</td>
</tr>
<tr>
<td>40</td>
<td>4090</td>
<td>378</td>
<td></td>
</tr>
<tr>
<td>PNNL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **a** HEC refers to samples collected on quartz fiber filters from the Harvard Environmental Chamber. PNNL refers to samples collected on Teflon filters from the Pacific Northwest National Laboratory Continuous-Flow Environmental Chamber.

- **b** The values of $\tau_{\text{exp,flow}}$ can vary between experiments but the slowest observed flows are reported here in order to calculate an upper limit to the viscosity.

- **c** A lower limit (378 Pa s) was established for 40-70% RH based on the lower 95 % prediction limit from the bead-mobility value at 70 % RH.

- **d** The upper limits to the viscosities were calculated using $\tau_{\text{exp,flow}}$, and the calibration curve shown in Fig. 3.2.

Simulations were carried out using the software package COMSOL Multiphysics (see Section 3.2.4) for a particle of half-torus geometry having similar physical dimensions as the experimental observations. Because of assumptions used in the simulations, the viscosities determined for 40-70 % RH were upper limits (see Section 3.2.4).

A lower limit (378 Pa s) was also established for 40-70 % RH based on the lower 95 % prediction limit from the bead-mobility value at 70 % RH. The upper limits (based on the poke-and-flow technique) and lower limits (based on the bead-mobility technique) to the viscosities for 40-70 % RH are listed in Table 3.2 and plotted in Fig. 3.3(a). At 40 % RH, the limits range from 378 Pa s to $5 \times 10^7$ Pa s, i.e., from approximately the viscosity
Figure 3.3: (a) Summary plot of the SOM viscosities determined by a combination of experiments using the bead-mobility technique (black empty squares and triangles for HEC and PNNL samples, respectively, where the black bars represent the 95% prediction intervals) and experiments using the poke-and-flow technique (where the blue bars represent the bounds of the viscosities). HEC refers to samples collected on quartz fiber filters from the Harvard Environmental Chamber. PNNL refers to samples collected on Teflon filters from the Pacific Northwest National Laboratory Continuous-Flow Environmental Chamber. Various common substances have been placed alongside the diagram, along with their approximate viscosities at room temperature, to provide points of reference following the idea of Koop et al. (2011). The secondary y-axes show (1) diffusion coefficients calculated using the Stokes-Einstein relation and (2) mixing times (τ_{mixing}) of the particles due to bulk diffusion in 100 nm particles of the same viscosity (see main text). The image of the pitch is a detail of an image from the pitch drop experiment (Wikimedia Commons, GFDL, University of Queensland, Australia, John Mainstone). (b) Typical relative humidities observed in the planetary boundary layer (Hamed et al., 2011; Held and Soden, 2000; Martin, 2000) and environmental chambers (Kostenidou et al., 2009; Tillmann et al., 2010). Originally published in Renbaum-Wolff et al. (2013a).
of peanut butter to that of pitch (Edgeworth et al., 2001).

For RH values of 25 to 30 %, the particles shattered when poked with a needle. Moreover, restorative flow did not occur, at least for the experimental timescale (8-10 h) (e.g. Fig. 2.7(d)). The fragments had sharp well-defined edges, and no smoothing of the edges was observed over the course of the experiments. In this case, modelling of the flow established a lower limit to the viscosity. This lower limit is included in Fig. 3.3(a), with a value comparable to that of pitch (Edgeworth et al., 2001).

3.4 Discussion

Amorphous solids have viscosities greater than $10^{12}$ Pa s, semi-solids such as gels or ultra-viscous liquids have viscosities between $10^{2}$ and $10^{12}$ Pa s, and liquids have viscosities less than or equal to $10^{2}$ Pa s (Koop et al., 2011; Shiraiwa et al., 2011a). These phases are represented by different patterns in Fig. 3.3, together with the RH-dependent viscosities. The viscosities of the studied SOM correspond to liquid for RH $\geq 80$ %, a semisolid for 40 % $\leq$ RH $<$ 80%, and a semisolid or solid for RH $\leq 30$ %. These findings are in agreement with the results of other recent studies suggesting that certain types of SOM do not behave as liquids under some conditions, such as low relative humidity (Abramson et al., 2013; Cappa and Wilson, 2011; Kuwata and Martin, 2012; Perraud et al., 2012; Saukko et al., 2012; Vaden et al., 2010, 2011; Virtanen et al., 2010, 2011).

The relationship between RH and viscosity in Fig. 3.3(a) can be rationalized by considering the hygroscopic nature of the studied SOM. SOM from $\alpha$-pinene ozonolysis is known to be hygroscopic, meaning the water content of the particles will increase as the RH increases (Cocker III et al., 2001; Saathoff et al., 2003; Varutbangkul et al., 2006; Virkkula et al., 1999). As the particles uptake water, the viscosity of the mixture is thus expected to decrease, since the viscosity of pure water is low ($1.002 \times 10^{-3}$ Pa s at 293 K (Kestin et al., 1978). This phenomenon may be described, at least to a first order approximation, by simple mixing rules (see Section A.2). The apparent step in viscosity between 30-40 % RH may be due to a phase tran-
3.4. Discussion

sition, such as the formation of a glass or gel, or may be due to non-ideal interactions in the complex mixture (see Section A.2).

Using the viscosities determined herein and an estimated hydrodynamic radius, the corresponding Stokes-Einstein-equivalent diffusion coefficients of organic molecules in SOM, $D_{org}$, have been calculated. These values correspond to the secondary $y$-axis of Fig. 3.3(a). The hydrodynamic radius was approximated as the molecular radius of 0.38 nm for a molar mass of 175 g mol$^{-1}$ (Cocker IIII et al., 2001), a density of 1.3 g cm$^{-3}$ (Saathoff et al., 2003; Varutbangkul et al., 2006; Virkkula et al., 1999), and molecular spherical symmetry. The obtained $D_{org}$ values ranged from $10^{-9}$ to $10^{-11}$ cm$^2$ s$^{-1}$ between 90 % and 70 % RH, from $10^{-11}$ to $10^{-16}$ cm$^2$ s$^{-1}$ between 70 % and 40 % RH, and to $<10^{-17}$ cm$^2$ s$^{-1}$ for RH $\leq$30 %. Three studies have estimated the diffusivity of organic compounds within SOM. Two of these studies, one looking at partitioning of organic nitrates into SOM particles (Perraud et al., 2012) and the other looking at the evolution of the chemical composition of SOM particles after they pass through a thermodenuder (Cappa and Wilson, 2011), have estimated an upper bound of $D_{org} <10^{-14}$ cm$^2$ s$^{-1}$ for the diffusion coefficient of organic molecules in SOM produced by $\alpha$-pinene ozonolysis under dry conditions (<3 % RH). These results are consistent with the results reported herein for RH $\leq$30 % ($D_{org} <10^{-17}$ cm$^2$ s$^{-1}$). The third study (Abramson et al., 2013) quantified the diffusivity of pyrene in SOM under low RH conditions to be $2.5 \times 10^{-17}$ cm$^2$ s$^{-1}$, similar to, but slightly higher than, the diffusion coefficient measured herein for the water-soluble component of $\alpha$-pinene at $\leq$30 % RH ($D_{org} <10^{-17}$ cm$^2$ s$^{-1}$). The small discrepancy is largely attributed to the hydrodynamic radius of pyrene used in the study by Abramson et al. (2013) compared to the hydrodynamic radius of SOM material used to calculate molecular diffusion coefficients from our viscosity data.

Detailed modelling studies are required to fully explore the implications of the new viscosity data. Here the viscosity data is used together with previous modelling studies or simple calculations to provide an initial assessment of the effect of the new viscosity data on (1) the mechanism of growth of SOM particles, (2) predictions of particle mass, and (3) rates of
3.4. Discussion

reactions in SOM particles.

Currently most models used for predicting the effect of SOM particles on air quality and climate assume that growth occurs by instantaneous equilibrium partitioning of SVOCs into the bulk of the SOM particles (Fig. 1.7(a), top image). For this mechanism to be accurate the mixing time of SVOCs within the particles must be short compared to the times scale for particle growth. The mixing times, $\tau_{\text{mixing}}$, by diffusion of large organic molecules within an SOM particle can be estimated from the viscosity data and the Stokes-Einstein relation (Bones et al., 2012),

$$\tau_{\text{mixing}} = \frac{3d^2\eta r}{2\pi kT} \quad (3.1)$$

in which $d$ is the particle diameter, $r$ is the hydrodynamic radius of a representative molecule of SOM within the SOM bulk matrix, $k$ is Boltzmanns constant, and $T$ is temperature. After the mixing time, the concentration of the representative molecule anywhere in the particles deviates by less than $1/e$ from the initial disequilibrium concentration (i.e., a homogenization process). It should be noted that Equation 3.1 may be inaccurate if the viscosity is close to that of a glass (Champion et al., 1997).

Shown in Fig. 3.3(a) (right-hand y-axis) are mixing times within 100 nm particles, calculated with Equation 3.1, the new viscosity data, and assuming a hydrodynamic radius of 0.38 nm. For an RH of 70 to 90 %, the mixing times are 0.01-1 s. In this case instantaneous equilibrium partitioning within the bulk of the SOM particles is likely a valid description of SOM growth (Fig. 1.7(a), top image). By comparison, the mixing times exceed 2.5 days for RH $\leq$30 %. At these relative humidities, gas-particle partitioning of large organic molecules such as pinonaldehyde (the most abundant product of $\alpha$-pinene ozonolysis) may be effectively confined to the surface of the particle (Fig. 1.7(a), bottom image). Hence, the mechanism of growth may not occur by instantaneous equilibrium partitioning within the particle bulk, as suggested for $\alpha$-pinene SOM studied under dry conditions (e.g. Perraud et al., 2012, and references therein). The mechanism of growth may have important consequences for the particle size distribution (Riipinen et al., 2012).
3.4. Discussion

et al., 2011), which may in turn affect the scattering and absorption of solar radiation and the ability of particles to act as nuclei for cloud condensation (Solomon et al., 2007).

At $\leq 30\%$ RH, because the viscosity of the particles may allow partitioning of SVOCs only within the top few molecular layers of the particle, the particles will take up less SVOCs compared to low viscosity particles where instantaneous equilibrium partitioning within the bulk of SOM particles may occur (Fig. 1.7(a)). As a result, models that assume equilibrium partitioning at $\leq 30\%$ RH, may over predict SOM particle mass and under predict gas-phase concentrations of SVOCs. Recently Shiraiwa and Seinfeld (2012) showed that when the viscosity of the particle is $\geq 5 \times 10^6$ Pa s, the particle-phase mass concentrations of semivolatile and low-volatility organic compounds may be overestimated by at least an order of magnitude compared to the assumption of instantaneous equilibrium partitioning within the bulk. The new viscosity data and the modelling results from Shiraiwa and Seinfeld (2012), suggest that at $\leq 30\%$ RH, the particle-mass concentrations of SVOCs and low-volatility organic compounds may be over predicted by an order of magnitude with implications for predictions of air quality and visibility.

Reactions between atmospheric oxidants, such as O$_3$, and particle-phase organic molecules can lead to chemical aging of SOM particles, with possible implications for particle hygroscopicity, optical properties, and toxicity (Shiraiwa et al., 2011b; Zahardis and Petrucci, 2007). The rates of these aging reactions may depend on the diffusion coefficients of the oxidants, $D_{ox}$, within the SOM (Pfrang et al., 2011; Shiraiwa et al., 2011a; Smith et al., 2002). The rates can also possibly depend on the diffusion coefficients of the organic molecules, $D_{org}$, in the case that the diffusion rates of the organic molecules are slow (Pfrang et al., 2011; Shiraiwa et al., 2011a). Based on our viscosity data and the Stokes-Einstein equation, $D_{org}$ decreases by more than eight orders of magnitude for a drop in RH from 90 % to 30 % RH. In organic matrices $D_{ox}$ is estimated based on previous measurements of the mobility of small molecules in different matrices to be $\approx 10^{-5}$ cm$^2$ s$^{-1}$ for a liquid, $10^{-7} - 10^{-9}$ cm$^2$ s$^{-1}$ for a semi-solid, and $10^{-10}$ cm$^2$ s$^{-1}$ for a
solid (see Shiraiwa et al. (2011a) and references therein). Based on these estimates and the phase information elucidated above, $D_{ox}$ is expected to decrease by at least two to five orders of magnitude for a change in RH from 90 % to $\leq$30 % RH as the particles transition from liquid to semisolid/solid. These changes in diffusion coefficients imply that the rates of chemical aging of SOM particles can depend strongly on RH, with a decrease in rates expected with a decrease in RH. In support of these implications, a recent study showed that the reaction rate of NH$_3$ with $\alpha$-pinene SOM particles decreases significantly for a drop in RH from 95 % to 5% (Kuwata and Martin, 2012).

Applying the viscosity measurements from the present study to $\alpha$-pinene SOM in the atmosphere or environmental chambers is subject to several caveats. First, the study focused on the water-soluble component of SOM. For $\alpha$-pinene SOM, however, the water-soluble material constitutes the major mass fraction SOM (see Section A.1). Second, collection of SOM from environmental chambers can be subject to both positive and negative sampling artifacts. Positive artifacts occur due to the adsorption of semivolatile organic material on the filters and are expected to be much less with Teflon filters than quartz fiber filters (Kirchstetter et al., 2001). Since the same viscosity results were obtained within the uncertainty of the measurements using both Teflon filters and quartz filters (Tables 3.1 and 3.2 and Fig. 3.3), positive artifacts seem unimportant in our experiments. Negative artifacts can include the partial evaporation of semivolatile SOM. This process cannot be ruled out for our experiments. As a result the material studied here may be the less volatile component of the water-soluble secondary organic material. These caveats notwithstanding, the results reported herein provide best estimates of $\alpha$-pinene SOM viscosities over a wide range of atmospherically relevant relative humidities. Information concerning viscosity and ultimately diffusion coefficients is needed for the accurate modelling of heterogeneous chemistry as well as particle growth and evaporation.
3.5 Summary

Two techniques, the bead-mobility technique and the poke-and-flow technique combined with simulations of fluid flow have been used to experimentally determine the viscosity of particles containing the water-soluble component of SOM at a range of RHs.

Firstly, the bead-mobility technique, which was initially described and validated previously (Renbaum-Wolff et al., 2013b), was used to determine the viscosity of SOM particles at RHs ≥70 %. At ≥80 % RH the particles were determined to have viscosities corresponding to that of a liquid, whilst at RHs between 70 and 80 % RH the particles were determined to have viscosities corresponding to that of a semisolid (Koop et al., 2011; Shiraiwa et al., 2011a).

Secondly a poke-and-flow technique was used to determine the viscosity of SOM particles at ≤70 % RH. At RHs between 40 % and 70 %, the material exhibited flow on an atmospheric timescale, whilst at RHs ≤30 % the material was observed to crack, and no flow was observed over the subsequent 8 h. Simulations of this behaviour suggest that the material is of viscosity corresponding to that of a semisolid between 40 and 70 % RH, and of viscosity corresponding to that of a semisolid or solid at ≤30 % RH (Koop et al., 2011; Shiraiwa et al., 2011a).

These experimental findings are in agreement with the results of other recent studies suggesting that certain types of SOM do not behave as liquids under some conditions, such as low relative humidity (Abramson et al., 2013; Cappa and Wilson, 2011; Kuwata and Martin, 2012; Perraud et al., 2012; Saukko et al., 2012; Vaden et al., 2010, 2011; Virtanen et al., 2010, 2011).

These results have important atmospheric implications. For example, if particles in the atmosphere are similar to those studied here then their mixing times would be rapid (on the order of seconds) for particles at ≥70 % RH, but become increasingly longer as RH is reduced, being on the order of days at ≤30 % RH, affecting the mechanism and rate of growth of the particles. Based on the viscosities and the phase information elucidated above, and for particles similar to those studied here, $D_{ox}$ is expected to decrease
3.5. Summary

by at least two to five orders of magnitude for a change in RH from 90% to \( \leq 30\% \) RH, as particles transition from liquid to semisolid/solid in phase, a direction of change in agreement with that suggested by prior research (Kuwata and Martin 2012). These changes in diffusion coefficients imply that the rates of chemical aging of SOM particles can depend strongly on RH, with possible implications for particle hygroscopicity, optical properties, and toxicity (Shiraiwa et al. 2011b; Zahardis and Petrucci 2007).
Chapter 4

Additional validation of the poke-and-flow technique combined with simulations of fluid flow for determining viscosities in samples with small volumes and high viscosities

4.1 Introduction

The importance of viscosity and diffusion within SOM particles is outlined in Chapter 1. The viscosity, \( \eta \), of SOM may span multiple orders of magnitude, from \( 10^{-3} \) to \( >10^{12} \) Pa s, across the ambient relative humidity range in the atmosphere through the uptake and release of water (Koop et al., 2011; Kuwata and Martin, 2012, and Chapter 3). Measuring such a wide range of viscosities presents a challenge, made more difficult by the small, milligram, scale of SOM samples typically collected in the atmosphere or chambers used to simulate atmospheric conditions. Currently, there is no commercially available technique capable of quantifying the viscosity of SOM samples across the entire viscosity range important in the atmosphere. However, a
few techniques have recently been developed, each of which is capable of covering at least part of the range of interest.

Renbaum-Wolff et al. (2013b) developed a bead-mobility technique, which can determine the viscosities of SOM samples with masses between 1-5 mg and viscosities between $10^{-3}$ and $10^3$ Pa s. This technique consists of determining the speed of circulation of micrometer sized beads within a particle as a shear stress is applied to the particle. In Chapter 2 the development of a poke-and-flow technique combined with simulations of fluid flow to constrain the viscosities of samples of 1-5 mg in mass is detailed. The technique consisted of generating a hole in a supermicron sized particle suspended on a surface and determining a characteristic time taken for the hole to close. In Chapter 3 simulations of fluid flow were performed to determine upper limits of viscosity for a particle based upon the time taken for the hole at its centre to close, and the measured upper limits of viscosity were consistent with literature values up to at least $10^4$ Pa s.

Power et al. (2013) used holographic optical tweezers to coalesce two suspended particles with a combined volume of $<500$ femtolitres. By measuring the time taken for the resulting particle to relax to a spherical shape, viscosities of sucrose-water or sucrose-salt-water particles were quantified across the range of $10^{-3}$-$10^9$ Pa s. In a subsequent publication, Power and Reid (2014) further outlined the application of optical tweezers for rheological measurements. In a similar vein, Pajunoja et al. (2014) used scanning electron microscopy images to determine the viscosity of secondary organic aerosols by studying the time taken for multiple particles to coalesce. Hosny et al. (2013) observed the behaviour of molecular rotors using fluorescence lifetime imaging microscopy to determine the viscosity of sodium chloride and sucrose-water particles. In addition, Kidd et al. (2014) estimated some limits to viscosities of particles from the extent to which material collected in the centerline of an impactor spreads under high airflow.

In Chapter 3 only a preliminary validation of the poke-and-flow technique combined with simulations of fluid flow was carried out for viscosities $<10^8$ Pa s due to the lack of suitable standards for validation at the time of publication. Specifically, in Chapter 3 sucrose-water particles over a narrow
4.2 Experimental

range of relative humidities to validate the approach for viscosities <10^8 Pa s. In addition, as mentioned above, for viscosities <10^8 Pa s, the work in Chapter 3 only showed that the approach was able to provide upper limits to the viscosity of the particles. No attempt was made to determine lower limits to the particle viscosity using the poke-and-flow technique combined with simulations of fluid flow when the viscosity was <10^8 Pa s.

The following expands on the initial validation and characterization of the poke-and-flow technique combined with simulations of fluid flow. First, the approach is used to determine the viscosity of sucrose-water particles over a wider range of relative humidities than previously done in Chapter 3. These results are compared to recent results published by Power et al. (2013) who reported viscosities of sucrose-water particles ranging from 10^{-3} - 10^9 Pa s, and Quintas et al. (2006) who measured a viscosity of 10^3 Pa s at 54 % RH using a rotational controlled stress rheometer. Second, the approach was used to determine the viscosity of two polybutene standards, and the results compared with viscosities measured by the manufacturer using a commercially available viscometer. The results for both the sucrose-water particles and the polybutene standards shows this approach is capable of providing both lower and upper limits of viscosity that are consistent with literature or measured values for particles of material that range in viscosity from \approx 5 \times 10^2 - \approx 3 \times 10^6 Pa s.

4.2 Experimental

4.2.1 Poke-and-flow technique

The poke-and-flow technique combined with simulations of fluid flow is detailed in Section 2.2. Super-micron sized sucrose particles were produced on hydrophobic glass substrates by nebulising sucrose-water solutions. Super-micron sized particles consisting of polybutene standards (N450000 and N2700000; Cannon Instrument Company, USA) were prepared on hydrophobic glass substrates using a pipette. The samples were heated to 60 - 70 °C over \approx 30 minutes to aid the production of particles by reducing the vis-
4.2. Experimental

Consistency of the material, with material being picked up on a pipette tip and the pipette being ‘flicked’ towards the substrate, resulting in particles being formed on the substrate. After particle production, the particles were allowed to equilibrate under dry (<0.5 % RH) conditions at room temperature for 60 minutes. Particles consisting of polybutene standards that were poked ranged in diameter from 40-70 µm.

4.2.2 Simulations of fluid flow

Simulations of fluid flow were performed as detailed in Section 2.2.3. The physical properties used in the simulations are detailed in Tables 4.1 (for particles of sucrose-water) and 4.2 (for particles of polybutene standards). The dimensions of \( R_0 \) and \( r_0 \) and the equilibrium contact angle were determined from measurements, and the values of surface tension (Surface 1, Fig. 2.8(b)), slip length (which describes the interaction at Surface 2 in Fig. 2.8(b)), and the density of the material were determined based on literature values. For each particle that was poked and formed a half-torus geometry, and was not significantly influenced by scratches (determined visually, as discussed in Section 2.2), lower and upper limits of viscosity were determined via simulations. Values from row 2 of Tables 4.1 and 4.2 were used for simulations of the lower limit of viscosity for a particle, whilst values from Row 3 of Tables 4.1 and 4.2 were used for simulations of its upper limit of viscosity.

A proportion (≈30 %) of the sucrose-water particles that were poked had dimensions where \( r_0/R_0 > \approx 0.4 \). Simulations of the lower limit of viscosity for many of these particles gave rise to a non-physical geometry whereby the inner edge of the half-torus geometry appeared jagged and wavy - a phenomena not observed during experiments. Further study of this phenomena revealed that this was the result of the stretching of the mesh elements at the moving front of the particle, and use of a finer mesh did not prevent this from occurring. As such, all sucrose-water particles of dimensions \( r_0/R_0 > \approx 0.4 \) were removed from the study. No particles of the polybutene standard fell into this size range.
Table 4.1: Experimental parameters used when simulating flow with COMSOL for the sucrose-water experiments. Originally published in Grayson et al. (2015a).

<table>
<thead>
<tr>
<th>Surface tension (mN m(^{-1}))</th>
<th>Slip length (m)</th>
<th>Density (kg m(^{-3}))</th>
<th>Contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of values</td>
<td>57.2 - 75.15</td>
<td>1490 - 1520</td>
<td>94.8 - 102.2</td>
</tr>
<tr>
<td>Value used to calculate lower limit of viscosity</td>
<td>57.2</td>
<td>5 x 10(^{-9})</td>
<td>1500</td>
</tr>
<tr>
<td>Value used to calculate upper limit of viscosity</td>
<td>75.15</td>
<td>1 x 10(^{-5})</td>
<td>1500</td>
</tr>
</tbody>
</table>

\(a\) MacDonald et al. (1996); Power et al. (2013)
\(b\) This range is based on the literature values included in Table 2.1.
\(c\) Tong et al. (2011); Zobrist et al. (2008). A density of 910 kg m\(^{-3}\) was used for all simulations as density was found to have no effect on simulated viscosities.
\(d\) Contact angles were determined by photographing a series of five sucrose-water particles, each on a separate hydrophobic slide. The mean contact angle was measured at the particle-substrate interface of both the right and left edges of the particle using ImageJ software. The mean contact angle was determined to be 98.5 °, and the lower and upper limits of contact angle were determined to be 94.8 and 102.2 ° (98.5 ° ± 1 σ). The relationship between the simulated viscosity of a particle and its contact angle is dependent upon the dimensions of the particle, more specifically the value of the ratio \((R_0-r_0)/r_0\). The lower limit of contact angle gave rise to the lower limit of viscosity for particles where \((R_0-r_0)/r_0<2\), whilst the upper limit of contact angle gave rise to the upper limit of viscosity for particles where \((R_0-r_0)/r_0>2\).
### Table 4.2: Experimental parameters used when simulating flow with COMSOL for experiments using polybutene standards. Originally published in Grayson et al. (2015a).

<table>
<thead>
<tr>
<th>Surface tension (mN m(^{-1}))</th>
<th>Slip length (m)</th>
<th>Density (kg m(^{-3}))</th>
<th>Contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Range of values</strong></td>
<td>25 - 50 (^a)</td>
<td>5 x 10(^{-9}) - 1 x 10(^{-5}) (^b)</td>
<td>910 - 913 (^c)</td>
</tr>
<tr>
<td><strong>Value used to calculate upper limit of viscosity</strong></td>
<td>25</td>
<td>5 x 10(^{-9})</td>
<td>910</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Value used to calculate upper limit of viscosity</strong></td>
<td>50</td>
<td>1 x 10(^{-5})</td>
<td>910</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Five studies have examined the surface tension of the polybutene, with the reported values ranging from 29 - 34.3 mN m\(^{-1}\) (Blunk and Wilkes, 2001; Jeong and Moffatt, 1992; Lewandowski and Dupuis, 1994; Mewis and Metzner, 2006; Roe, 1968). As the polybutene standards studied here are unlikely to differ much from those studied elsewhere, a conservative value of 25 mN m\(^{-1}\) has been used as the lower limit of surface tension. Blunk and Wilkes (2001) studied three different polybutene resins of differing viscosities. Measured surface tension values suggested a direct, though weak, relationship between surface tension and viscosity (surface tension increased from 29.3 - 30.0 mN m\(^{-1}\) as the viscosity of the resins increased from 4 to 16.4 Pa s). As the resins studied by Blunk and Wilkes (2001) were two orders of magnitude less viscous than those measured herein, a conservative upper estimate of 50 mN m\(^{-1}\) has been used in simulations for the surface tension of the polybutene standards. 

\(^b\) This range is based on the literature values included in Table 2.1.

\(^c\) Measured by Cannon Instrument company. A density of 910 kg m\(^{-3}\) was used for all simulations as density was found to have no effect on simulated viscosities.

\(^d\) Contact angles were determined as for sucrose-water particles (Table 4.1). For Standard #1 (N450000) the lower and upper limits of contact angle were determined to be 53.6 and 66.4 ° (i.e. 60.0 ° ± 1 σ), whilst the corresponding values for Standard #2 (N2700000) were determined to be 48.8 and 57.4 ° (i.e. 53.1 ° ± 1 σ).
4.3 Results and discussion

4.3.1 Sucrose-water particles

Shown in Figure 4.1 are examples of optical images of sucrose-water particles at 48.8, 52.7, and 58.8 % RH recorded during typical poke-and-flow experiments. Prior to being poked the particles may be described geometrically as a spherical cap (Fig. 4.1, Panels a1, b1, and c1). Just after being poked the geometry of the particles can be described as a half-torus - a ring of material with a hole at its centre (Fig. 4.1, Panels a2, b2, and c2), which

<table>
<thead>
<tr>
<th>% RH</th>
<th>Particle pre-poking</th>
<th>Particle poked</th>
<th>First frame post-poke</th>
<th>Frame at $\tau_{exp,flow}$</th>
<th>Final frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 48.8%</td>
<td>(a1)</td>
<td>(a2)</td>
<td>t = 0.00 sec</td>
<td>(a3)</td>
<td>t = 11.25 sec</td>
</tr>
<tr>
<td>(b) 52.7%</td>
<td>(b1)</td>
<td>(b2)</td>
<td>t = 0.00 sec</td>
<td>(b3)</td>
<td>t = 3.75 sec</td>
</tr>
<tr>
<td>(c) 58.8%</td>
<td>(c1)</td>
<td>(c2)</td>
<td>t = 0.00 sec</td>
<td>(c3)</td>
<td>t = 1.25 sec</td>
</tr>
</tbody>
</table>

Figure 4.1: Optical images of sucrose-water particles poked at RHs of (a) 48.8, (b) 52.7, and (c) 58.8 % recorded during typical poke-and-flow experiments. Images a1, b1, and c1 correspond to the particles before they are poked. Images a2, b2, and c2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3, b3, and c3 correspond to images of the experimental flow time, $\tau_{exp,flow}$, the point at which the equivalent area diameter of the hole at the centre of the particle has decreased to 50 % of its original size. Images a4, b4, and c4 correspond to the final frame recorded, at which point each particle has re-attained its original spherical cap geometry. Scale bar: 20 µm. Originally published in Grayson et al. (2015a).
4.3. Results and discussion

is energetically unfavourable compared to that of a spherical cap. For the particles in Fig. 4.1, $\tau_{\text{exp,flow}}$ was determined to be 11.25, 3.75, and 1.25 seconds at 48.8 %, 52.7 %, and 58.8 % RH, respectively (Fig. 4.1; Panels a3, b3, and c3). Following $\tau_{\text{exp,flow}}$ the material continued to flow, and eventually re-attained its initial, energetically favourable, spherical cap geometry (Fig. 4.1; Panel a4, b4, and c4).

The $\tau_{\text{exp,flow}}$ values of each of the individual sucrose-water particles poked and analysed is shown in Figure 4.2(a). Experimental flow times increased from $\approx 150$ milliseconds at 59 % RH to $\approx 40$ minutes at 37 % RH. The millisecond time resolution of the camera precluded experiments being performed at RH >60 % as the closure time for the sucrose-water particles was too fast to measure. Lower and upper limits of viscosity were determined for each individual particle using their dimensions and $\tau_{\text{exp,flow}}$ (Figure 4.2(b)). Between 59 % RH and 36 % RH, the viscosities for individual sucrose-water particles range from $\approx 1.0 \times 10^1$ - $6.6 \times 10^6$ Pa s with the upper limit of viscosity for a given particle being a factor of 16 to a factor of 140 larger than the corresponding lower limit of viscosity, with the uncertainty mainly due to the uncertainties of the values of the physical properties used in the simulations.

In Figure 4.2(c), the viscosities of individual particles are grouped by RH, and previously reported values of the viscosity of sucrose-water particles are included for comparison (Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958). Viscosities have been determined by grouping particles based upon RH, with lower and upper limits of viscosity from particles in the group reported. The lower and upper limits of viscosity of the group of particles poked at $\approx 59$ % RH are 1.0 x 10^1 Pa s and 1.6 x 10^4 Pa s, whilst at 37 % RH the corresponding values are 7.2 x 10^4 and 4.7 x 10^6 Pa s, respectively. As shown in Fig. 4.2(c), the results are in good agreement with Quintas et al. (2006) who measured a viscosity of $10^3$ Pa s at 54 % RH using a rotational controlled stress rheometer, and Power et al. (2013) who recently reported mean measured viscosities of $\approx 5 \times 10^2$ Pa s to $\approx 3 \times 10^6$ Pa s between 60 % RH and 37 % RH using holographic optical tweezers.
4.3. Results and discussion

Figure 4.2: (a) $\tau_{exp,flow}$ as a function of RH for individual sucrose-water particles. (b) Calculated viscosities for the individual sucrose-water particles in (a), where red bars represent the calculated lower and upper limits of viscosity. (c) Lower and upper limits of viscosity for the particles shown in (b), grouped by RH. The error bars on the $x$-axis represent the range of RHs at which particles in the group were poked. Lower and upper limits of viscosity were determined for each particle via simulation, with the bottom of a bar on the $y$-axis representing the lowest lower limit of viscosity for any of the particles in the group, and the top of the bar representing the highest upper limit of viscosity for any of the particles in the group. Literature values (Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958) are provided for comparison, with error bars representing $1\sigma$ for Power et al. (2013) and 95 % confidence intervals for Quintas et al. (2006). Originally published in Grayson et al. (2015a).
4.3. Results and discussion

4.3.2 Particles of polybutene standards

Figure 4.3 shows examples of optical images of particles of the polybutene standards recorded during poke-and-flow experiments at <0.5 % RH. As for sucrose-water particles, the geometry of the particles of standard solution could be described as a spherical cap prior to being poked (Fig. 4.3; Panels a1 and b1), and a half-torus after being poked (Fig. 5; Panels a2 and b2). Upon removal of the needle the material flowed, with the size of the hole at the centre of the half-torus geometry decreasing over time. For the particles in Fig. 4.3, $\tau_{\text{exp,flow}}$ was determined to be 2.50 and 6.00 seconds, respectively (Fig. 4.3 Panels a3 and b3). The particle continued to flow after $\tau_{\text{exp,flow}}$ and eventually re-attained it’s initial, energetically favourable, spherical cap geometry (Fig. 4.3; Panels a4 and b4). The mean experimental flow times, $\tau_{\text{exp,flow}}$, were 2.79 ($\sigma = 0.39$) seconds for the lower viscosity.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Particle pre-poking</th>
<th>Particle poked</th>
<th>First frame post-poke</th>
<th>Frame at $\tau_{\text{exp,flow}}$</th>
<th>Final frame</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td><img src="image-a1" alt="Image" /></td>
<td><img src="image-a2" alt="Image" /></td>
<td><img src="image-a3" alt="Image" /></td>
<td><img src="image-a4" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>Standard #1 (N400000)</td>
<td></td>
<td>10 sec</td>
<td>2.50 sec</td>
<td>8 sec</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td><img src="image-b1" alt="Image" /></td>
<td><img src="image-b2" alt="Image" /></td>
<td><img src="image-b3" alt="Image" /></td>
<td><img src="image-b4" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>Standard #2 (N2700000)</td>
<td></td>
<td>10 sec</td>
<td>6.00 sec</td>
<td>21 sec</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.3: Optical images of particles of polybutene standards (a) Standard #1 (N450000), and (b) Standard #2 (N2700000), being poked at 0 % RH recorded during typical poke-and-flow experiments. Images a1 and b1 correspond to particles prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, $\tau_{\text{exp,flow}}$, the point at which the equivalent area diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Images a4 and b4 correspond to the final frame recorded of each particle, at which point each particle has re-attained its original spherical cap geometry. Scale bar: 20 $\mu$m. Originally published in Grayson et al. (2015a).
4.3. Results and discussion

standard #1, and 7.86 (σ = 1.65) seconds for the higher viscosity standard #2.

As for the sucrose-water experiments, $\tau_{exp,flow}$ values from individual particles were converted into viscosities using simulations. To determine upper and lower limits for the viscosities of the standards, the upper and lower limits of the viscosities determined from the individual particles were used. Using this approach, and the parameters listed in Table 4.2 the simulated lower and upper limits of viscosity for the particles poked were $2.0 \times 10^2$ and $1.2 \times 10^4$ Pa s for standard #1 (N450000), and $3.1 \times 10^2$ and $2.4 \times 10^4$ Pa s for standard #2 (N2700000). These values are in good agreement with those reported by the manufacturer, Cannon Instrument Company (Figure 4.4).

![Figure 4.4: Viscosity as a function of temperature for experiments with the polybutene standards. Results from standard #1 (N450000) are in black whilst results from Standard #2 (N2700000) are in red. Symbols represent values measured by Cannon Instrument Company using a manual capillary viscometer. Bars represent viscosities determined herein. For the bar that represents each standard the bottom of the bar represents the lowest lower limit of viscosity of all the particles examined, whilst the top of the bar represents the highest upper limit of viscosity of all of the particles examined. Originally published in Grayson et al. (2015a).](image-url)
4.4 Summary

The poke-and-flow technique combined with simulations of fluid flow provides the advantage of being able to measure viscosities of samples that are both highly viscous and available only in small sample volumes. The combination of these characteristics provides a challenge that is beyond the reach of current commercially available viscometers. In Chapter 3, only a preliminary validation of the poke-and-flow technique combined with simulations of fluid flow was carried out for viscosities up to $10^4$ Pa s, due to the lack of suitable standards for validation at the time of publication. The current manuscript expands on the initial validation experiments in Chapter 3.

First, the approach was used to determine the viscosity of sucrose-water particles over a wider range of relative humidities than previously done in Chapter 3. The lower and upper limits of viscosity at $\approx 59\%$ RH were $1.0 \times 10^1$ Pa s and $1.6 \times 10^4$ Pa s, whilst at $37\%$ RH the corresponding values were $7.2 \times 10^4$ and $4.7 \times 10^6$ Pa s, respectively. The results are in good agreement with Quintas et al. (2006) who measured a viscosity of $10^3$ Pa s at $54\%$ RH using a rotational controlled stress rheometer, and Power et al. (2013) who recently reported that mean measured viscosities of $\approx 5 \times 10^2$ Pa s to $\approx 3 \times 10^6$ Pa s between $60\%$ RH and $37\%$ RH using holographic optical tweezers.

Second, the approach was used to determine the viscosity of two polybutene standards. The simulated lower and upper limits of viscosity for standard #1 was $2.0 \times 10^2$ and $1.6 \times 10^4$ Pa s and for standard #2 $1.6 \times 10^2$ and $2.6 \times 10^4$ Pa s. These values are in good agreement with value reported by Cannon Instrument Company (See Fig. 4.4).

The results for both the sucrose-water particles and the polybutene standards shows the poke-and-flow technique combined with simulations of fluid flow is capable of providing both lower and upper limits of viscosity that are consistent with literature or measured values when the viscosity is in the range of $\approx 5 \times 10^2$ - $\approx 3 \times 10^6$ Pa s. This covers an important part of the range of viscosities of secondary organic material generated in environmental chambers. For example, this range of viscosities have been measured.
at atmospherically relevant RHs for both the water-soluble fraction of the SOM produced via the ozonolysis of α-pinene (Chapter 3), as well as the total SOM produced via the oxidation of isoprene (Song et al., 2015). In addition, this technique has several advantages including being low in cost and the experimental setup affording compatibility with cascade impactors for particle collection.

Whilst the poke-and-flow technique combined with simulations of fluid flow gives good agreement with measured values the upper limit of viscosity for a given particle is typically a factor of 16-140 larger than the corresponding lower limit of viscosity. Thus, the limits of viscosity determined using this approach are wide. The largest source of uncertainty in the approach is the values of surface tension and slip length used in the simulations. Constraining these values would lead to a reduction in the uncertainty of the measurements.
Chapter 5

Effect of varying experimental conditions on the viscosity of α-pinene derived secondary organic material

5.1 Introduction

In Chapter 3 the viscosity of the water-soluble component of SOM produced from the ozonolysis of α-pinene in an environmental chamber was determined. The current manuscript is an extension of the work in Chapter 3. Similar to Chapter 3 the viscosity of SOM particles derived via the ozonolysis of α-pinene is studied; however, in contrast, the current study focuses on particles consisting of the whole SOM, meaning both the water-soluble fraction and water-insoluble fraction.

In the first set of experiments, the effect of relative humidity (RH) on the viscosity of the whole SOM was investigated. SOM was generated via the ozonolysis of α-pinene. Reported here are viscosity measurements as a function of RH between <0.5 % and 50 % RH, using SOM with production mass concentrations of 520 and 121 µg m⁻³. The results add to the few existing measurements of the effect of RH on the viscosity of SOM produced via the ozonolysis of α-pinene (Bateman et al., 2015; Kidd et al., 2014; Zhang et al., 2015 and Chapter 3). Understanding the effect of RH on the viscosity
of SOM is important as RH in the boundary layer regularly varies between roughly 20 % and 100 % RH with varied time and location in the planetary boundary layer (Hamed et al., 2011).

In the second set of experiments, the effect on viscosity of the production mass concentration of SOM particles (in units of micrograms of SOM per m$^3$ of gas) used when generating SOM was investigated. Experiments have shown that the composition of SOM particles can change with production mass concentration (Shilling et al., 2009), possibly affecting the viscosity of the SOM particles. The production mass concentrations of the SOM in the current study ranged from 121 to 14,000 µg m$^{-3}$.

5.2 Experimental

SOM particles were produced either in a flow tube (particle mass concentrations of 520 to 14,000 µg m$^{-3}$) or a chamber (particle mass concentrations of 121 and 230 µg m$^{-3}$) at <5 % RH and collected on hydrophobic substrates with an impactor (see Sections 5.2.1 and 5.2.2, and Fig. 3.1). The poke-and-flow technique in conjunction with simulations of fluid flow was used to determine the viscosity of the SOM (see Sections 5.2.3 and 5.2.4).

5.2.1 Production and collection of SOM generated at production mass concentrations from 520 to 14,000 µg m$^{-3}$

For SOM generated at production mass concentrations from 520 to 14,000 µg m$^{-3}$, a previously described flow tube was used (Shrestha et al., 2013) to generate the SOM. Alpha-pinene (Sigma-Aldrich, >99.5 % purity, 97 % enantiomeric excess) and 2-butanol (Sigma-Aldrich, >99.5 % purity; used as an OH scavenger) were introduced into the flow tube at an α-pinene:2-butanol ratio of 1:49, using a dry air flow rate of 0.50 sLpm. Ozone was produced prior to the inlet of the flow tube by passing dry air through an ozone generator (Jetlight, Model 600) at a rate of 3.0 sLpm, resulting in an ozone concentration of 12 ppm at the inlet of the flow tube, as measured by
5.2. Experimental

an ozone sensor (Ecosensors, UV-100). Residence time in the flow tube was 38 ± 1 s. The concentration of the \( \alpha \)-pinene entering the flow tube was varied to produce samples at a total of five different particle mass concentrations (as measured using an SMPS; TSI, model 3934), with the ozone concentration being kept in constant excess. Table 5.1 shows the mass concentrations and collection times used in the flow tube experiments, as well as the mean geometric size of the particles produced in the flow (Sample names Flow tube #1 - Flow tube #5).

After exiting the flow tube the 2 Lpm of dry flow was diluted with an 8 Lpm flow of humidified air, giving a total airflow of 10 Lpm with a humidity of 68 ± 2 % RH, as measured using an RH meter (Rotronic, HC2-S). The airflow then passed through a single stage impactor (MSP Corp.), within which a hydrophobic glass substrate was mounted. Over the course of an experiment sub-micron sized SOM particles impacted on a hydrophobic glass substrate, with the humidified gas serving to reduce the fraction of particles that bounced in the impactor. Over time the particles coagulated to form super-micron sized particles. The production mass concentration, mode diameter, geometric standard deviation, and collection times are detailed in Table 5.1. After collection, the samples were stored at 253 K until use. All samples were used within 4 weeks of production. To determine the impact of storing samples at 253 K, the viscosity of one sample (produced using a mass concentration of 6,000 µg m\(^{-3}\)) was measured first after four days of storage and again after 24 further days of storage. The measured lower and upper limits of viscosity differed by <20 % (which is within experimental uncertainty) when measured at both 30 % and <0.5 % RH.

5.2.2 Production and collection of SOM generated at production mass concentrations of 121 and 230 µg m\(^{-3}\)

For production mass concentrations <500 µg m\(^{-3}\), the time required to collect enough material for the poke-and-flow experiments was >12 hours using the flow tube setup described above. As a result, to collect SOM using
Table 5.1: Conditions used for generating and collecting samples of SOM generated via the ozonolysis of α-pinene. The whole SOM (both water soluble and water insoluble component of the SOM) was collected. Originally published in Grayson et al. (2015b).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Samples studied</th>
<th>Production mass concentration ($\mu g m^{-3}$)</th>
<th>Mode diameter (nm)</th>
<th>Geometric standard deviation</th>
<th>Collection time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow tube sample #1</td>
<td>3</td>
<td>$(1.4 \pm 0.1) \times 10^4$</td>
<td>265 ± 7</td>
<td>1.43</td>
<td>20</td>
</tr>
<tr>
<td>Flow tube sample #2</td>
<td>3</td>
<td>$(5.9 \pm 0.7) \times 10^3$</td>
<td>194 ± 5</td>
<td>1.47</td>
<td>90</td>
</tr>
<tr>
<td>Flow tube sample #3</td>
<td>3</td>
<td>$(3.4 \pm 0.1) \times 10^3$</td>
<td>163 ± 2</td>
<td>1.46</td>
<td>150</td>
</tr>
<tr>
<td>Flow tube sample #4</td>
<td>3</td>
<td>$(1.2 \pm 0.2) \times 10^3$</td>
<td>121 ± 8</td>
<td>1.46</td>
<td>450</td>
</tr>
<tr>
<td>Flow tube sample #5</td>
<td>3</td>
<td>$(5.2 \pm 0.2) \times 10^2$</td>
<td>132 ± 2</td>
<td>1.52</td>
<td>800</td>
</tr>
<tr>
<td>Chamber sample #1</td>
<td>2</td>
<td>$(2.3 \pm 0.1) \times 10^2$</td>
<td>181 ± 12</td>
<td>1.52</td>
<td>95</td>
</tr>
<tr>
<td>Chamber sample #2</td>
<td>2</td>
<td>$(1.2 \pm 0.1) \times 10^2$</td>
<td>169 ± 12</td>
<td>1.52</td>
<td>180</td>
</tr>
</tbody>
</table>
production mass concentrations less than 500 µg m\(^{-3}\) the Leipzig Aerosol Chamber (LEAK), a cylindrical 19 m\(^3\) Teflon bag (Iinuma et al., 2009), was used. The LEAK chamber could be sampled at higher flow rates than the flow tube (16 Lpm as opposed to 2 Lpm), reducing the required collection time.

First, ozone was introduced into LEAK, which was operating under dry conditions (<5 % RH). The ozone concentration was held between 64-72 ppb (ozone monitor; 49c Ozone Analyzer, Thermo Scientific, USA). Afterwards \(\alpha\)-pinene (Sigma-Aldrich, >99.5 % purity, 97 % enantiomeric excess) was injected into LEAK, and the formation and growth of SOM particles within LEAK was monitored using an SMPS (TROPOS-type). No OH scavenger was used during experiments. After 80 minutes of reaction, the submicron sized particles were collected by pumping air from the chamber at a flow rate of 16 Lpm. At the exit of LEAK the air passed through a humidifier unit (FC300-1660-15-LP-01, Perma Pure LLC, NJ, USA), and upon exiting the humidifier unit the air was determined to be at 91 \(\pm\) 2.5 % RH, as measured using a handheld RH meter (RH85, Omega, USA). The airflow then passed through a single stage impactor, as described in Section 5.2.1. Particles collected and coagulated on a hydrophobic slide located with the impactor. After collection, the samples were stored at 253 K until use. All samples were used within 10 weeks of production. The production mass concentration, mode diameter, and collection times are detailed in Table 5.1 (Samples named Chamber sample #1 and Chamber sample #2).

5.2.3 Poke-and-flow technique

The viscosities of the SOM collected on the hydrophobic slides were determined with the poke-and-flow technique combined with simulations of fluid flow, which has been described in Section 2.2. As experiments were performed between <0.5 % and 50 % RH, the dewpoint monitor was calibrated using the deliquescence dewpoint of potassium carbonate, and found to give readings within 0.1 K of the expected value at 43 % RH and 293 K.

During poke-and-flow experiments the SOM was exposed to a dry or hu-
mid gas flow over a period of 3-15 h. During this time semivolatile components of the SOM may undergo evaporation. If the semivolatile components were behaving as plasticizers within the SOM, the viscosity of the SOM may change. To determine whether this process occurred here and, if so, whether it had a significant effect on the results, the volumes of particles consisting of whole SOM and produced with a mass concentration of 6,000 µg m\(^{-3}\) were determined for up to 45 h while exposed to a dry (<0.5 % RH) flow of nitrogen gas (see Section B.1 for further experimental details). Within experimental uncertainty the volume of the particles remained unchanged (Figure B.1).

In addition, the viscosity of particles consisting of whole SOM and produced with a mass concentration of 6,000 µg m\(^{-3}\) were determined after both 1 h and 45 h of exposure to a dry (<0.5 % RH) flow of nitrogen gas. The mean lower and upper limits of viscosity were determined to be roughly double after 45 h of exposure compared to their values after 1 h of exposure (Table B.1). This result suggests it is possible that a small volume of semivolatile material may have evaporated during the exposure to dry nitrogen, below the detection limit of the measurements of particle volume, but enough to result in a small increase in viscosity. Alternatively, oligomerisation or polymerisation could occur within the samples at room temperature, with the products of this process being of higher viscosity than their precursors. This doubling in viscosity should be considered as a conservative upper limit to the effect of evaporation in the rest of the experiments reported here, which were carried out on a time scale of 3-15 h.

Two or three samples were analyzed per set of conditions, and the results of the three samples combined to give the values reported here. In total, this study contains the results from experiments on a total of 436 particles.

5.2.4 Simulations of fluid flow

Simulations of fluid flow were performed as detailed in Section 2.2.3. Shown in Table 5.2 are the estimates of the physical properties (i.e., particle-substrate slip length, surface tension, particle-substrate contact angle, and
Table 5.2: Physical parameters used when simulating particles that exhibited flow with COMSOL. Originally published in Grayson et al. (2015b).

<table>
<thead>
<tr>
<th>Density / kg m(^{-3}) (^{a})</th>
<th>Slip length / m (^{b})</th>
<th>Surface tension / mN m(^{-1}) (^{c})</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value used to determine lower limit of viscosity</td>
<td>1,300</td>
<td>5 \times 10^{-9}</td>
<td>40</td>
</tr>
<tr>
<td>Value used to determine upper limit of viscosity</td>
<td>1,300</td>
<td>1 \times 10^{-5}</td>
<td>75</td>
</tr>
</tbody>
</table>

\(^{a}\) Density was varied from 1,000-1,400 kg m\(^{-3}\) based on the work of Chen and Hopke (2009) and determined to have no effect upon viscosities determined via simulation. As such a median value of 1300 kg m\(^{-3}\) was used.

\(^{b}\) For references and rationale see Chapter 4.

\(^{c}\) Range of surface tension values based on work on Tuckermann and Cammenga (2004).

\(^{d}\) The lower value from Table B.2 is used for particles of geometry \((R_{0} - r_{0}) / r_{0} < 2\), and the upper value from Table B.2 is used for particles of geometry \((R_{0} - r_{0}) / r_{0} > 2\).

\(^{e}\) The upper value from Table B.2 is used for particles of geometry \((R_{0} - r_{0}) / r_{0} < 2\), and the lower value from Table B.2 is used for particles of geometry \((R_{0} - r_{0}) / r_{0} > 2\).
5.3. Results and discussion

density) of SOM used during simulations. In addition images acquired during each experiment were used to determine the dimensions of each particle and its value of $\tau_{exp,flow}$ as inputs for simulations. Contact angles were determined using 3-D images of the super-micron particles suspended on hydrophobic surfaces using a confocal fluorescence microscope (Leica SP5 II) with a 20x objective, a schematic of which is shown in Figure B.2(a). An excitation wavelength of 458 nm was used, causing moieties within the SOM to fluoresce, and a range of emission wavelengths, from 500-700 nm, were used to produce the image. A z-stack series of images with a step size of 0.5 $\mu$m, was acquired for each particle. Contact angles were subsequently measured from the 2-D cross-sections in the y-z plane using the LB-ADSA plugin for ImageJ (Fig. B.2(b)). Contact angles were determined by measuring multiple particles from each sample and are reported in Table B.2. The values used during simulations of a given particle are those determined for particles of the corresponding sample.

The main source of uncertainty in the viscosity of the SOM arises from uncertainty in the physical properties of SOM that are used in simulations, including the slip length, the particle-substrate contact angle, and the surface tension at the particle-gas interface. The variability in viscosity from particle to particle was only a small component of the overall uncertainty (discussed further in Section B.2).

5.3 Results and discussion

5.3.1 Effect of relative humidity on the viscosity of SOM

The effect of relative humidity on the viscosity of SOM was determined for SOM produced with production mass concentrations of 520 $\mu$g m$^{-3}$ and 121 $\mu$g m$^{-3}$. Shown in Figure 5.1 are images of SOM produced in the flow tube with a production mass concentration of 520 $\mu$g m$^{-3}$ and studied at <0.5 % and 50 % RH. Shown in Fig. 5.1(a) (Panels a1-a3) is SOM being studied at <0.5 % RH. Prior to poking the SOM is in a hemispherical geometry (Fig. 5.1, Panel a1). The act of poking the SOM with the needle led to the
5.3. Results and discussion

Figure 5.1: Optical images recorded during typical poke-and-flow experiments of whole SOM produced at a production mass concentration of 520 µg m\(^{-3}\) being poked at (a) <0.5 %, and (b) 50 %, RH. Images a1 and b1 correspond to SOM prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, \(\tau_{\text{exp,flow}}\), the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: 20 µm. Originally published in Grayson et al. (2015b).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle pre-poking</th>
<th>Particle poked</th>
<th>First frame post-poke</th>
<th>Frame of (\tau_{\text{exp,flow}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) &lt; 0.5 % RH</td>
<td><img src="a1.png" alt="Image" /></td>
<td><img src="a2.png" alt="Image" /></td>
<td><img src="a3.png" alt="Image" /></td>
<td><img src="a4.png" alt="Image" /></td>
</tr>
<tr>
<td>(b) 50 % RH</td>
<td><img src="b1.png" alt="Image" /></td>
<td><img src="b2.png" alt="Image" /></td>
<td><img src="b3.png" alt="Image" /></td>
<td><img src="b4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 5.1: Optical images recorded during typical poke-and-flow experiments of whole SOM produced at a production mass concentration of 520 µg m\(^{-3}\) being poked at (a) <0.5 %, and (b) 50 %, RH. Images a1 and b1 correspond to SOM prior to poking. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3 and b3 correspond to images of the experimental flow time, \(\tau_{\text{exp,flow}}\), the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: 20 µm. Originally published in Grayson et al. (2015b).

formation of a half-torus geometry (Fig. 5.1 Panel a2). Upon removal of the needle the material flowed and the hole began to close, with a \(\tau_{\text{exp,flow}}\) of 1,074 s (Fig. 5.1 Panel a3). Shown in Fig. 5.1(b) (Panels b1-b3) is SOM being studied at 50 % RH. As for the SOM in Fig. 5.1(a), the SOM was hemispherical in geometry prior to being poked (Fig. 5.1 Panel b1), and the act of poking the SOM also lead to the formation of a half-torus geometry (Fig. 5.1 Panel b2). However, in this case the flow rate was clearly faster, and the SOM was determined to have a \(\tau_{\text{exp,flow}}\) of 4.3 s (Fig. 5.1 Panel a3).

Figure 5.2 summarizes the RH dependent studies. For SOM produced at a production mass concentration of 520 µg m\(^{-3}\) the mean \(\tau_{\text{exp,flow}}\) value was a factor of 460 lower at 50 % RH than at <0.5 % RH (Fig. 5.2(a)). By
5.3. Results and discussion

Figure 5.2: Summary of poke-and-flow experiments from <0.5 \% to 50 \% RH performed on samples of whole SOM produced at mass concentrations of 520 µg m\(^{-3}\) (Panels (a) and (c)) and 121 µg m\(^{-3}\) (Panels (b) and (d)). Panels (a) and (b) show box plots of observed \(\tau_{\text{exp,flow}}\) as a function of RH. Panels (c) and (d) show simulated lower (filled symbols) and upper (open symbols) limits of viscosity. Y-error bars represent 95 \% confidence intervals, and x-error bars represent the range of RH at which measurements were made. The shaded regions are included to guide the eye of the reader. The viscosities of common substances at room temperature have been added to (d) to provide points of reference, as per Koop et al., 2011. The image of pitch is part of an image from the pitch drop experiment (image courtesy of Wikimedia Commons, GNU Free Documentation License, University of Queensland, John Mainstone). Originally published in [Grayson et al.] (2015b).
5.3. Results and discussion

Comparison, SOM produced at a production mass concentration of 121 \( \mu g \ m^{-3} \) the mean \( \tau_{exp,flow} \) value was a factor of 3,600 lower at 50 % RH than at <0.5 % RH (Fig. 5.2(b)).

Based on simulations of the poke-and-flow experiments the viscosities of SOM produced at a production mass concentration of 520 \( \mu g \ m^{-3} \) the viscosity was between \( 3 \times 10^5 \) and \( 2 \times 10^7 \) Pa s at <0.5 % RH and between \( 4 \times 10^2 \) and \( 3 \times 10^4 \) Pa s at 50 % RH (Fig. 5.2(c)). The viscosity of SOM produced at a production mass concentration of 121 \( \mu g \ m^{-3} \) was determined to be between \( 2 \times 10^6 \) and \( 6 \times 10^7 \) Pa s at <0.5 % RH and between \( 1.8 \times 10^2 \) and \( 1.4 \times 10^4 \) Pa s at 50 % RH. The results suggest the viscosity of both samples was between that of window putty and tar pitch at <0.5 % RH and that of ketchup and window putty at 50 % RH. The RH-dependent results are consistent with previous work that has shown that the viscosity of SOM can depend strongly on RH (Bateman et al., 2015; Saukko et al., 2012; Song et al., 2015; Zhang et al., 2015; and Chapter 3), with the dependence of the viscosity on RH likely being a combination of water behaving as a plasticizer and the fraction of water present in a particle increasing with RH (Koop et al., 2011).

5.3.2 Effect of production mass concentration used when generating the SOM on the viscosity of SOM

Viscosity of SOM as a function of production mass concentration used to generate SOM was studied at 30 % RH and <0.5 % RH. Figure 5.3 shows examples of SOM generated at production mass concentrations of 14,000, 520, and 121 \( \mu g \ m^{-3} \) being poked at <0.5 % RH. In all cases the SOM exhibited flow, and there is a trend of increasing experimental flow time with decreasing production mass concentration.

A summary of the \( \tau_{exp,flow} \) and viscosity values as a function of production mass concentration at <0.5 % RH is shown in Figure 5.4. Considering all the data together, as the production mass concentration decreases from 14,000 \( \mu g \ m^{-3} \) to 121 \( \mu g \ m^{-3} \), the mean \( \tau_{exp,flow} \) values increase by a factor of 45 (Fig. 5.4(a)). Based on simulations of the poke-and-flow experiments
5.3. Results and discussion

Table 5.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle pre-poking</th>
<th>Particle poked</th>
<th>First frame post-poke</th>
<th>Frame of $\tau_{\text{exp,flow}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Whole SOM produced with a production mass concentration of 14,000 µg m$^{-3}$</td>
<td><img src="a1" alt="Image" /></td>
<td><img src="a2" alt="Image" /></td>
<td><img src="a3" alt="Image" /></td>
<td><img src="a4" alt="Image" /></td>
</tr>
<tr>
<td>(b) Whole SOM produced with a production mass concentration of 520 µg m$^{-3}$</td>
<td><img src="b1" alt="Image" /></td>
<td><img src="b2" alt="Image" /></td>
<td><img src="b3" alt="Image" /></td>
<td><img src="b4" alt="Image" /></td>
</tr>
<tr>
<td>(c) Whole SOM produced with a production mass concentration of 121 µg m$^{-3}$</td>
<td><img src="c1" alt="Image" /></td>
<td><img src="c2" alt="Image" /></td>
<td><img src="c3" alt="Image" /></td>
<td><img src="c4" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 5.3: Optical images recorded during typical poke-and-flow experiments of particles of the whole SOM produced at production mass concentrations of (a) 14,000 µg m$^{-3}$, (b) 520 µg m$^{-3}$, and (c) 121 µg m$^{-3}$ being poked at <0.5 % RH. Images a1, b1 and c1 correspond to SOM prior to poking. Images a2, b2 and c2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). Images a3, b3 and c3 correspond to images of the experimental flow time, $\tau_{\text{exp,flow}}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1, b1 and c1: 20 µm. Originally published in Grayson et al. (2015b).

The viscosities of the SOM samples are between $4 \times 10^4$ and $1.5 \times 10^6$ Pa s for SOM produced at a production mass concentration of 14,000 µg m$^{-3}$ and between $6 \times 10^5$ and $5 \times 10^7$ Pa s for SOM produced at a production mass concentration of 121 µg m$^{-3}$ (Fig. 5.4(b)).

The inverse relationship between viscosity and production mass concentration is consistent with results of Shilling et al. (2009), who observed an inverse relationship between production mass concentration and the oxida-
5.3. Results and discussion

Figure 5.4: Summary of poke-and-flow experiments performed on samples of whole SOM at $<0.5$ % RH. Black symbols represent results from particles produced in a flow tube, whilst red symbols represent results from particles produced in a chamber. Panel (a) shows box plots of observed $\tau_{\text{exp,flow}}$ times at different production mass concentrations for particles poked $<0.5$ % RH. Boxes represent the 25, 50, and 75 percentiles, open circles represent median values, and whiskers represent the 5 and 95 percentiles. Panel (b) shows the simulated lower (filled squares) and upper (open squares) limit of viscosity for particles at each production mass concentration poked at $<0.5$ %. Symbols represent mean values. The y error bars represent 95 % confidence intervals. The shaded regions are included to guide the eye of the reader. Also included in (b) are literature viscosities for SOM produced via the ozonolysis of $\alpha$-pinene (Renbaum-Wolff et al., 2013a; Zhang et al., 2015). Originally published in Grayson et al. (2015b).
5.3. Results and discussion

tion level of the resulting SOM. As previously mentioned, higher oxidation levels are linked to higher glass transition temperatures and an increased likelihood that a particle rebounds from an impactor surface.

The results for SOM produced in the flow tube (production mass concentrations of 14,000 to 520 µg m$^{-3}$) and produced in the chamber (production mass concentrations of 230 and 121 µg m$^{-3}$) each exhibit the same trend: $\tau_{exp, flow}$ increases as production mass concentration decreases. However, the data are not in perfectly aligned. If the data from the flow tube are extrapolated to lower particle mass concentrations, slightly higher $\tau_{exp, flow}$ values are predicted compared to observations using samples from the chamber (roughly a factor of 2-3 higher). This difference could be due to some differences in experimental conditions. For example, the flow tube studies were carried out in the presence of an OH scavenger, 2-butanol, whereas no OH scavenger was used in the chamber studies. The presence of 2-butanol decreases the SOM yield from a given amount of precursor (Henry and Donahue, 2011; Jonsson et al., 2008). The reaction of OH with both $\alpha$-pinene, as well as first generation products of $\alpha$-pinene ozonolysis, can alter the chemical composition of the SOM produced (Vereecken and Peeters, 2012). Another difference in experimental conditions between the flow tube and the chamber studies was the RH at which the SOM was collected - 68 ± 2 % in flow tube studies and 91 ± 2.5 % in chamber studies. The increased humidity while SOM was being collected during the chamber studies may have resulted in a larger fraction of the more volatile components being present in the particle phase as material was collected, possibly explaining the lower than expected viscosity of the samples collected during chamber studies.

Also included in Fig. 5.4 are previous measurements of the viscosity of $\alpha$-pinene derived SOM measured under dry conditions. Zhang et al. (2015) studied material produced in the same flow tube as the material used here using a production mass concentration of $\approx$70 µg m$^{-3}$, and in Chapter 3 the viscosity of the water-soluble component of SOM produced at a production mass concentration of $\approx$50 µg m$^{-3}$ in an environmental chamber was determined. The results of Zhang et al. (2015) are consistent with the results obtained here. The results from Chapter 3 are not inconsistent with the
current results due to the observed inverse relationship between viscosity and production mass concentration.

Other researchers have measured diffusion rates (Abramson et al., 2013; Cappa and Wilson, 2011; Perraud et al., 2012), or mixing times under dry conditions (Robinson et al., 2013; Saleh et al., 2013) within SOM produced via the ozonolysis of α-pinene. In Section B.3 these measurements have been converted to viscosities using the Stokes-Einstein relationship. It should be kept in mind that the Stokes-Einstein relationship may break down for small molecules (Bones et al., 2012; Price et al., 2015) and for large molecules when the viscosity is high and near the glass transition temperature (Champion et al., 1997; Corti et al., 2008). Further discussion on the conversion of reported diffusion coefficients or mixing times to viscosities for each of these studies is given in Section B.3. Figure B.3 shows that most of these previous studies (Cappa and Wilson, 2011; Perraud et al., 2012; Saleh et al., 2013) are not inconsistent with those presented here. Some of the results are outside of the range reported here (Abramson et al., 2013; Robinson et al., 2013) suggesting factors beyond just a simple relationship between viscosity and production mass concentration are required to explain previous measurements. Differences may be due to invalid assumptions made when using the Stokes-Einstein relationship or other factors.

The effect of production mass concentration on viscosity was also studied at 30% RH (Figure 5.5). At this RH, the effect of particle mass concentration was not as dramatic. For the samples produced in a flow tube, as the production mass concentration decreases from 14,000 µg m\(^{-3}\) to 520 µg m\(^{-3}\), the mean \(\tau_{exp,flow}\) values increase by a factor of 5 (Fig. 5.5(a)). For the samples produced in the chamber, as the production mass concentration decreased from 230 µg m\(^{-3}\) and 121 µg m\(^{-3}\), the mean \(\tau_{exp,flow}\) values increase by a factor of 1.5. Similar to the experiments at <0.5% RH, if the results from the flow tube are extrapolated to lower particle mass concentrations, they predict larger \(\tau_{exp,flow}\) values than observed from the chamber studies. As mentioned above, these differences may be due to small differences in experimental conditions between the flow tube and chamber.

Based on simulations the viscosity of the SOM at 30% RH is between
5.3. Results and discussion

Figure 5.5: Summary of poke-and-flow experiments performed on particles of whole SOM at 30 % RH. Black symbols represent results from particles produced in a flow tube, whilst red symbols represent results from particles produced in a chamber. Panel (a) shows box plots of observed $\tau_{\text{exp,flow}}$ times as a function of SOM mass concentrations for particles studied using the poke-and-flow technique at 30 % RH. Panel (b) shows the simulated lower (filled squares) and upper (open squares) limit of viscosity for particles at each SOM mass concentration studied using the poke-and-flow technique at 30 % RH. Symbols represent mean values, whilst the y error bars represent 95 % confidence intervals. The shaded region is included to guide the eye of the reader. Also included in (b) are literature viscosities from Renbaum-Wolff et al. (2013a) and Zhang et al. (2015), for SOM produced via the ozonolysis of $\alpha$-pinene and studied at 30 % RH. Originally published in Grayson et al. (2015b).
5.3. Results and discussion

1.0 x 10³ and 9 x 10¹ Pa s at a production mass concentration of 14,000 µg m⁻³ and between 1.2 x 10³ and 1.2 x 10⁵ Pa s at a production mass concentration of 121 µg m⁻³ (Fig. 5.5(b)). The smaller dependence of viscosity on production mass concentration at 30 % RH compared to <0.5 % RH can be explained by the dependence of the viscosity on the water content of the SOM. Under dry conditions the measured viscosity is due only to the viscosity of the SOM. However, as RH is increased the SOM uptakes water, and the viscosity of the different SOM samples become increasingly dependent on the viscosity of water and converge, finally approaching the viscosity of water, ≈10⁻³ Pa s, at 100 % RH.

Also included in Fig. 5.5(b) are viscosities of α-pinene-derived SOM measured at 30 % RH by Zhang et al. (2015) and reported in Chapter 3. As mentioned above Zhang et al. (2015) studied material produced in the same flow tube as the material used here, and in Chapter 3 the water-soluble component of SOM produced in an environmental chamber was studied. One possible explanation of the results shown in Fig. 5.5(b) is a very strong dependence of viscosity on production mass concentration in the range of 50 and 121 µg m⁻³. To determine if a strong dependence of viscosity in the range of 50 and 121 µg m⁻³ shown in Fig. 5.5(b) exists or due to other factors, additional studies are needed. More importantly, additional studies are needed to determine if the viscosity of the water-soluble component of SOM is the same as the viscosity of the whole SOM (water-soluble and water insoluble components) produced at production mass concentrations around 50 µg m⁻³. In addition, further comparison studies using the technique introduced by Zhang et al. (2015) and the poke-and-flow technique used here would be beneficial. Finally, the studies here are carried out at production mass concentrations greater than those found under ambient conditions (Hallquist et al. 2009, Slowik et al. 2010), and studies carried out using material produced using ambient concentrations would provide further useful information.
5.3. Results and discussion

5.3.3 Effect of the water-insoluble component on the viscosity of SOM

To better understand the difference between the viscosity of water-soluble SOM and SOM containing both the water-soluble and water-insoluble components, additional measurements were carried out using just the water-soluble component of SOM generated by the ozonolysis of α-pinene at a production mass concentration of 14,000 µg m⁻³. Particles were generated using the flow tube as discussed in Section 5.2.1, and particles from the outlet of the flow tube were collected on a Teflon filter. After collection, SOM was extracted from the Teflon filter by placing it in a clean glass jar and immersing the filter in 10 mL of Millipore (18.2 MΩ cm) water. The jar was shaken for 1.5 h, with the filter being flipped over half way through, after which the filter was removed from the jar, resulting in a solution of the water-soluble component of the SOM. The solution was then nebulised and sprayed onto a hydrophobic glass substrate, producing super-micron sized particles. The particles were then studied using the poke-and-flow technique and their viscosities determined using simulations of fluid flow as described in Section 2.2.

Shown in Figure 5.6 are images of a particle comprised of the water-soluble fraction of SOM (Fig. 5.6(a)) and a particle comprised of the whole SOM, both the water-soluble and water-insoluble fractions (Fig. 5.6(b)). Both were produced at a production mass concentration of 14,000 µg m⁻³ and studied at <0.5 % RH. Although the production of both the water-soluble SOM and the whole SOM took place using equivalent flow tube conditions, the images of the SOM during the poke-and-flow experiments were clearly different, with the water-soluble SOM cracking and showing no observable flow over the course of 14 hours (Fig. 5.6(a), Panels a2 & a3), whilst the whole SOM exhibited flow, with a $\tau_{exp,flow}$ of 1074 s (Fig. 5.6(b), Panels b2 & b3).
5.3. Results and discussion

Figure 5.6: Optical images recorded during poke-and-flow experiments using particles consisting of (a) the water-soluble component of the SOM and (b) the whole SOM (i.e., both the water-soluble and the water-insoluble components). In both experiments the SOM was produced using a mass concentration of 14,000 µg m\(^{-3}\) and was poked at <0.5 % RH. Images a1 and b1 correspond to the SOM prior to being poked. The brightness in Image a1 is due to reflection of the source light by the needle positioned just above the particle. Images a2 and b2 correspond to the first frame post-poke (i.e. the first frame after the needle has been removed). The particle comprised of the water-soluble component of SOM exhibited cracking behaviour and, as shown in Image a3, no change in the size or shape of the cracks can be observed 14 hours after the particle has been poked. The particle comprised of whole SOM exhibited flow, and Image b3 corresponds to an image of the particle at its experimental flow time, \(\tau_{exp,flow}\), the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. Scale bar in Images a1 and b1: 20 µm. Originally published in Grayson et al. (2015b).

Table 5.3 summarizes experimental results at <0.5 % RH for both the water-soluble SOM and the whole SOM produced at a production mass concentration of 14,000 µg m\(^{-3}\). The \(\tau_{exp,flow}\) and viscosity of the water-soluble
component were both at least a factor of 300 greater than the $\tau_{\text{exp,flow}}$ and viscosity of the whole SOM.

The difference in viscosity between the whole SOM and the water-soluble SOM may arise from differences in the extent of oxidation of the SOM. Water-soluble SOM is assumed to be composed of the more oxidized components of the whole SOM and literature suggests that higher oxidation is related to a warmer glass transition temperature (Berkemeier et al., 2014; Dette et al., 2014; Koop et al., 2011), implying that viscosity increases with oxidation level.

The results in Table 5.3 correspond to a high production mass concentration. At lower SOM particle concentrations such as concentrations used in Chapter 3, the difference between water-soluble SOM and whole SOM is likely smaller, since as the production mass concentration decreases, the extent of oxidation in the particle phase is expected to increase and hence the amount of water insoluble material in the particle phase should decrease. In addition, literature suggests that the SOM formed from the ozonolysis of $\alpha$-pinene is largely composed of water-soluble organic compounds (Hall and Johnston, 2011) produced using a production mass concentration of $<500$

<table>
<thead>
<tr>
<th>Water-soluble SOM</th>
<th>Viscosity (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt;4.3 \times 10^4$</td>
<td>$&gt;4.8 \times 10^8$</td>
</tr>
</tbody>
</table>

| Whole SOM | 90 (57, 144) | 3.8 x 10$^4$ - 1.5 x 10$^9$ |

Table 5.3: Summary of $\tau_{\text{exp,flow}}$ times and viscosities of whole SOM and water-soluble SOM produced in the flow tube at a production mass concentration of 14,000 $\mu$g m$^{-3}$ and studied at $<0.5$ % RH. Originally published in Grayson et al. (2015b).

For the whole SOM, $\tau_{\text{exp,flow}}$ values represent experimental values in the form ”mean (5th percentile, 95th percentile)”. For the water-soluble SOM, the lower limit to $\tau_{\text{exp,flow}}$ represents the shortest experimental time that the particles were observed.

For whole SOM, the lower limit of viscosity represents the lower 95 % confidence interval of the lower limit of viscosity, whilst the upper limit of viscosity represents the upper 95 % confidence interval of the upper limit of viscosity. For water-soluble SOM the lower limit of viscosity was calculated for the particles observed over the shortest experimental time.
5.4 Summary

The effect of various experimental parameters on the viscosity of SOM derived via the ozonolysis of α-pinene have been studied. First, the effect of relative humidity on the viscosity of the whole SOM was studied. For each sample studied the \( \tau_{\text{exp,flow}} \) values were larger and the simulated viscosities higher as the RH was decreased from 50 % to <0.5 % (Figs. 5.1 and 5.2). Specifically, for SOM produced at a production mass concentration of 121 \( \mu \text{g m}^{-3} \), the \( \tau_{\text{exp,flow}} \) increased by a factor of 3,600 as the relative humidity (RH) decreased from 50 % to <0.5 % RH. Based on simulations, the viscosities of the particles were between \( 3 \times 10^2 \) and \( 9 \times 10^3 \) Pa s at 50 % RH and between \( 6 \times 10^5 \) and \( 5 \times 10^7 \) Pa s at <0.5 % RH.

Second, the effect on viscosity of the production mass concentration used during the production of SOM was investigated at 30 % and <0.5 % RH. The measurements provide evidence of an inverse relationship between production mass concentration in the reaction vessel and viscosity of the SOM material (Figs. 5.3 and 5.4). The effect was most prominent at <0.5 % RH where \( \tau_{\text{exp,flow}} \) increased by a factor of 45 as the particle mass concentration decreased from 14,000 \( \mu \text{g m}^{-3} \) to 121 \( \mu \text{g m}^{-3} \). From simulations of the poke-and-flow experiments, the viscosity of the SOM produced at a production mass concentration of 14,000 \( \mu \text{g m}^{-3} \) are between \( 4 \times 10^4 \) and \( 1.5 \times 10^6 \) Pa s and the viscosity of SOM produced at a production mass concentration of
5.4. Summary

121 µg m\(^{-3}\) are between 6 \times 10^5 and 5 \times 10^7 Pa s at <0.5 \% RH (Fig. 5.4).

The \(\tau_{\text{exp,flow}}\) and viscosity of the water-soluble component of SOM was also observed to be at least a factor of 300 greater than the \(\tau_{\text{exp,flow}}\) and viscosity of the whole SOM when using a production mass concentration of 14,000 µg m\(^{-3}\) (Fig. 5.6). This result should be considered as a upper limit to the difference between the viscosity of water-soluble SOM and whole SOM produced at production mass concentrations lower than 14,000 µg m\(^{-3}\).

Overall the results suggest that the RH at which the viscosity was determined and the mass concentration at which the SOM was produced should be considered when laboratory experiments are being compared or when used to infer viscosities of atmospheric particles.
Chapter 6

Viscosity of a tetraol and saccharide-water mixtures

6.1 Introduction

As outlined in Chapter [1], an improved understanding of the viscosity of SOM particles over the range of relative humidities found in the atmosphere is required to improve our ability to predict the atmospheric effects of SOM (Adler et al., 2013; Bodsworth et al., 2010; Koop et al., 2011; Kuwata and Martin, 2012; Riipinen et al., 2011; Shiraiwa et al., 2011a; Zelenyuk et al., 2012).

The numerous oxidation mechanisms in the atmosphere result in SOM having a complex composition, with hundreds or thousands of individual species and a range of chemical structures and functionalities (Hallquist et al., 2009). Only \( \approx 10\% \) of the SOM mass has been identified at the molecular level (Hallquist et al., 2009). Molecules that have been identified include alkane, alkene, alcohol, carboxylic acid, aldehyde, ketone, ester, ether, and acid anhydride functional groups, as well as both aromatic and non-aromatic cyclic molecules (Aschmann and Atkinson, 1998; Chan et al., 2010; Chen et al., 2011b; Christoffersen et al., 1998; Day et al., 2009; Russell et al., 2011; Surratt et al., 2006). A wide range of molar masses have been observed for individual species, with some being of molar mass >1000 g mol\(^{-1}\), although smaller compounds are thought to account for the majority of the SOM mass fraction (Gao et al., 2004; Praplan et al., 2015; Schobesberger et al., 2013). The average elemental oxygen-to-carbon ratio (O:C) of SOM has been determined to range from 0.3-1.1 (Chen et al.,
6.1. Introduction

The high values of O:C can be explained by organic compounds with multiple oxygen containing functional groups (Christoffersen et al., 1998; Hoffmann et al., 1997; Yu et al., 1999). Recent studies have identified the presence of extremely low volatility organic compounds (ELVOCs) in SOM, which can be of O:C ≥1 and may account for a significant fraction of SOM mass (Ehn et al., 2012, 2014; Praplan et al., 2015; Schobesberger et al., 2013).

In the following the viscosities of a tetraol (2-methyl-1,2,3,4-butanetetrol) and three saccharides (glucose, raffinose, and maltohexaose) mixed with water are determined. These systems are used as proxies for highly oxidized components of ambient SOM. The saccharides and the tetraol studied are listed in Table 6.1 as well as their relevant physical properties. Although the viscosity of sucrose has been measured over a wide range of relative humidities (RHs) (e.g. Först et al., 2002; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007), similar studies for glucose, maltohexaose and raffinose have yet to be carried out. Furthermore, we are not aware of previous studies of the viscosity of tetraols.

The saccharides studied have an O:C of 0.86-1.0, which is similar to that of the more highly oxidized components of SOM, and molar mass ranging from 180-990 g mol\(^{-1}\), which covers the range of molar mass of components that account for the majority of the mass of SOM. Saccharides including levoglucosan, glucose, xylose, sucrose, and maltose have been identified in smoke produced during the combustion of wood under both controlled con-

Table 6.1: Properties of saccharide and tetraol compounds studied experimentally.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>O:C</th>
<th>Molar mass / g mol(^{-1})</th>
<th>RH range of viscosity measurements / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>C(<em>6)H(</em>{12})O(_6)</td>
<td>1.00</td>
<td>180</td>
<td>28</td>
</tr>
<tr>
<td>Raffinose</td>
<td>C(<em>{18})H(</em>{32})O(_{16})</td>
<td>0.89</td>
<td>342</td>
<td>40-85</td>
</tr>
<tr>
<td>Maltohexaose</td>
<td>C(<em>{36})H(</em>{62})O(_{31})</td>
<td>0.86</td>
<td>991</td>
<td>50-77</td>
</tr>
<tr>
<td>2-Methyl-1,2,3,4-butanetetrol</td>
<td>C(<em>5)H(</em>{12})O(_4)</td>
<td>0.80</td>
<td>134</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
6.2 Experimental

6.2.1 Determination of viscosity of super-micron sized particles comprised of a tetraol or a saccharide mixed with water

The bead-mobility technique and the poke-and-flow technique combined with simulations of fluid flow have been used to measure the viscosities of particles comprised of 2-methyl-1,2,3,4-butanetetrol or a saccharide (glucose, maltohexaose and raffinose) mixed with water. The bead-mobility technique is described in Section 2.1 and the poke-and-flow technique combined with simulations of fluid flow is described in Section 2.2. The physical properties used when simulating the poke-and-flow experiments are summarised in Tables 6.2 and 6.3.

B-D-Glucose (≥99.5 % purity), raffinose (≥98 % purity), and maltohexaose (≥65 % purity) were obtained from Sigma-Aldrich. 2-methyl-1,2,3,4-tetraol was prepared in diastereomerically pure form starting from pro-
Table 6.2: Physical parameters used to simulate the flow of material during poke-and-flow experiments where a half-torus geometry was formed and the material subsequently observed to flow. R and r represent dimensions of a half-torus, with R representing the radius of the tube of material, and r representing the radius of the hole at the centre of the tube.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Slip length / nm</th>
<th>Surface tension / mN m$^{-1}$</th>
<th>Density / g cm$^{-3}$</th>
<th>Contact angle / degrees $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glucose</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower limit</td>
<td>5 $^b$</td>
<td>72.0 $^c$</td>
<td>1.0 $^d$</td>
<td>66 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73 (if r&gt;2R)</td>
</tr>
<tr>
<td>Upper limit</td>
<td>10,000 $^b$</td>
<td>95.1 $^e$</td>
<td>1.7 $^d$</td>
<td>73 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>66 (if r&gt;2R)</td>
</tr>
<tr>
<td><strong>Raffinose</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower limit</td>
<td>5 $^b$</td>
<td>57.2 $^f$</td>
<td>1.0 $^d$</td>
<td>58 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67 (if r&gt;2R)</td>
</tr>
<tr>
<td>Upper limit</td>
<td>10,000 $^b$</td>
<td>125.8 $^e$</td>
<td>1.9 $^d$</td>
<td>67 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>58 (if r&gt;2R)</td>
</tr>
<tr>
<td><strong>Maltohexaose</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower limit</td>
<td>5 $^b$</td>
<td>57.2 $^f$</td>
<td>1.0 $^d$</td>
<td>63 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>73 (if r&gt;2R)</td>
</tr>
<tr>
<td>Upper limit</td>
<td>10,000 $^b$</td>
<td>138.2 $^e$</td>
<td>2.0 $^d$</td>
<td>73 (if r&lt;2R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>63 (if r&gt;2R)</td>
</tr>
</tbody>
</table>

$^a$ Contact angles determined using photographic images of particles on a hydrophobic substrate.

$^b$ This range is based on the literature values included in Table 2.1.

$^c$ Lee and Hildemann (2013).

$^d$ The density of water.

$^e$ As predicted by ACD/Labs.

$^f$ Lower limit of the surface tension of sucrose (Power et al., 2013, and Chapter 4).
Table 6.3: Physical parameters used to simulate a lower limit of viscosity for poke-and-flow experiments where particles cracked when impacted by the needle, and no observable flow of material was observed over the course of the experiment.

<table>
<thead>
<tr>
<th>Slip length</th>
<th>Surface tension</th>
<th>Density</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>/ nm</td>
<td>/ mN m$^{-1}$</td>
<td>/ g cm$^{-3}$</td>
<td>/ $^\circ$</td>
</tr>
<tr>
<td>0.01 x l $^a$</td>
<td>57.2</td>
<td>1.7</td>
<td>90</td>
</tr>
</tbody>
</table>

$l$ is the grid spacing of the mesh, which ranged from 1-1.7 µm.

Protected cis-2-methylbut-2-ene-1,4-diol (Fontana et al., 2000; Surratt et al., 2010). Protection of the alcohol moieties of cis-2-methylbut-2-ene-1,4-diol with benzyl groups was followed by dihydroxylation using osmium tetroxide and N-methyl morpholine-N-oxide. Deprotection with H$_2$ over Pd/C resulted in the formation of the desired 2-methyl-1,2,3,4-tetraol. The purity of the tetraol was determined based on $^1$H and $^{13}$C spectra generated using NMR spectroscopy. In order to test stability, solutions containing 100 mM of the tetraol in 1 M (NH$_4$)$_2$SO$_4$ and D$_2$O were stirred at room temperature for one week and monitored by NMR spectroscopy. No changes in composition were observed during this time. Saccharide-water and tetraol-water solutions for nebulising were prepared using high purity (18.2 MΩ) water.

The range of relative humidites at which viscosities have been measured for each of the compounds are detailed in Table 6.1. Glucose was studied only at 28 % RH as viscosity at higher RH values can be extracted from literature data and below 28 % RH the particles stuck to the needle and were removed from the substrate during the poke-and-flow experiments, meaning their viscosity could not be determined. Raffinose particles were studied between 40 and 85 % RH. At 40 % RH the particles cracked when poked, and did not flow on a laboratory timescale. The same results were expected at lower RH values, and so experiments at lower RH values were not carried out. Maltohexaose particles were studied at RH values ranging from 50 to 80 %. As the particles cracked and did not flow at both 60 % RH and 50 % RH, experiments were not carried out at lower RH values. 2-Methyl-1,2,3,4-butanetetrol was studied only under dry conditions, though future studies...
6.2. Experimental

of viscosity as a function of RH for this compound are required as RH in the planetary boundary layer ranges from approximately 20 to 100 % ([Hamed et al., 2011] and [Martin, 2000]).

6.2.2 Predictions of viscosity using quantitative structure-property relationship models

Two quantitative structure-property relationship (QSPR) models were used to estimate the viscosity of 2-methyl-1,2,3,4-butanetetrol. QSPR models relate physical, chemical, or physicochemical properties of compounds to their structures. The first QSPR model used, which was proposed by [Sastri and Rao, 1992], estimates the viscosity of a compound based on its vapour pressure, along with the number and type of functional groups in the molecule. Experimental measurements of the vapour pressure of 2-methyl-1,2,3,4-butanetetrol are not available, and so its vapour pressure was estimated using the three QSPR models employed by the E-AIM calculator ([http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php](http://www.aim.env.uea.ac.uk/aim/ddbst/pcalc_main.php)). Each of the QSPR models used to estimate vapour pressure is based on the boiling point of the molecule along with group contributions from the functional groups present in its structure. The first model uses the method of [Nannooolal et al., 2004] to predict the boiling point, and the method of [Moller et al., 2008] to predict vapour pressure, the second uses the method of [Nannooolal et al., 2004] to predict the boiling point and the method of [Nannooolal et al., 2008] to predict vapour pressure, and the third uses the method of [Stein and Brown, 1994] to predict the boiling point and the method of [Myrdal and Yalkowsky, 1997] to predict vapour pressure. The three models each gave rise to a different estimation of the vapour pressure of 2-methyl-1,2,3,4-butanetetrol, and the lower and upper estimations of vapour pressure were used to estimate lower and upper limits of viscosity.

The second QSPR model used, which was proposed by [Marrero-Morejón and Pardillo-Fontdevila, 2000], estimates a compound's viscosity based on its molar mass and the type and number of bonds and functional groups within the molecule.
6.3 Results and discussion

6.3.1 Measured viscosities of saccharides at a range of RHs

Particles comprised of saccharides were studied using the bead-mobility and poke-and-flow techniques across a range of RHs. Shown in Figure 6.1 are examples of images for poke-and-flow experiments for maltohexaose-water and raffinose-water particles at RHs of 54 and 50 %, respectively. Markedly

![Figure 6.1: Optical images recorded during poke-and-flow experiments using particles of (a) maltohexaose and (b) raffinose. Images a1 and b1 correspond to the particles prior to being poked, with the white haloes being an optical effect. Images a2 and b2 correspond to the first frame after the needle has been remover. The particle composed of maltohexaose and studied at 50 % RH exhibited cracking behaviour and, as shown in Image a3, no change in the size or shape of the cracks can be observed 3 h after the particle has been poked. The particle comprised of raffinose and studied at 54 % RH exhibited flow, and Image b3 corresponds to an image of the particle at its experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. The scale bar in images a1 and b1 corresponds to 20 $\mu$m.](image)
different behaviour was observed in the particles. Maltol hexaose cracked, and showed no observable flow over the subsequent three hours. In contrast, raffinose flowed upon removal of the needle, with a calculated experimental flow time, $\tau_{exp, flow}$, of 112 s.

The behaviour observed in images like the examples in Fig. 6.1 was simulated and the viscosity of each saccharide-water particle determined. The simulated viscosities for each of the saccharide particles are grouped by RH and summarised in Table 6.4, and shown in Figure 6.2(a).

Also included in Fig. 6.2(a) are literature data for the viscosity of glucose-water mixtures at $\geq 75$ % RH (Barbosa-Cánovas et al. 2007; Haynes 2015; Achard et al. 1992) and sucrose-water mixtures for RH values $\geq 25$ % RH ( Först et al., 2002; Power et al., 2013; Quintas et al., 2006; Swindells et al. 1958; Telis et al., 2007). The viscosity of each of the saccharides was observed to increase as RH is decreased, with the viscosity at 28 % RH at least four orders of magnitude greater than at 78 % RH. This inverse relationship between viscosity and RH is due to the behaviour of water as a plasticiser (a component that reduces the viscosity of a solution) and the greater water content in particles at higher relative humidities.

Figure 6.2(b) is a plot of viscosity vs. molar mass of the saccharides (primary $x$-axis) at three RHs for saccharide-water particles. At 28 % RH, the viscosity increased by 3.6-6.0 orders of magnitude as molar mass of the saccharide increased from 180 to 342 g mol$^{-1}$. At 77-80 % RH the viscosity increased by 4.3-6.2 orders of magnitude as the molar mass of the saccharide increased from 180 to 991 g mol$^{-1}$. These observations are consistent with prior studies that suggest viscosity and molar mass are related through a power function (Hiemenz and Lodge 2007; Pachaiyappan et al., 1967).

Shown as a secondary $x$-axis on Fig. 6.2(b) is the number of saccharide units in a compound’s structure. Molar mass increased as the number of saccharide units in a compound’s structure increased, and a relationship was observed between viscosity and number of saccharide units. At 28 % RH, glucose, which is comprised of one saccharide unit, was determined to have a viscosity between $2 \times 10^3$ and $1 \times 10^5$ Pa s, whilst sucrose, comprised of two saccharide units, was determined to have a viscosity between $3 \times 10^8$
Table 6.4: Summary of experimental viscosity measurements using the bead-mobility and poke-and-flow techniques for the tetraol and the saccharide-water particles studied here, with results from individual particles grouped by RH. For experiments using the bead-mobility technique the mean is reported along with the 95% confidence intervals. For experiments using the poke-and-flow technique lower and upper limits of viscosity are reported, taking account of the 95% confidence limits of the simulated lower and upper limits of viscosity for the group of particles studied at each RH. N/A is reported for all experiments performed using the poke-and-flow technique, for which no mean viscosity is calculated, and for upper limits of viscosity for experiments with the poke-and-flow technique where the particle cracked, as only a lower limit of viscosity can be calculated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RH / %</th>
<th>Viscosity / Pa s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Glucose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28 *</td>
<td>N/A</td>
</tr>
<tr>
<td>Raffinose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85 +</td>
<td>1.9e-1</td>
</tr>
<tr>
<td></td>
<td>80 +</td>
<td>4.3e0</td>
</tr>
<tr>
<td></td>
<td>61 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48 *</td>
<td></td>
</tr>
<tr>
<td>Maltohexaose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>77 *</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>74 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 *</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1,2,3,4-</td>
<td>&lt;0.5 +</td>
<td>2.4e2</td>
</tr>
<tr>
<td>butanetetrol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Experiment carried out using the bead-mobility technique.

* Experiment carried out using the poke-and-flow technique.
6.3. Results and discussion

Figure 6.2: Plots of $\log_{10}(\text{viscosity})$ vs. (a) relative humidity and (b) both molar mass and number of saccharide units for glucose, sucrose, raffinose, and maltohexaose. Results determined in the current study using the bead-mobility technique are shown using circle symbols, and those determined using the poke-and-flow technique are shown using squares, with filled squares representing upper limits of viscosity and open squares representing lower limits of viscosity, with y-error bars representing 95% confidence intervals for both techniques, as detailed for Table 3. Also included are literature viscosity values for sucrose ( Först et al., 2002; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007) and glucose (Achard et al., 1992; Barbosa-Cánovas et al., 2007; Haynes, 2015), with the viscosity of glucose at 47% shown in (b) being determined using a polynomial fit of the literature data. The viscosity of water is added to (a), and shaded regions are added to (a) and (b) to guide the reader's eye.

and $2 \times 10^9$ Pa s. At 77-80% RH, glucose was determined to have a viscosity of $1 \times 10^{-1}$ Pa s, and maltohexaose, which is comprised of six saccharide units, was determined to have a viscosity between $3 \times 10^3$ and $2 \times 10^5$ Pa s.
6.3. Results and discussion

6.3.2 Measured viscosity of a tetraol

The viscosity of 2-methyl-1,2,3,4-butanetetrol, a compound containing four hydroxyl functional groups, was measured at <0.5 % RH using the bead-mobility technique. Under these conditions the 2-methyl-1,2,3,4-butanetetrol had a viscosity of 240 Pa s (95 % confidence intervals of 160-575 Pa s) (Table 6.4), roughly between that of ketchup and peanut butter (Koop et al., 2011). Recently Song et al. (2015) studied SOM produced via the oxidation of isoprene and determined the SOM to have a viscosity between $2 \times 10^4$ and $4 \times 10^6$ Pa s at <1 % RH. This viscosity is greater than that measured for the tetraol compound measured here, suggesting that SOM produced via the oxidation of isoprene contains some components that are of greater viscosity than that of the tetraol.

Plotted in Figure 6.3 is the viscosity of 2-methyl-1,2,3,4-butanetetrol, along with 2-methyl-butane and 1-hydroxy-2-methyl-butane, as a function of the number of hydroxyl groups in the structure. Also included on the figure is a line that passes through the points of 2-methylbutane and 1-hydroxy-2-methyl-butane. The viscosity of 2-methyl-1,2,3,4-butanetetrol is 5.9-6.4 orders of magnitude greater than that of 2-methylbutane, and is 0.6-1.2 orders of magnitude greater than would be predicted by the extrapolated line, suggesting that the increase in log(viscosity) may not be a linear function of the number of hydroxyl functional groups in its structure.

Shown in Figure 6.4 is a plot similar to Fig. 6.3, which shows the viscosity as a function of the number of hydroxyl groups added to n-alkanes with three to eight carbons. Fig. 6.3 illustrates that the viscosity increases by approximately 1.2 orders of magnitude when a n-alkane with three to eight carbons incorporates one hydroxyl group, by approximately 2.5 orders of magnitude when a C$_3$-C$_8$ alkane incorporates two hydroxyl functional groups, and by approximately 4 orders of magnitude when a C$_3$ or C$_6$ alkane incorporates three hydroxyl functional groups. Based on these values, oxidation reactions in the atmosphere that lead to the addition of a hydroxyl group to alkanes should lead to at least one order of magnitude increase in viscosity.
6.3. Results and discussion

Figure 6.3: A plot of log(viscosity) vs. number of hydroxyl functional groups added to 2-methylbutane. The symbols correspond to 2-methylbutane (square), 1-hydroxy-2-methylbutane (upward pointing triangle), and 2-methyl-1,2,3,4-tetraol (leftward pointing triangle). The solid line is a fit of the data for 2-methylbutane and 1-hydroxy-2methylbutane.

Figure 6.4: Plot of log(viscosity) vs. number of hydroxyl groups added to C₃-C₈ alkanes. Symbols correspond to alkanes (squares), monoalcohols (upward pointing triangles), diols (downward pointing triangles), and triols (diamonds), with lines drawn between compounds with the same number of carbons.
6.3. Results and discussion

6.3.3 Comparison of the measured and predicted viscosity of a tetraol

Two QSPR models have been used to predict the viscosity of 2-methyl-1,2,3,4-butanetetrol. The first QSPR (Sastri and Rao, 1992) relates viscosity to the molecular structure and vapour pressure of a compound, and predicts a viscosity of $1 \times 10^{10} - 5 \times 10^{14}$ Pa s for 2-methyl-1,2,3,4-butanetetrol, 8-12 orders of magnitude greater than the experimental value.

The second QSPR (Marrero-Morejón and Pardillo-Fontdevila, 2000) relates viscosity to the molecular structure and molar mass of a compound, and predicts a viscosity of $4 \times 10^1$ Pa s for 2-methyl-1,2,3,4-butanetetrol, 0.5-1.5 orders of magnitude lower than the experimental value.

Figure 6.5 is a plot of experimental vs. predicted viscosity for 2-methyl-1,2,3,4-butanetetrol for the two QSPR models. Also included in this figure are the measured and predicted viscosities of the same organics shown in Figs. 6.3 and 6.4. Literature vapour pressure values (Cai et al., 2015; Cammenga et al., 1977; Perry and Green, 2008; Verevkin, 2004) were used to predict the viscosities of the alkanes, mono, di, and tri alcohols. The QSPR model of Sastri and Rao predicts the viscosity of compounds containing zero

![Figure 6.5](image.png)

Figure 6.5: Plot of experimental vs. predicted log(viscosity) of C$_3$-C$_8$ alkanes, monoalcohols, and polyols for the models derived by (a) Sastri and Rao (1992) and (b) Marrero-Morejón and Pardillo-Fontdevila (2000). Dashed 1:1 lines are shown on each plot to guide the reader’s eye.
or one hydroxyl functional groups well, however, it increasingly over-predicts the viscosity of compounds as the number of hydroxyl functional groups increased, over-predicting the viscosity of compounds containing three hydroxyl functional groups by approximately 6 orders of magnitude (Fig. 6.5(a)). These over-estimations may be due to the model over-estimating the effect of multiple hydroxyl compounds being present in the same molecule. In theory there could also be error in the calculated vapour pressure of 2-methyl-1,2,3,4-butanetetrol, however, this would not account for the large over-estimation in the viscosity of compounds containing three hydroxyl functional groups.

Shown in Fig. 6.5(b) are predicted viscosities using the QSPR model of Marrero-Morejón and Pardillo-Fontdevila (2000). The model provides more accurate predictions than that of Sastri and Rao, with the predicted log(viscosity / Pa s) of all compounds bar 2-methyl-1,2,3,4-butanetetrol being within 0.2 of their experimental values.

6.4 Summary

The viscosity of particles consisting of a tetraol (2-methyl-1,2,3,4-butanetetrol) and particles containing one of three saccharides (glucose, raffinose and maltotetraose) mixed with water have been determined. These systems serve as proxies for highly oxidized components of ambient SOM. In addition, tetraols are a component of secondary organic material produced via the photooxidation of isoprene, and saccharides have been observed in atmospheric organic particulate matter.

The viscosity of saccharide-water particles was at least four orders of magnitude greater at a RH of 28 % than at 78 % RH, indicating that water is acting as a plasticizer. At 28 % RH, the viscosity of saccharide-water particles was observed to increase by approximately 4-6 orders of magnitude as molar mass of the saccharide is increased from 180 to 342 g mol$^{-1}$ or the number of saccharide units increased from one to two. At 77-80 % RH the viscosity increased by approximately 4-6 orders of magnitude as the molar mass of the saccharide increases from 180 to 991 g mol$^{-1}$ or the
number of saccharide units increased from one to six. These results suggest oligomerisation of highly oxidized compounds in atmospheric SOM could lead to large increases in viscosity, and could be at least partially responsible for high viscosities in SOM.

The tetraol studied under dry conditions was determined to have a viscosity of 240 Pa s, approximately 6 orders of magnitude greater than 2-methylbutane, which shares a carbon backbone with 2-methyl-1,2,3,4-butanetetrol but contains zero hydroxyl functional groups. The measured viscosity of 2-methyl-1,2,3,4-butanetetrol is lower than the viscosity of SOM produced via the oxidation of isoprene, suggesting SOM produced via the oxidation of isoprene contains some components of greater viscosity than that of the tetraol. Finally, two quantitative structure-property relationship models, which were previously developed to predict the viscosity of organic liquids, was used to predict the viscosity of 2-methyl-1,2,3,4-butanetetrol. The viscosity of 2-methyl-1,2,3,4-butanetetrol is vastly over-predicted by 8-12 orders of magnitude by the model of Sastri and Rao (1992), and is under-predicted by 0.6-1.2 orders of magnitude by the model of Marrero-Morejón and Pardillo-Fontdevila (2000).
Chapter 7

Predicting the viscosity of organic compounds using their oxygen-to-carbon elemental ratio and saturation vapour concentration

7.1 Introduction

Aerosol particles are ubiquitous throughout the atmosphere and affect the Earth’s climate directly, through the scattering and absorption of incoming solar radiation, and indirectly, by acting as nuclei for liquid and ice clouds (Stocker et al., 2013). Atmospheric particulate matter is formed in the atmosphere, in part through the oxidation of volatile organic compounds (VOCs) emitted from the planet’s surface. These oxidation reactions result in the formation of secondary organic material and SOM is typically estimated to account for 30-70 % of the mass fraction of submicron particulate matter in most regions of the atmosphere (Kanakidou et al., 2005).

Due to the complexity of SOM (see Section 1.2), explicit description of its formation, evolution, and physical properties of SOM cannot currently be incorporated into large-scale models (Hallquist et al., 2009). As a result, researchers have used simple methods to describe these processes and
properties. Two properties that are currently being used to describe and model the formation, evolution, and hygroscopic properties of SOM are O:C and saturation vapour concentration (C*) (Donahue et al., 2011, 2006, 2012; Jimenez et al., 2009; Napier et al., 2014; Zhao et al., 2015). C* defines the concentration above which a species will partition to the particle phase (Donahue et al., 2009; Hallquist et al., 2009; Pankow, 1994), and is calculated for a given compound as follows,

\[
C^* = \frac{P_L^0 M_w < 10^6}{RT}
\]

(7.1)

where \(P_L^0\) is the saturated vapour pressure (units of atm) of the compound, \(M_w\) is its molar mass (g mol\(^{-1}\)), \(\varsigma\) is its activity coefficient (typically assumed to be 1), \(R\) is the ideal gas constant (J K\(^{-1}\) mol\(^{-1}\)), and \(T\) is the temperature (K).

The use of O:C and C* is a convenient method for predicting the formation, evolution, and hygroscopic properties of SOM as they are simple enough to be incorporated into large-scale models, and they may also be validated with field and laboratory experiments.

The viscosity of SOM has recently become a topic of interest in the scientific literature as viscosity is important for predicting the environmental impact of SOM. For example viscosity can affect the mechanism and rate of growth of particles containing SOM (Riipinen et al., 2011; Shiraiwa and Seinfeld, 2012; Shiraiwa et al., 2013; Zaveri et al., 2014) as well as their ability to uptake water (Bones et al., 2012; Hawkins et al., 2014; Lu et al., 2014; Price et al., 2014; Tong et al., 2011). The importance of the viscosity of SOM is further outlined in Chapter 1.

Due to the importance of the viscosity of SOM, researchers have begun to measure the viscosity of specific types of SOM under specific laboratory conditions (Bateman et al., 2015; Pajunoja et al., 2014; Song et al., 2015; Zhang et al., 2015, and Chapters 3 and 5), however, tools to predict the viscosity of SOM particles for a range of environmental conditions are currently limited.

The relationship between viscosity and the physical property of com-
7.1. Introduction

Compounds has been studied previously (Katritzky et al., 2010). For example, Suzuki et al. (1996) studied the correlation between 18 different physical properties and viscosity for a selection of 237 organic compounds. The physical properties determined to correlate most strongly with viscosity were the enthalpy of vaporisation of a compound at its boiling point, the cohesive energy of a compound at 298 K, and the vapour pressure of a compound at 293 K. Approaches to predict viscosity that combine multiple physical properties have also been used - for example, Katritzky et al. (2000) derived an equation combining five physical properties, with the most important property determined to be a measure of the proportion of the compound available to form hydrogen bonds.

The following investigates whether an organic compound’s O:C and C* are good predictors of its viscosity, which would potentially allow viscosity to be incorporated into atmospheric models. Additionally, the predictive ability of a multivariate relationship between viscosity and both O:C and C* is considered.

A relationship has previously been established between a molecule’s O:C and its glass transition temperature \( T_g \) (Koop et al., 2011), as has a relationship between the viscosity and vapour pressure of organic compounds (Sastri and Rao, 1992; Suzuki et al., 1996), however, neither the relationship between viscosity and O:C, nor the relationship between viscosity and C*, have been studied. The common characteristics between O:C and C*, and physical properties shown to be correlated with viscosity suggest O:C and C* may be good candidates for predicting the viscosity of organic compounds. A greater O:C ratio increases the proportion of a compounds structure that is available to hydrogen bond, which was determined to be an important measure by Katritzky et al. (2000). Vapour pressure is used to calculate a compound’s C*, and has been determined by Suzuki et al. (1996) to be strongly correlated to the viscosity of organic compounds. Also included in the calculation of C* is molar mass which, though observed to give rise to a lower correlation than vapour pressure, was also observed by Suzuki et al. (1996) to be correlated to viscosity.
7.2 Methods

7.2.1 Selection of compounds

Based on the elemental composition and functional groups of secondary organic material outlined in the introduction of this Chapter, and the goal of determining the relationship between viscosity, O:C and C*, the following criteria were used when selecting compounds from the literature:

i) compounds must contain only carbon and hydrogen or only carbon, hydrogen, and oxygen atoms,

ii) compounds must contain only the following functional groups: alkanes, alkenes, alcohols, carboxylic acids, aldehydes, ketones, esters, ethers, and acid anhydrides, as well as both aromatic and non-aromatic cyclic molecules, to be consistent with functional groups associated with SOM (see introduction to this Chapter),

iii) compounds must have viscosities reported in the literature at 298 K, or viscosities reported at more than three other temperatures, with at least one measurement being above 298 K and at least one measurement being below 298 K, allowing their viscosity at 298 K to be interpolated using a polynomial fit,

iv) compounds must have vapour pressures reported in the literature at 298 K, or vapour pressures reported at more than three other temperatures, with at least one measurement being above 298 K and at least one measurement being below 298 K, allowing their vapour pressure at 298 K to be interpolated using a polynomial fit.

Application of these criteria resulted in data for 156 suitable compounds that range in molar mass from 32-600 g mol$^{-1}$ and in O:C from 0.0 to 2.0, consistent with the properties of components of SOM outlined in the introduction. The compounds also range in $\log(C^*/\mu g\ m^{-3})$ from 0 to 10, and in $\log(\eta/\ Pa\ s)$ from -4 to 0.5. The compounds, along with their properties, are detailed in Table C.1, whilst Table 7.1 provides a summary of the functional groups represented in the compounds.

Components of SOM produced during the ozonolysis of $\alpha$-pinene are predicted to have $\log\ (C^*/\mu g\ m^{-3})$ at least as low as 2.5 [Jimenez et al., 107].
Table 7.1: A summary of the functional groups featured in the 156 compounds used to determine the relationship between viscosity and either O:C or C*. A compound with multiple oxygen containing functional groups is counted once for each type of functional group it contains, and once in the multiple oxygen containing functional group row. As such, the total sums to >156.

<table>
<thead>
<tr>
<th>Organic compound class</th>
<th>Number of compounds containing functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>23</td>
</tr>
<tr>
<td>Alkene</td>
<td>21</td>
</tr>
<tr>
<td>Cyclic (non-aromatic)</td>
<td>18</td>
</tr>
<tr>
<td>Cyclic (aromatic)</td>
<td>19</td>
</tr>
<tr>
<td>Alcohol</td>
<td>36</td>
</tr>
<tr>
<td>Acid</td>
<td>10</td>
</tr>
<tr>
<td>Acid anhydride</td>
<td>2</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>9</td>
</tr>
<tr>
<td>Ketone</td>
<td>10</td>
</tr>
<tr>
<td>Ester</td>
<td>19</td>
</tr>
<tr>
<td>Ether</td>
<td>16</td>
</tr>
<tr>
<td>Multiple oxygen containing functional groups</td>
<td>19</td>
</tr>
</tbody>
</table>

and may be significantly lower (Schobesberger et al., 2013). The viscosity of individual components has yet to be measured, though α-pinene has a log(η / Pa s) of -2.89 and experimental studies of the total SOM produced via the ozonolysis of α-pinene suggest it to be of log(η / Pa s) ≥6 (Zhang et al., 2015, and Chapter 4).

7.2.2 Parameterisation of data

Parameterisations were determined using Origin software. Linear fits were used to determine the relationship between log(η) and O:C and between log(η) and log(C*), whilst a multiple linear regression was used to determine the relationship between log(η) and a combination of O:C and log(C*). The form of each of these parameterisations is detailed in Table 7.2.
7.3 Results

Table 7.2: Summary of the parameterisations used in this study. In each case \( \log(\eta / \text{Pa s}) \) is used as the dependent variable, and O:C and \( \log(C^* / \mu g \text{ m}^{-3}) \) are the independent variables. RMSE refers to the root mean square error between the \( \log(\eta / \text{Pa s}) \) predicted by the parameterisation for each of the compounds in the study and the experimental viscosities.

<table>
<thead>
<tr>
<th>Equation form, including independent variables</th>
<th>Values of constants (standard error)</th>
<th>Statistical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log_{10}(\eta) = a + b(O:C) )</td>
<td>( a = -3.09 ) (6.74e-2) ( b = 0.776 ) (0.189)</td>
<td>R value = 0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adjusted ( R^2 = 0.09 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p)-value &lt; 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSE = 0.49</td>
</tr>
<tr>
<td>( \log_{10}(\eta) = a + b \times \log_{10}(C^*) )</td>
<td>( a = 0.164 ) (0.141) ( b = -0.407 ) (1.83e-2)</td>
<td>R value = -0.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adjusted ( R^2 = 0.76 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p)-value &lt; 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSE = 0.23</td>
</tr>
<tr>
<td>( \log_{10}(\eta) = a + b(O:C) + c \times \log_{10}(C^*) )</td>
<td>( a = -2.49e-4 ) (0.147) ( b = 0.301 ) (9.72e-2) ( c = -0.394 ) (1.83e-2)</td>
<td>R value = 0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adjusted ( R^2 = 0.77 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( p)-value &lt; 0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMSE = 0.26</td>
</tr>
</tbody>
</table>

7.3 Results

7.3.1 The relationship between viscosity and O:C

Figure 7.1(a) is a plot of \( \log(\eta) \) vs O:C for the compounds used for this study (Table C.1). Though a general trend can be observed, with \( \log(\eta) \) and O:C being directly related, the relationship has a R value of 0.31, suggesting O:C explains only \( \approx 9\% \) of the observed variance in \( \log(\eta / \text{Pa s}) \). The equation of the best fit to Fig. 7.1(a) is detailed in Table 7.2. Figure 7.1(b) is a plot of experimental viscosities vs. the viscosities predicted using the best fit equation. The predicted viscosities have a root mean square error (RMSE) of 0.49 units of \( \log(\eta / \text{Pa s}) \), with the predicted \( \log(\eta / \text{Pa s}) \) of 58 of the 156 compounds observed to deviate by >0.5 from their experimental values.
7.3. Results

Figure 7.1: Plots detailing the relationship between viscosity (log(\(\eta / \text{ Pa s}\))) and ((a) and (b)) O:C, and ((c) and (d)) log saturation vapour concentration (log(C*)) for a range of compounds comprised only of carbon and hydrogen or carbon, hydrogen, and oxygen atoms, and containing atmospherically relevant functional groups. Lines of best fit are included on plots (a) and (c). 1:1 lines are included on plots (b) and (d) to guide the eye of the reader. Statistical values from the plots are reported in Table 7.2.
7.3. Results

7.3.2 The relationship between viscosity and C*

Shown in Figure 7.1(c) is a plot of $\log(\eta)$ vs $\log(C^*)$ for the compounds used in this study (Table C.1). The linear regression between $\log(\eta)$ and $\log(C^*)$ exhibits a stronger correlation than that between $\log(\eta)$ and O:C, with a $R$ value of -0.87 (Table 7.2) suggesting $\log(C^*)$ explains $\approx76\%$ of the variation in $\log(\eta)$ for the compounds used in this study, a much greater proportion than O:C. This correlation occurs over a wide range of values, with viscosities spanning almost 5 orders of magnitude, and $C^*$ values spanning more than 10 orders of magnitude. Figure 7.1(d) is a plot of experimental viscosities and the viscosities predicted using a compounds $C^*$. A much tighter grouping about the 1:1 line is observed than for O:C (Fig. 7.1(b)), and the best fit equation (Table 7.2) predicts viscosities with a RMSE of 0.23 units of log($\eta$), smaller than that predicted using O:C. Of the 156 compounds studied, the predicted $\log(\eta)$ of 20 compounds deviated by $>0.5$ from their experimental viscosities.

Suzuki et al. (1996) has previously demonstrated a strong correlation between viscosity and vapour pressure for a range of organic compounds. Vapour pressure and $C^*$ are related as detailed in equation 7.1, and thus the results here can be considered consistent with those of Suzuki et al. (1996).

7.3.3 Multivariate relationship between viscosity and both O:C and C*

A tool often used in modelling is multiple linear regression (MLR), which simultaneously optimises the weight given to numerous independent properties to create a single equation to estimate the value of a dependent property. The MLR approach has been applied to the study of the viscosity of organic compounds previously, using models that contain up to nine properties (Katritzky et al., 2010). As such, a combination of O:C and $C^*$ has been used to determine whether they result in an improved relationship with viscosity.

Figure 7.2(a) is a 3-D contour plot with O:C and $\log(C^*)$ on the $x$- and $y$-axes, respectively, and the colour scale on the plot indicating the viscosity.
7.3. Results

Figure 7.2: (a) is a 3-D contour plot with O:C and $\log_{10}(C^* / \mu g m^{-3})$ on the $x$- and $y$-axes, respectively, and the colour scale on the plot indicating the viscosity predicted using an MLR with experimental $\log(\eta / Pa s)$ as the dependent variable and O:C and $\log(C^* / \mu g m^{-3})$ as the independent variables. (b) is a residual plot showing the difference for each compound between its experimental viscosity and the viscosity predicted by the regression. (c) is a plot of the predicted viscosities for each of the compounds vs. their experimental viscosities, with a 1:1 line to guide the readers eye.
predicted using an MLR with log(η / Pa s) as the dependent variable, and log(C* / µg m\(^{-3}\)) and O:C as independent variables (Table 7.2). Also plotted are the O:C and log(C*) values of the compounds used in this study.

Fig. 7.2(b) is a residual plot showing the difference between the experimentally determined viscosities and those predicted by the MLR that incorporates O:C and log(C*) as predictors of log(η / Pa s). The RMSE of the predicted viscosities (0.26 log units) is similar, though slightly larger than the RMSE of C* alone (0.23 log units). Though the correlation to viscosity between the MLR featuring both O:C and C* is higher (adjusted R\(^2\) = 0.77) than the parameterisation featuring solely C* (adjusted R\(^2\) = 0.76), the small increase suggests O:C plays at best a negligible role in improving the ability to predict viscosities using log(C*).

The viscosities predicted by the regression model are plotted against their experimental viscosities in Fig. 7.2(c). This data is also, expectedly, centred on the 1:1 line, and a tight grouping is observed, with the predicted viscosities of only 17 of the 156 compounds deviating by >0.5 log units from their experimental viscosities.

### 7.4 The predicted viscosity of products of α-pinene ozonolysis

The plot of log(η / Pa s) vs log(C* / µg m\(^{-3}\)) shown in Fig. 7.1(c) is plotted again as Figure 7.3, with the pink area representing the area bounded by the 95 % prediction interval of the linear relationship. The 95 % prediction intervals suggest log(η / Pa s) to range from 0.9 to -0.6 when log(C* / µg m\(^{-3}\)) equals 0, and -3.2 to -4.6 when log(C* / µg m\(^{-3}\)) equals 10.

Shown on the bottom x-axis is the structure of α-pinene, as well as three products formed during the ozonolysis of α-pinene, cis-pinic acid, cis-pinonic acid, and pinonaldehyde. Shown along the top x-axis are the regions of the log(C*) scale attributed to semivolatile organic compounds (SVOCs), intermediate volatility organic compounds (IVOCs), and volatile organic compounds (VOCs), as defined by Donahue et al. (2009, 2012).
7.4. The predicted viscosity of products of α-pinene ozonolysis

Figure 7.3: Plot of log(η / Pa s) vs. log(C* / µg m⁻³) for the compounds detailed in Table C.1. The shaded pink region represents the 95 % prediction interval of the linear regression between log(C* / µg m⁻³) vs. log(η / Pa s). Shown on the x-axis are the regions of the log(C*) scale attributed to semivolatile organic compounds (SVOCs), intermediate volatility organic compounds (IVOCs), and volatile organic compounds (VOCs). Also shown is the position of α-pinene (dark blue circle) (per Donahue et al., 2009), as well as first generation products from α-pinene ozonolysis, cis-pinic acid (green), cis-pinonic acid (red), and pinonaldehyde (cyan) (C* values calculated from Hartonen et al., 2013).

Compounds in the SVOC region may be in either the particle or gas phase under ambient atmospheric conditions, whilst IVOCs and VOCs are almost exclusively in the gas phase. The C* of α-pinene suggests it should
be classified as a VOC, whilst those of the three reaction products shown on Fig. 7.3 suggest they should be classified as IVOCs. The 95 % prediction limit of the regression equation suggests the upper limit of log(\(\eta / \text{ Pa s}\)) for IVOCs to be -0.2, suggesting both IVOCs and VOCs occupy the liquid regime of viscosities (Shiraiwa et al., 2011a, and Chapter 3). These values are consistent with the multiple linear regression incorporating both O:C and C* shown in Fig. 7.2, which predicts the log(\(\eta / \text{ Pa s}\)) of \(\alpha\)-pinene to be -3.0, and the log(\(\eta / \text{ Pa s}\)) of cis-pinic acid, cis-pinonic acid, and pinonaldehyde to be between -1.4 and -2.3, all of which are in the liquid regime of viscosities.

The lower limit of log(C* / \(\mu\)g m\(^{-3}\)) for SVOCs is defined as -0.5 (Donahue et al., 2012). Though the dataset of compounds used here, and shown in Fig. 7.3 only covers compounds of log(C* / \(\mu\)g m\(^{-3}\)) >0, extrapolation of the regression equation and 95 % prediction limits suggests an upper limit of log(\(\eta / \text{ Pa s}\)) of 1.1 when log(C* / \(\mu\)g m\(^{-3}\)) equals -0.5, suggesting that SVOCs also occupy the liquid regime of viscosities, although additional studies are needed to confirm whether this is the case.

7.5 Summary

Literature data has been used to determine the relationship between viscosity and O:C, as well as between viscosity and C*, for 156 organic compounds. The compounds studied have viscosities that span a range of almost five orders of magnitude, O:C values that range from 0.0-2.0, and values of C* that span a range of ten orders of magnitude.

The relationship between log(viscosity) and O:C was determined to have a R value of 0.31, suggesting O:C explained 9 % of the observed variance in log(viscosity). The linear relationship between log(viscosity) and O:C was subsequently used to predict the viscosity of each of the compounds. The predicted viscosities had a RMSE of 0.49 for log(viscosity), and of the 154 compounds studied, 58 had a predicted log(viscosities / Pa s) that deviated by >0.5 from its experimental log(viscosity / Pa s). The relationship between log(viscosity) and C* was determined to be stronger that that be-
7.5. Summary

tween log(viscosity) and O:C, having a R value of -0.87, suggesting log(C*) explained 76 % of the observed variance in log(viscosity). The linear relationship between log(viscosity) and log(C*) was subsequently used to predict the viscosity of each of the compounds. The predicted viscosities had a RMSE of 0.23 for log(viscosity), and of the 154 compounds studied, 20 had a predicted log(viscosities / Pa s) that deviated by >0.5 from its experimental log(viscosity / Pa s).

Finally, MLR was used to determine the relationship between viscosity and a combination of O:C and log(C*). The statistical results were similar to that observed for C* alone, with an R value of 0.88, suggesting the combination of O:C and C* explained 77 % of the observed variance in log(viscosity). The viscosities predicted by the MLR had a RMSE of 0.26 for log(viscosity), and of the 154 compounds studied, 17 had a predicted log(viscosities / Pa s) that deviated by >0.5 from its experimental log(viscosity / Pa s).

These results suggest, for the compounds studied here, C* is a potentially useful property with which to predict viscosities, whilst O:C was observed to play a negligible role in improving the ability to predict viscosities.

Whilst the parameterisations and results presented here provide an initial framework for predicting viscosities of the components observed in SOM, a greater number of experimental values for compounds of higher viscosity, lower C*, and containing multiple oxygen containing functional groups are required in order to further evaluate the usefulness of C* for predicting the viscosity of SOM.
Chapter 8

Conclusions and future work

8.1 Conclusions

8.1.1 Development and validation of the poke-and-flow technique

Chapters [2-4] detail the development and validation of the poke-and-flow technique combined with simulations of fluid flow, a novel method for measuring small samples of high viscosities. The technique is capable of measuring a wide range of viscosities yet requires only micrograms of material, presenting the opportunity to provide the first direct measurements of the viscosity of SOM.

In Chapter 3 the technique was used to determine the upper limit of viscosity for particles that formed a half-torus geometry on being poked by the needle, and subsequently exhibited flow to re-attain a hemispherical morphology. An initial validation showed the simulated viscosities to be in agreement with literature viscosities for sucrose-water mixtures with viscosities of approximately $10^4 \, \text{Pa s}$. The technique was also used to determine the lower limit of viscosity for particles that cracked upon impaction by the needle, that exhibit no observable flow over subsequent hours. The simulated lower limit of viscosity for raffinose-water particles at low RHs was $5 \times 10^8 \, \text{Pa s}$, not inconsistent with literature data suggesting them to be of viscosity $>10^{12} \, \text{Pa s}$.

In Chapter 4 simulations of particles that took on a half-torus geometry and subsequently exhibited flow were extended to also include an estimated lower limit of viscosity. The technique was also validated across a wider range of viscosities, with simulated viscosities of sucrose-water particles ob-
served to be in agreement with literature values at least across the range of \( \approx 5 \times 10^2 - \approx 3 \times 10^6 \) Pa s. Simulated viscosities obtained using the poke-and-flow technique combined with simulations of fluid flow were also shown to be in agreement with measured viscosities for two commercially available polybutene high viscosity standards.

8.1.2 Measuring the viscosity of SOM and atmospherically relevant compounds

The viscosity of SOM produced via the ozonolysis of \( \alpha \)-pinene was measured in Chapters 3 and 5 and the viscosity of atmospherically relevant compounds, a tetraol and numerous saccharide-water mixtures was measured in Chapter 6. These results add to the limited values in literature for SOM as well as highly oxidized atmospherically relevant compounds.

In Chapter 3, the poke-and-flow technique combined with simulations of fluid flow was used along with a second novel technique, the bead-mobility technique, which was also detailed in Chapter 2. The viscosity of the water-soluble component of the SOM was determined to be strongly dependent on RH, and range in viscosity from approximately \( 10^0 \) Pa s at 90 % RH, roughly equivalent to that of honey, to \( > 10^8 \) Pa s at \( \leq 30 \) % RH, greater than that of tar pitch.

In Chapter 5, the viscosity of the whole SOM, comprised of both the water-soluble and water-insoluble components, was collected and measured using the poke-and-flow technique in combination with simulations of fluid flow. The effect on viscosity of varying experimental conditions was also studied. The viscosity of the total SOM was determined to be dependent on RH, with the viscosity of the sample produced under the most atmospherically relevant conditions observed to be three to four orders of magnitude greater at \( < 0.5 \) % RH than at 50 % RH. The viscosity of the total SOM was determined to be dependent on the SOM particle mass concentration at which the SOM was produced, with viscosities measured at \( < 0.5 \) % RH ranging by greater than an order of magnitude for the range of production mass concentrations studied. Finally, the viscosity of the whole SOM was
determined to be lower than the viscosity of the water-soluble component of the SOM.

In Chapter 6, the bead-mobility and poke-and-flow technique in combination with simulations of fluid flow were used to measure the viscosity of a tetraol and some saccharide-water mixtures. These measurements add to the limited measurements that exist in literature for the viscosity of highly oxidized atmospherically relevant compounds. The viscosities of the saccharide-water mixtures were determined to be dependent upon RH, with viscosities determined to be at least four orders of magnitude greater at 28% RH than at 78% RH. The viscosities of the saccharide-water mixtures was also determined to be dependent upon the molar mass of the saccharide. The viscosity measurement of the tetraol studied were compared to literature data to demonstrate viscosity is strongly dependent upon the number of hydroxyl functional group in a molecule, suggesting oxidation reactions in the atmosphere that lead to the addition of a hydroxyl group to alkanes should lead to at least one order of magnitude increase in viscosity.

8.1.3 Predicting the viscosity of SOM

Chapter 7 details the application of literature data in order to determine the relationship between viscosity and elemental oxygen-to-carbon ratio (O:C), as well as between viscosity and saturation vapour concentration (C*), the mass based equivalent of saturation vapour pressure. The relationship between log(viscosity) and O:C had a R value of 0.31, compared with a R value of -0.87 between log(viscosity) and log(C*). A multivariate linear regression comprising both O:C and log(C*) was similar to log(C*) in terms of its correlation to, and ability to predict, viscosities, suggesting O:C played a negligible role in improving the ability to predict viscosities. Finally, the relationship between log(viscosity) and log(C*) suggests that volatile organic compounds (VOCs), and intermediate volatility organic compounds (IVOCs) will be liquids (viscosities <10^2 Pa s). An extrapolation of this relationship a short distance beyond the compounds included in the study of Chapter 7 suggests the same to be true for at least some semivolatile
organic compounds (SVOCs).

8.2 Directions for future work

The samples and relationships studied here provide a starting point for predicting the viscosity of SOM in the atmosphere, however, further experiments would be beneficial.

Studies of the physical properties of SOM typically report the values for SOM produced and studied under a limited set of conditions, for example produced at dry RH and studied at room temperature (see Chapter 3 as well as Abramson et al., 2013; Cappa and Wilson, 2011; Perraud et al., 2012; Zhang et al., 2015), and caution must be taken when applying these results to the atmosphere, where conditions such as RH and temperature exhibit significant spatial and temporal variation. The results presented in Chapter 5 outline the effect on the viscosity of SOM of varying experimental conditions, and Kidd et al. (2014) have reported changing the RH at which SOM is produced also plays a role in dictating the chemical composition of the SOM. Further, viscosity and temperature are known to be inversely related (Viswanath et al., 2007). Whilst the majority of laboratory studies are performed at room temperature, the temperature in the troposphere can be as low as -56 °C (Seinfeld and Pandis, 2006), suggesting SOM in the atmosphere would be of higher viscosity than at room temperature. Initial observations supporting this theory have recently been provided by Järvinen et al. (2015), who observed the transition of SOM particles from non-spherical to spherical as RH was increased, and determined an increase in the RH at which the transition occurred as temperature was decreased. This relationship was also in agreement with those prior estimations (Koop et al., 2011; Wang et al., 2015). Due to the effect on viscosity of varying experimental parameters, the effect on viscosity of varying production RH should be studied in more detail, as well as the effect on viscosity of the temperature at which SOM is both produced and studied.

In order to better understand and predict the viscosity of the individual components of SOM, additional measurements of the viscosity of at-
mospherically relevant compounds are required. For example, the recent experimental discovery and identification of extremely low volatility organic compounds in SOM, which may be of O:C $\geq$ 1.0 and account for a significant fraction of SOM mass (Elm et al., 2012, 2014; Praplan et al., 2015; Schobesberger et al., 2013), has highlighted the lack of experimental viscosity measurements of compounds that contain certain types of oxygen containing functional groups, compounds containing multiple oxygen containing functional groups, or compounds that have low volatilities. For example, ELVOC compounds are known to contain multiple hydroperoxide functional groups, whilst organonitrate and organosulfate functional groups are also known to be present in components of SOM (e.g. Russell et al., 2011), however, few literature measurements of viscosity are available for compounds containing these functional groups. Furthermore, due to a lack of available literature data no compounds considered to be of low volatility (per Donahue et al., 2009, 2012) could be included in the study in Chapter 7. Literature data for a greater number of compounds containing multiple oxygen containing functional groups or of low volatility would allow the relationship between viscosity and saturation vapour concentration ($C^*$) observed in Chapter 7 to be established over a wider range of values. The results presented in Chapters 4 and 6 here, as well as the viscosities of sucrose reported by Power et al. (2013) and the vapour pressures of atmospherically relevant compounds reported by Bilde et al. (2015), are some of the examples of early steps in providing some of these measurements.
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Appendix A

Appendix to chapter 3

A.1 Composition of SOM from ozonolysis of α-pinene

SOM formed from the ozonolysis of α-pinene is largely composed of water-soluble organic compounds. Hall and Johnston (2011) determined that 63 (±27) % of the total particle mass is extractable from filters with water. Heaton et al. (2007) compared the mass spectra from extracts using 100 % water and 50:50 methanol:water and showed that there was little difference in the chemical composition of the two extracts. Cloud condensation measurements suggest that secondary organic material generated from the ozonolysis of α-pinene is not limited by solubility of the organic material in water under similar conditions as used in our experiments (King et al., 2009). Finally, SOM produced by limonene ozonolysis, a species structurally related to α-pinene, has been shown to be nearly completely water-soluble by comparing water and acetonitrile extracts (Bateman et al., 2010).

A.2 Viscosity prediction using mixing rules

A common approach to estimating the viscosity of mixtures ($\eta_{mix}$) is to apply mixing rules to the viscosities of the pure components of the mixture based on experimental data and/or theory. Among the simplest of mixing rules for complex mixtures was first proposed by Arrhenius (1885) and considered the mole fraction of each component ($x_i$) and the viscosity of each pure component ($\eta_i$) (Equation A.1) (Grunberg and Nissan, 1949):
A.2. Viscosity prediction using mixing rules

\[ \log(\eta_{mix}) = \sum_{i=1}^{n} x_i \log(\eta_i) \] (A.1)

Equation [A.1] was later modified by (Grunberg and Nissan, 1949) to include a group interaction parameter, G, accounting for non-ideality of the complex mixture, the result of which was a closer fit to the experimental data (Equation [A.2]):

\[ \log(\eta_{mix}) = \sum_{i=1}^{n} x_i \log(\eta_i) + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j G_{i,j} \] (A.2)

If the interaction parameter, \( G_{i,j} \), between the SOM components is small, and the mole fraction of water is a linear function of RH, Equation [A.2] predicts a linear dependence of \( \log(\eta_{SOM-H_2O}) \) vs. RH, roughly consistent with what is observed in Fig. 3.3, where \( \log(\eta_{SOM-H_2O}) \) is the viscosity of the SOM-water mixture. Any deviation from linearity, for instance between 30 and 40 % RH, may be due to non-ideality and/or a gel or glass transitions in that RH regime. Accurate predictions of viscosities in aqueous mixtures may require an additional interaction term in Equation [A.2], the result of which is further non-linearity in the plots of \( \log(\eta_{mix}) \) (or \( \log(\eta_{SOM-H_2O}) \)) (Marczak et al., 2012).

It should be noted that the use of equations such as Equations [A.1] and [A.2] for mixtures containing components with very large differences in the viscosities of the pure components is not well established and are used here only for a first-order approximation of the trend in the viscosity expected with changing RH. However, other formulations modelling the viscosity of specific polar mixtures such as sucrose-water mixtures predict a linear correlation between \( \log(\eta_{mix}) \) and concentration even with a large difference in pure component viscosities Longinotti and Corti (2008).
Appendix B

Appendix to chapter 5

B.1 Effect of carrier gas flow on SOM particle properties

To determine whether particles evaporate whilst being exposed to a flow of N₂ gas, a sample (generated with a mass concentration of 6,000 µg m⁻³) was mounted in the flow cell and exposed to dry (<0.5 % RH) N₂ gas for a period of 45 h. A series of nine images were taken of each of five particles over a time period of 45 h. The area at the particle-substrate interface of each particle was measured using Leica software, and equilibrium contact angle measurements of particles in the sample were made after the completion of the experiment. From this information, the volume of each of the particles was determined at each time point, with the equilibrium contact angle assumed to remain constant during the duration of the experiment. To remove the potential of photo-induced changes to the sample the light source was only turned on when acquiring images. poke-and-flow experiments were also performed after 1 h and 45 h of exposure to the dry N₂ gas flow to determine whether the viscosity of the particles changed due to the extended exposure. The results of these studies are shown in Figure B.1 and Table B.1.
B.2 Variability between particles in the same sample, and between all particles produced under equivalent conditions

To determine the variability in $\tau_{\text{exp,flow}}$ and the variability in the simulated lower and upper limits of viscosity for particles produced using equivalent conditions, the percent relative standard deviations (% RSD) have been calculated for poke-and-flow experiments performed at <0.5 % RH, and are reported in Table B.3.

Table B.3 shows the % RSD for all particles produced under equivalent conditions ranged from 26-117 %. For samples on the same substrate, the % RSD ranged from 14-83 %. In general there appears to be a reasonable level of reproducibility in results both between particles on the same substrate, and between particles on separate substrates produced under equivalent conditions. The majority of the uncertainty in the reported viscosities is due to uncertainty in the physical parameters used during simulations, rather than experimental variability or error, as can be seen in Figs. 5.2(b), 5.4(b), and B.3(b).

B.3 Calculation of viscosity for prior studies of $\alpha$-pinene derived SOM

Saleh et al. (2013) and Robinson et al. (2013) reported mixing times for particles of a given size, which have been used to calculate diffusion coefficients through the relationship,

$$ D = \frac{d_p^2}{4\pi^2 \tau_{\text{mixing}}} \quad \text{(B.1)} $$

where $d_p$ is the diameter of the particle (m), and $\tau_{\text{mixing}}$ is the mixing time in s (Shiraiwa et al., 2011a). The calculated diffusion coefficients for Saleh et al. (2013) and Robinson et al. (2013) should be considered as lower limits, as the mixing times used were the upper limit of those reported,
and other processes besides molecular diffusion within the particles may have been the rate determining step for mixing in their experiments. These calculated upper limits to diffusion coefficients were then converted to lower limits of viscosities through the Stokes-Einstein relationship,

\[ \mu = \frac{k_B T}{x \pi r D} \]

where \( k_B \) is the Boltzmann constant (J K\(^{-1}\)), \( T \) is the temperature (K), \( x \) is a coefficient ranging from 4-6 dependent upon the assumption of slip or no-slip at the surface of the diffusing species, and \( r \) is the hydrodynamic radius of the diffusing molecule (m). A summary of the values used to calculate viscosities is included in Table B.4.

As the size of the diffusing molecules were not known in Saleh et al. (2013) and Robinson et al. (2013), a hydrodynamic radius of 0.38 nm was assumed, which corresponding to the radii of a symmetrically spherical molecule of molar mass 175 g mol\(^{-1}\) (Huff-Hartz, 2005) and density 1.3 g cm\(^{-3}\) (Chen and Hopke, 2009). Further, \( x \) has been given a value of 4, to give conservative upper limits to viscosity.

Abramson et al. (2013) determined the diffusion coefficient for pyrene molecules in particles of SOM generated via the ozonolysis of \( \alpha \)-pinene. The hydrodynamic radius of pyrene is 0.4 nm, whilst, as suggested by Abramson et al. (2013) pyrene may form clusters consisting of up to 1,000 molecules, with a 1000 molecule cluster having a radius of \( \approx 4 \) nm. Hence, when calculating viscosity using Equation B.2, for the studies of Abramson et al., values of \( r = 0.4 \) and 4 nm were used. Further, values of \( x = 4-6 \) were used in Equation B.2 to calculate conservative lower and upper limits of viscosity.

Cappa and Wilson (2011) observed the change in chemical composition of SOM particles produced via the ozonolysis of \( \alpha \)-pinene as the particles were heated, and conservatively estimated an upper limit of diffusion coefficient for the particles. A value of \( x = 6 \) has been used in Equation B.2, along with a value of \( r = 4 \) nm, in order to determine a lower limit of viscosity.

Perraud et al. (2012) studied the particulate nitrate concentration in SOM particles generated via the ozonolysis of \( \alpha \)-pinene and determined an
B.4 Simulations of fluid flow for particles that exhibit cracking

upper limit for the diffusion coefficient of the particles. A value of $x = 6$ has been used in Equation [B.2] along with a value for $r$ of 4 nm, in order to determine a lower limit of viscosity.

B.4 Simulations of fluid flow for particles that exhibit cracking

In some cases (for the water-soluble SOM at low RH) the needle did not penetrate the particle. Instead, the needle caused the particle to 'crack', resulting in sharp, defined edges in the SOM (see Fig. 5.6, panel b2 for an example). In cases where cracking occurred, the material was observed for an extended period of time (at least 12 h). If, over that time, the sharp, defined, edges exhibited no detectable movement, the observation time was taken as a lower limit of $\tau_{\text{exp,flow}}$.

Particles that exhibited cracking behaviour and no detectable flow over the course of an experiment were simulated using a particle of quarter-sphere geometry, with one flat surface in contact with a solid substrate (see Fig. 2.10, and Movie S5 in Renbaum-Wolff et al., 2013a). The bottom surface, which represented the material-substrate interface, was allowed to undergo free deformation in the horizontal plane. All other surfaces were allowed to undergo free deformation in all directions. In these simulations the viscosity of the particle was varied until the sharp edge at the top of the particle moved by 0.5 $\mu$m over the experimental time. A value of 0.5 $\mu$m was chosen because this amount of movement is a clearly detectable threshold for the microscopy. Thus, for experiments for which no detectable movement was observed in microscope images, the viscosity determined via this method is a lower limit. The values of density, particle-substrate slip length, surface tension, and contact angle used when simulating the lower limit of viscosity for these particles are detailed in Table [B.5]
### B.5 Tables and figures

#### B.5 Tables and figures

Table B.1: Summary of $\tau_{\text{exp, flow}}$ times and viscosities of sample analysed after both 1 hour and 45 hours of exposure to a dry (<0.5 % RH) flow of Nitrogen gas. Originally published in [Grayson et al. (2015b)].

<table>
<thead>
<tr>
<th>Exposure time</th>
<th>$\tau_{\text{exp, flow}}$ (sec) $^a$</th>
<th>Mean simulated viscosity ± 95 % confidence intervals (Pa s) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lower limit  Upper limit</td>
</tr>
<tr>
<td>1 hour</td>
<td>104.3 (80.3, 120.5)</td>
<td>$1.5 \times 10^1 \pm 5.0 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.4 \times 10^5 \pm 9.0 \times 10^4$</td>
</tr>
<tr>
<td>45 hours</td>
<td>107.8 (80.6, 141.1)</td>
<td>$3.0 \times 10^4 \pm 9.3 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.0 \times 10^6 \pm 2.3 \times 10^5$</td>
</tr>
</tbody>
</table>

$^a$ $\tau_{\text{exp, flow}}$ values represent experimental values in the form "mean (5th percentile, 95th percentile)."

Table B.2: Experimentally determined contact angles for each of the samples studied. The range of values represent the 95 % confidence intervals of the values measured for multiple particles. Originally published in [Grayson et al. (2015b)].

<table>
<thead>
<tr>
<th>Sample name (production mass concentration during SOM production)</th>
<th>Particle-substrate contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1    Sample 2    Sample 3</td>
</tr>
<tr>
<td>Water-soluble SOM (14,000 µg m$^{-3}$)</td>
<td>43.5 - 50.0 47.2 - 53.3 50.5 - 72.0</td>
</tr>
<tr>
<td>Flow tube sample #1 (14,000 µg m$^{-3}$)</td>
<td>57.5 - 63.7 49.6 - 55.4 18.3 - 21.4</td>
</tr>
<tr>
<td>Flow tube sample #2 (6,000 µg m$^{-3}$)</td>
<td>59.8 - 61.3 60.5 - 66.9 63.3 - 67.2</td>
</tr>
<tr>
<td>Flow tube sample #3 (3,200 µg m$^{-3}$)</td>
<td>41.2 - 52.2 38.5 - 45.3 49.2 - 51.1</td>
</tr>
<tr>
<td>Flow tube sample #4 (1,100 µg m$^{-3}$)</td>
<td>31.4 - 35.6 61.5 - 65.5 44.3 - 47.8</td>
</tr>
<tr>
<td>Flow tube sample #5 (520 µg m$^{-3}$)</td>
<td>55.5 - 61.8 56.2 - 60.6 36.1 - 47.0</td>
</tr>
<tr>
<td>Chamber sample #1 (230 µg m$^{-3}$)</td>
<td>64.5 - 69.0 64.1 - 66.5</td>
</tr>
<tr>
<td>Chamber sample #2 (121 µg m$^{-3}$)</td>
<td>60.2 - 65.1 60.7 - 80.1</td>
</tr>
</tbody>
</table>

158
Table B.3: Summary of the percent relative standard deviation (% RSD) in $\tau_{exp,flow}$, lower limits of viscosity, and upper limits of viscosity for particles produced using equivalent conditions and studied via the poke-and-flow technique in combination with simulations of fluid flow at $<0.5$ % RH. Three samples were studied per production mass concentration in the flow tube. Values prior to parentheses represent the relative standard deviation between all particles studied that were produced at a given mass concentration, whilst the values inside each parenthesis represent the average relative standard deviation between particles on the same substrate. Originally published in Grayson et al. (2015b).

<table>
<thead>
<tr>
<th>SOM mass particle concentration ($\mu g , m^{-3}$)</th>
<th>% RSD of $\tau_{exp,flow}$</th>
<th>% RSD of simulated lower limit of viscosity</th>
<th>% RSD of simulated upper limit of viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>54 (30)</td>
<td>68 (67)</td>
<td>56 (39)</td>
</tr>
<tr>
<td>1,100</td>
<td>89 (24)</td>
<td>117 (44)</td>
<td>96 (27)</td>
</tr>
<tr>
<td>3,200</td>
<td>27 (22)</td>
<td>67 (42)</td>
<td>45 (30)</td>
</tr>
<tr>
<td>6,000</td>
<td>26 (20)</td>
<td>103 (47)</td>
<td>58 (29)</td>
</tr>
<tr>
<td>14,000</td>
<td>31 (27)</td>
<td>57 (27)</td>
<td>40 (28)</td>
</tr>
</tbody>
</table>
Table B.4: Summary of parameters used to estimate viscosity from literature studies of SOM produced via the ozonolysis of α-pinene. Originally published in Grayson et al. (2015b).

<table>
<thead>
<tr>
<th>Reference</th>
<th>$d_p$ (nm)</th>
<th>$\tau_{mixing}$ (sec)</th>
<th>$x$</th>
<th>$r$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cappa and Wilson (2011)</td>
<td>N/A</td>
<td></td>
<td>6</td>
<td>4.0</td>
</tr>
<tr>
<td>Perraud et al. (2012)</td>
<td>N/A</td>
<td></td>
<td>6</td>
<td>4.0</td>
</tr>
<tr>
<td>Saleh et al. (2013)</td>
<td>112</td>
<td>3,600</td>
<td>4</td>
<td>0.38</td>
</tr>
<tr>
<td>Saleh et al. (2013)</td>
<td>38</td>
<td>3,600</td>
<td>4</td>
<td>0.38</td>
</tr>
<tr>
<td>Abramson et al. (2013)</td>
<td>N/A</td>
<td></td>
<td>4 - 6</td>
<td>0.4 - 4.0</td>
</tr>
<tr>
<td>Robinson et al. (2013)</td>
<td>&gt;158</td>
<td>60</td>
<td>4</td>
<td>0.38</td>
</tr>
</tbody>
</table>

$^a$ Values for experiments conducted with an SOM mass concentration of 350 $\mu$g m$^{-3}$.

$^b$ An aerodynamic diameter was reported, and has been converted to a geometric diameter here.

$^c$ Values for experiments conducted with an SOM mass concentration of 1-12 $\mu$g m$^{-3}$. 
Table B.5: Physical parameters when simulating particles that don’t exhibit flow in COMSOL. Originally published in [Grayson et al. (2015b)].

<table>
<thead>
<tr>
<th>Value used to determine lower limit of viscosity</th>
<th>Density (kg m(^{-3})) (^{a})</th>
<th>Slip length (m) (^{b})</th>
<th>Surface tension (mN m(^{-1})) (^{c})</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,300</td>
<td>1 - 1.7 x 10(^{-8})</td>
<td>40</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Density was varied from 1,000 - 1,400 kg m\(^{-3}\) based on the work of [Chen and Hopke (2009)] and determined to have no effect upon simulations values. As such a median value of 1300 kg m\(^{-3}\) was used.

\(^{b}\) For references and rationale see Chapter 4.

\(^{c}\) Surface tension value based on work on [Tuckermann and Cammenga (2004)].
Figure B.1: A plot of particle volume vs. time for five particles exposed to a dry (<0.5 % RH) N₂ gas flow. Dotted lines represent the measured mean size of a particle. Error bars on the y-axis represent the uncertainty in measuring both the area of the particle, and the equilibrium contact angle, at the particle-substrate interface. Originally published in Grayson et al. (2015b).
Figure B.2: (a) Schematic representation of instrumental setup for contact angle images. (b) Fluorescence image obtained of an SOM particle. The green overlay is used to determine the contact angle of the particle, in this case 60°, and was produced using the LB-ADSA plugin for ImageJ. Originally published in Grayson et al. (2015b).
B.5. Tables and figures

Figure B.3: Plot of production mass concentration vs. viscosity for whole SOM produced via the ozonolysis of α-pinene and studied at <5 % RH. Shown are the results determined here along with those previously reported in literature (Abramson et al., 2013; Cappa and Wilson, 2011; Perraud et al., 2012; Renbaum-Wolff et al., 2013a; Robinson et al., 2013; Saleh et al., 2013; Zhang et al., 2015). Originally published in Grayson et al. (2015b).
Appendix C

Appendix to chapter 7

C.1 Table

Table C.1: A list of compounds included in the study, along with selected chemical and physical properties.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional group(s)</th>
<th>$M_w$ / g mol $^{-1}$</th>
<th>O:C</th>
<th>$\log_{10}(P_L^0)$ / Pa</th>
<th>$\log_{10}(\eta)$ / Pa s</th>
<th>References $P_L^0$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>1</td>
<td>58</td>
<td>0</td>
<td>5.38</td>
<td>-3.78</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>4.96</td>
<td>-3.67</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Isopentane</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>4.95</td>
<td>-3.67</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>Pentane</td>
<td>1</td>
<td>72</td>
<td>0</td>
<td>4.57</td>
<td>-3.65</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>2-Methyl pentane</td>
<td>1</td>
<td>86</td>
<td>0</td>
<td>4.18</td>
<td>-3.55</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Hexane</td>
<td>1</td>
<td>86</td>
<td>0</td>
<td>4.3</td>
<td>-3.53</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>3-Methyl pentane</td>
<td>1</td>
<td>86</td>
<td>0</td>
<td>4.15</td>
<td>-3.51</td>
<td>a</td>
<td>b</td>
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</table>

Continued on next page
<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional group(s)</th>
<th>( M_w ) / g mol (^{-1})</th>
<th>O:C</th>
<th>( \log_{10}(P_{L0}) ) / Pa</th>
<th>( \log_{10}(\eta) ) / Pa s</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methyl hexane</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>4.02</td>
<td>-3.46</td>
<td>c</td>
</tr>
<tr>
<td>2,2-Dimethyl butane</td>
<td>1</td>
<td>86</td>
<td>0</td>
<td>4.33</td>
<td>-3.45</td>
<td>a, b</td>
</tr>
<tr>
<td>2,4-Dimethyl pentane</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>3.9</td>
<td>-3.44</td>
<td>d</td>
</tr>
<tr>
<td>2,3-Dimethyl butane</td>
<td>1</td>
<td>86</td>
<td>0</td>
<td>4.29</td>
<td>-3.42</td>
<td>d, b</td>
</tr>
<tr>
<td>2-Methyl hexane</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>3.72</td>
<td>-3.42</td>
<td>d, d</td>
</tr>
<tr>
<td>Heptane</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>3.73</td>
<td>-3.41</td>
<td>a, b</td>
</tr>
<tr>
<td>2,2,4-Trimethyl pentane</td>
<td>1</td>
<td>114</td>
<td>0</td>
<td>3.47</td>
<td>-3.32</td>
<td>a, b</td>
</tr>
<tr>
<td>Octane</td>
<td>1</td>
<td>114</td>
<td>0</td>
<td>3.24</td>
<td>-3.3</td>
<td>a, b</td>
</tr>
<tr>
<td>2,2,3-Trimethyl pentane</td>
<td>1</td>
<td>114</td>
<td>0</td>
<td>3.4</td>
<td>-3.28</td>
<td>d, d</td>
</tr>
<tr>
<td>2,2,3-Trimethyl butane</td>
<td>1</td>
<td>100</td>
<td>0</td>
<td>3.92</td>
<td>-3.24</td>
<td>d, d</td>
</tr>
<tr>
<td>Nonane</td>
<td>1</td>
<td>128</td>
<td>0</td>
<td>2.73</td>
<td>-3.18</td>
<td>c, c</td>
</tr>
<tr>
<td>2,7-Dimethyl octane</td>
<td>1</td>
<td>142</td>
<td>0</td>
<td>2.65</td>
<td>-3.08</td>
<td>a, b</td>
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<tr>
<td>Decane</td>
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<td>142</td>
<td>0</td>
<td>2.25</td>
<td>-3.07</td>
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<td>Undecane</td>
<td>1</td>
<td>156</td>
<td>0</td>
<td>1.74</td>
<td>-2.97</td>
<td>a, b</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1</td>
<td>170</td>
<td>0</td>
<td>1.25</td>
<td>-2.86</td>
<td>a, b</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>1</td>
<td>198</td>
<td>0</td>
<td>0.26</td>
<td>-2.68</td>
<td>a, b</td>
</tr>
<tr>
<td>Tridecane</td>
<td>1</td>
<td>184</td>
<td>0</td>
<td>0.75</td>
<td>-2.65</td>
<td>a, b</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>1</td>
<td>212</td>
<td>0</td>
<td>2.8</td>
<td>-2.6</td>
<td>a, b</td>
</tr>
<tr>
<td>Compound</td>
<td>Functional group(s)</td>
<td>$M_w$ / g mol$^{-1}$</td>
<td>O:C</td>
<td>$\log_{10}(P_L^0)$ / Pa</td>
<td>$\log_{10}(\eta)$ / Pa s</td>
<td>References</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------------------</td>
<td>----------------------</td>
<td>-----</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Propylene</td>
<td>2</td>
<td>42</td>
<td>0</td>
<td>6.06</td>
<td>-4.09</td>
<td>a e</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>2</td>
<td>54</td>
<td>0</td>
<td>5.41</td>
<td>-3.85</td>
<td>a b</td>
</tr>
<tr>
<td>1-Butene</td>
<td>2</td>
<td>56</td>
<td>0</td>
<td>5.47</td>
<td>-3.85</td>
<td>a e</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>2</td>
<td>70</td>
<td>0</td>
<td>4.73</td>
<td>-3.71</td>
<td>d d</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>2</td>
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